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# The low primordial heavy noble gas and $^{244}$Pu-derived Xe contents of Earth's convecting mantle

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A R T I C L E I N F O

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A B S T R A C T

Clues to unraveling the origin and history of terrestrial volatiles lie in the noble gas record of Earth's mantle. However, the low abundance of heavy noble gases (Ar-Kr-Xe) in mantle-derived rocks presents a major analytical challenge that limits our understanding of mantle volatile evolution. Here, we employ a new technique of ultrahigh precision dynamic mass spectrometry to measure Ar-Kr-Xe isotopes in mantle-derived gas collected from Mt. Etna (Italy) and Eifel (Germany), which both tap depleted convecting mantle reservoirs. We find that the fractions of primordial Kr-Xe from accretionary sources ($\leq$ 7 % of non-radiogenic, non-fissiogenic isotopes) and $^{244}$Pu-derived $^{136}$Xe ($\leq 9.8 \pm 9.3$ % of total fissiogenic Xe) are both markedly lower than previously estimated. For Mt. Etna, we find an apparent lack of detectable primordial Xe, which could reflect an additional contribution from recycled atmospheric volatiles from nearby subduction. In addition, slight excesses of $^{238}$U-derived fissiogenic Xe relative to the upper mantle composition may reflect the contribution of a crustal component related to the occurrence of a HIMU ("high μ" where $\mu = {}^{238}U/{}^{204}Pb$)-type source in Mt. Etna volcanic products. The low primordial heavy noble gas and $^{244}$Pu-derived Xe contents of Earth's convecting mantle, as derived from these new data, requires extensive volatile loss during terrestrial accretion, followed by long-term degassing and pervasive overprinting of primordial heavy noble gases by subduction recycling. In addition, we suggest that quantitative incompatible element (including Pu, U) extraction to the Hadean crust and subsequent reintroduction of U via subduction could have contributed to lowering the ultimate fraction of $^{244}$Pu-derived $^{136}$Xe in the upper mantle. The differences observed between this study and other upper mantle Xe studies may reflect mantle source heterogeneities (e.g. due to the heterogeneous overprinting of mantle volatiles by subduction) but could also result from analytical inconsistencies and/or subsurface isotope fractionation in natural systems. Future studies are crucial to gain insight into the origin of these different results.

## 1. Introduction

Since planetary accretion, primordial (accretionary) and secondary (radiogenic and fissiogenic) noble gas isotopes have been preserved and accumulated within Earth's mantle, respectively (Mukhopadhyay and Parai, 2019). Being inert, highly volatile, and showing resolvable isotopic and elemental compositions between different accretionary sources (e.g., solar, chondritic, cometary; Bekaert et al., 2020), noble gases represent key tools for understanding the origin of volatiles on Earth. Furthermore, the relative proportions of $^{129}$Xe derived from radioactive decay of extinct $^{129}$I ($t_{1/2}$=16 Myr) and $^{136}$Xe from fission of extinct $^{244}$Pu ($t_{1/2}$=80 Myr) as well as extant $^{238}$U ($t_{1/2}$=4.46 Gyr) provide crucial timestamps for mantle volatile loss to the atmosphere (Pepin and Porcelli, 2006). Given that $^{244}$Pu became extinct ~500 Myr after Solar System formation, whilst $^{238}$U remains extant, the fraction of fissiogenic $^{136}$Xe originating from $^{244}$Pu (hereafter $^{136}Xe_{Pu}/^{136}Xe_{TF}$, where TF refers to "total fission") provides diagnostic information about the timing and extent of degassing experienced by distinct mantle reservoirs (Parai

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et al., 2019), including the deep (primitive) and convecting upper (depleted) mantle. Variations in mantle Xe isotopes have been used to suggest that the convecting mantle experienced extensive degassing to the atmosphere within the first 100 Myr of planetary evolution, and has remained isolated from the more primitive lower mantle sampled by mantle plumes for most of Earth's history (Parai et al., 2019; Mukhopadhyay, 2012). In addition, $^{129}Xe_{I}/^{136}Xe_{Pu}$ variations across the solid Earth are considered to potentially reflect (i) accretionary heterogeneities (i.e., predominant accretion of volatile-poor differentiated planetesimals followed by later addition of volatile-rich (high I/Pu) material (Liu et al., 2023)), (ii) sequestration of I from the lower mantle into the core (Jackson et al., 2018), and/or (iii) rapid degassing of mantle volatiles to the surface (Clay et al., 2017). However, measuring heavy noble gas isotopes from mantle-derived rocks and minerals is inherently challenging due to the low concentrations of gas available for analysis. These analyses are further complicated by the widespread occurrence of subduction-derived atmospheric volatiles, thought to account for ~80 % of non-radiogenic heavy noble gases in the depleted mantle (Parai and Mukhopadhyay, 2021; Holland and Ballentine, 2006; Bekaert et al., 2021). To achieve sufficient analytical precision, gas accumulation techniques have recently been employed (Péron and Moreira, 2018), but re-analyses of the same basaltic glass sample (e.g., popping rock 2∏D43; Parai and Mukhopadhyay, 2021) with different techniques have yielded inconsistent $^{136}Xe_{Pu}/^{136}Xe_{TF}$ estimates for the upper mantle, ranging from U-dominated (Parai and Mukhopadhyay, 2021) to Pu-dominated (Péron and Moreira, 2018) compositions. These discrepancies leave major open questions about the Xe isotope composition of distinct mantle reservoirs, highlighting the need for new constraints that inform our understanding on the evolution of volatile elements within Earth's interior.

One promising method to overcome sample size limitations is the analysis of volcanic gas emissions (hereafter, "volcanic gas" refers to any free gas of mantle origin), which provide a practically limitless supply of mantle-derived noble gases. However, this approach is not without its own challenges. Volcanic gas emanations often inherit atmosphere-derived noble gases from physical interaction with groundwater systems, making it difficult to disentangle mantle-derived from atmosphere-derived heavy noble gas signals at the analytical precision of traditional static noble gas mass spectrometers. Although repeat analysis of the same gas sample may help improve the analytical precision, the accurate detection of mantle-derived heavy noble gas signals (e.g., $^{136}Xe_{Pu}/^{136}Xe_{TF}$) remains challenging (Bekaert et al., 2019). Marked enrichments in light Xe isotope have been observed in mantle-derived samples and attributed to the occurrence of a chondritic primordial component (Holland and Ballentine, 2006; Péron and Moreira, 2018; Caffee et al., 1999; Caracausi et al., 2016; Broadley et al., 2020). Distinguishing between an asteroidal and a solar-like origin of primordial Xe in mantle-derived samples could have far-reaching implications for our understanding of the origin of volatiles (e.g., water, nitrogen) on Earth. However, the identification of primordial Xe within mantle-derived samples is challenging due to all potential cosmochemical sources of terrestrial Xe being highly enriched in light Xe isotopes relative to the present-day atmosphere, as a result of atmospheric Xe's protracted isotope evolution during the Hadean and Archean eons (Avice et al., 2017). The extrapolation of mantle-derived Xe isotope data towards potential cosmochemical precursors induces large uncertainties that do not allow firmly distinguishing between chondritic, solar, and cometary sources. Difficulties in precisely defining the composition of chondritic (e.g., average carbonaceous chondrites, AVCC) and solar-derived (Meshik et al., 2020) end-members may also lead to variable conclusions depending on the "choice" of the primordial end-member compositions. In addition, some studies (Caracausi et al., 2016) have shown a propensity for analytical bias during repeat gas analysis via static noble gas mass spectrometry (Bekaert et al., 2019), leading to contentious interpretations regarding the heavy noble gas composition of distinct mantle domains and the detection of primordial heavy noble gas components within the solid Earth. Recently, we demonstrated that subsurface fractionation of noble gases in hydrothermal systems can also generate light noble gas isotope enrichments (Bekaert et al., 2023), mimicking potential primordial Xe contributions, requiring high-precision measurements of multiple Ar, Kr, and Xe isotopes to robustly identify and correct for this subsurface fraction.

One way of overcoming this challenge is to investigate primordial Kr isotope systematics. This is because the Kr isotopic signatures of chondritic and solar endmembers are heavier and lighter than atmosphere respectively, therefore constituting a powerful tool for distinguishing between chondritic and solar volatile sources in the terrestrial mantle (Péron and Moreira, 2018; Broadley et al., 2020; Holland et al., 2009; Péron et al., 2021). For example, previous analyses of Bravo Dome well gas (Holland and Ballentine, 2006) show marked enrichments in light Xe isotopes paired with enrichments in heavy Kr isotopes. These opposite isotopic enrichments cannot be explained by mass dependent fractionation (which would similarly affect Kr and Xe isotopes by causing either light or heavy isotope enrichments), thus requiring mixing between at least two components (primordial and atmospheric). While the primordial Kr isotope component identified in gas samples from the upper (Holland et al., 2009) and lower (Broadley et al., 2020)) mantle broadly resemble AVCC, the extent to which potential fractionation processes in volcanic gas (Bekaert et al., 2023) could obscure primordial signals and led to contentious interpretation remains to be explored. Based on basaltic glass analyses, the exact isotopic composition of Kr in the solid Earth has also been suggested to exhibit an exotic (i.e., $^{86}Kr$-depleted) signature, tentatively attributed to the occurrence of a nucleosynthetic anomaly (Péron et al., 2021). Accurately determining the primordial origin of Kr and Xe isotopes in the mantle therefore has the potential to unlock vital information on the origin of volatiles on Earth as well as the different processes that have modified the mantle volatile budget throughout Earth's history.

To overcome some of the intrinsic limitations associated with the analysis of mantle-derived heavy noble gases by static mass spectrometry, we have developed a new analytical procedure to precisely and accurately measure noble gases in volcanic and magmatic gas samples by dynamic dual-inlet isotope-ratio mass spectrometry (DMS) (Seltzer and Bekaert, 2022; Bekaert et al., 2023). This technique enables high-precision gas isotope ratio measurements via rapid switching between reference and sample gas streams (McKinney et al., 1950), resulting in a substantial improvement in analytical precision compared to classical techniques for volcanic noble gas geochemistry. The DMS method is also anchored by rigorous evaluations of two external standards (air and air-saturated water) with markedly different elemental ratios, but similar and well-established noble gas isotopic composition, providing a crucial check on high measurement accuracy, in addition to precision (Seltzer et al., 2023). Here, we present the Ar-Kr-Xe isotope compositions of pristine volcanic gases collected from Victoriaquelle ($n = 1$, Eifel, Germany) and the Naftia well ($n = 3$, Mt. Etna, Sicily, Italy) using the Giggenbach method (Giggenbach, 1975) and analyzed by DMS (Seltzer and Bekaert, 2022; Bekaert et al., 2023). Information about the geological contexts of both sampling locations is provided as part of the *Supplementary Information*. On the one hand, the Eifel volcanic province is located in a continental rift fed by the melting of convecting, upper mantle material with potential contributions from upwelling mantle plumes (Bräuer et al., 2013; Bekaert et al., 2019). On the other hand, Mt. Etna, the largest and most active volcano in Europe (Caracausi et al., 2003), is located in a complex subduction zone setting (*Supplementary Information*). Even if Mt. Etna volcano is not subduction-related in the sense that it is not part of the magmatic arc, its activity could result from the "suction" of mantle material associated with the slab rollback that is produced at the corner between the African and European tectonic plates (Gvirtzman and Nur, 1999). Despite these specific geological contexts, both volcanic sources have been shown to exhibit clear geochemical affinities with the convecting (depleted) upper mantle, with, for example, Ne isotope systematics that are indistinguishable from Mid-Ocean Ridge Basalts (MORBs) (Bekaert et al., 2019; Nakai et al., 1997). The pristine nature of these volcanic gases thus represents a unique opportunity to document the heavy noble gas isotope composition of the upper mantle. While some studies have reported Ar and Xe isotope data for Eifel and Mt. Etna gas using conventional static mass spectrometry (SMS), no data exist in the literature for the Kr isotope compositions of either volcanic gas sources, thus offering an opportunity to provide new insight into the origin and evolution of volatiles within the convecting mantle.

## 2. Material and methods

### 2.1. Sample collection

We collected volcanic gas from the Victoriaquelle well in Germany (August 2021; (Bekaert et al., 2019)) and the Naftia well in Sicily, Italy (November 2021), the latter having previously been analyzed by Nakai et al. (1997). The volcanic gas at the Naftia well, located 40 km south of Mt. Etna, displays the same small-scale temporal variation in He isotopes (in the range 6.2-6.7 $R_a$, where $R_a$ refers to the atmospheric $^3He/^4He$) as volcanic emissions from the Mt. Etna flanks and crater fumaroles Caracausi et al. (2003), Paonita et al. (2021) suggesting they are fed from the same magmatic source beneath Mt Etna. In contrast to the crater fumarole, the Naftia samples exhibit consistently high $^{40}Ar/^{36}Ar$. We used 1.5 L Giggenbach bottles, following the sampling method presented by Bekaert et al., (2019). These large-volume sample vessels are pre-evacuated glass flasks equipped with double Teflon stopcocks and partially filled with 250 mL of 5N NaOH solution (Giggenbach, 1975). This procedure of gas sampling vastly increases both the "purity" and total amount of volcanic noble gas available for analysis (by about three orders of magnitude), since most reactive species ($H_2O$, $CO_2$, $SO_2$, $H_2S$, HCl, HF) are removed from the pristine gas by reacting with the NaOH solution. As there is no practical limit on the size of Giggenbach bottles, a virtually unlimited amount of clean gas can be collected for analysis, which is ideally suited for DMS measurements.

### 2.2. Analytical approach

Giggenbach samples were analyzed using a recently developed technique for DMS analysis (Seltzer and Bekaert, 2022) in the Seltzer Lab at Woods Hole Oceanographic Institution. This analytical technique (Seltzer and Bekaert, 2022) takes advantage of the fact that >99.8 % of all the heavy noble gases in volcanic gas is $^{40}Ar$ by matching $^{40}Ar$ ion beam intensities between sample and reference gases to ensure that the total pressure is balanced during analysis. In other words, Kr and Xe isotopes can be analyzed with an assurance of balanced pressure, independent of the Kr/Ar and Xe/Ar (which can vary widely in volcanic gases). Corrections for instrumental non-linearity and matrix effects are thus key to the new technique (Seltzer and Bekaert, 2022).

## 3. Results and discussion

### 3.1. Radiogenic and fissiogenic excesses

Analyses of Ar isotopes from Eifel ($^{40}Ar/^{36}Ar = 10{,}177.38 \pm 0.89$) and Mt. Etna ($^{40}Ar/^{36}Ar = 1881.44 \pm 0.13, 1911.58 \pm 0.12, 1921.43 \pm 0.12$; Table 1) gases show large $^{40}Ar$ excesses relative to air ($^{40}Ar/^{36}Ar_{air} = 298.56 \pm 0.31$ (Lee et al., 2006)) due to the decay of $^{40}K$ in the mantle, in line with previous investigations (Bekaert et al., 2019; Nakai et al., 1997). Because of issues with the isobaric interference of $^{38}Ar$ and $^{36}Ar$ by the low energy $^{40}Ar$ tail, $^{38}Ar/^{36}Ar$ data are not presented in this study (see Seltzer and Bekaert 2022) for a detailed explanation of the $^{40}Ar$ tail issue for high $^{40}Ar/^{36}Ar$ samples)

Xenon isotope spectra show clear radiogenic (e.g., $^{129}I$-derived Xe, hereafter $^{129}Xe_I$; $t_{1/2}$=16 Myr) and fissiogenic ($^{131\text{-}136}Xe_{TF}$) isotope excesses originating from the convecting mantle (Fig. 1a–c). Comparing the relative ratios of fissiogenic Xe isotope excesses in Eifel and Naftia samples to the fission yields of $^{238}U$ and $^{244}Pu$ indicates a clear upper mantle affinity with $^{238}U$ fission, with no requirement for a significant contribution of $^{244}Pu$ fission (Fig. 1d). Fig. 2 further illustrates this point by showing a comparison of Xe isotope systematics for some previously published (SMS) and ultrahigh precision (DMS) mantle noble gas data with the isotopic trends for $^{238}U$ and $^{244}Pu$ fission. For both Mt. Etna and Eifel, new Xe isotope data acquired by DMS show a marked improvement in analytical precision compared to previously available data acquired by SMS (Fig. 1a,c). This improvement in analytical precision is further illustrated by extrapolating all the measured Xe isotope compositions of Eifel and Mt. Etna gas to the $\delta^{129}Xe/^{130}Xe$ of the MORB source (Parai and Mukhopadhyay, 2021; Péron and Moreira, 2018), which is considered as representative of the convecting mantle (Fig. 3). The MORB mantle source and extrapolated Eifel compositions have identical magnitudes of $\delta^{136}Xe/^{130}Xe$ excesses, confirming that the Eifel mantle source represents the convecting upper mantle, with limited (if any) addition of $^{238}U$-derived fissiogenic Xe from the crust. Basically, the

**Table 1**
Mt. Etna and Eifel volcanic noble gas isotope data, measured by dynamic mass spectrometry, reported in delta notation relative to air (Ozima and Podosek, 2002).

| | Sample | $^{40}Ar/^{36}Ar$ | ±1σ | $\delta\ ^{84}Kr/^{36}Ar$ | | $\delta\ ^{132}Xe/^{36}Ar$ | |
|---|---|---|---|---|---|---|---|
| **(a)** | Mt. Etna **1** | 1880 | 21 | 876.7 | 2.9 | 2886.1 | 12.574 |
| | Mt. Etna **2** | 1910 | 21 | 875.2 | 2.9 | 2878.1 | 12.581 |
| | Mt. Etna **3** | 1920 | 21 | 868.9 | 2.9 | 2863.8 | 12.587 |
| | **Eifel** | 10,177 | 112 | 557.0 | 3.1 | 2433.8 | 15.879 |
| | | $\delta^{82}Kr/^{84}Kr$ | ±1σ | $\delta^{86}Kr/^{84}Kr$ | ±1σ | $\delta^{86}Kr/^{82}Kr$ | ±1σ |
| **(b)** | Mt. Etna **1** | -0.182 | 0.088 | 0.406 | 0.075 | 0.589 | 0.106 |
| | Mt. Etna **2** | -0.302 | 0.090 | 0.420 | 0.076 | 0.723 | 0.108 |
| | Mt. Etna **3** | -0.206 | 0.091 | 0.453 | 0.077 | 0.659 | 0.109 |
| | **Eifel** | -0.193 | 0.508 | -0.136 | 0.431 | 0.057 | 0.605 |
| | | $\delta^{128}Xe/^{130}Xe$ | ±1σ | $\delta^{129}Xe/^{130}Xe$ | ±1σ | $\delta^{131}Xe/^{130}Xe$ | ±1σ |
| **(c)** | Mt. Etna **1** | 0.048 | 0.322 | 11.279 | 0.116 | 0.427 | 0.131 |
| | Mt. Etna **2** | -0.315 | 0.325 | 11.254 | 0.118 | 0.174 | 0.133 |
| | Mt. Etna **3** | 0.042 | 0.327 | 11.502 | 0.118 | 0.335 | 0.134 |
| | **Eifel** | 1.523 | 0.896 | 71.510 | 0.514 | 2.148 | 0.632 |
| | | $\delta^{132}Xe/^{130}Xe$ | ±1σ | $\delta^{134}Xe/^{130}Xe$ | ±1σ | $\delta^{136}Xe/^{130}Xe$ | ±1σ |
| | Mt. Etna **1** | 2.538 | 0.116 | 9.862 | 0.144 | 14.055 | 0.131 |
| | Mt. Etna **2** | 2.296 | 0.118 | 9.712 | 0.146 | 13.799 | 0.133 |
| | Mt. Etna **3** | 2.612 | 0.118 | 10.072 | 0.147 | 14.373 | 0.134 |
| | **Eifel** | 13.778 | 0.514 | 49.767 | 0.594 | 70.248 | 0.608 |

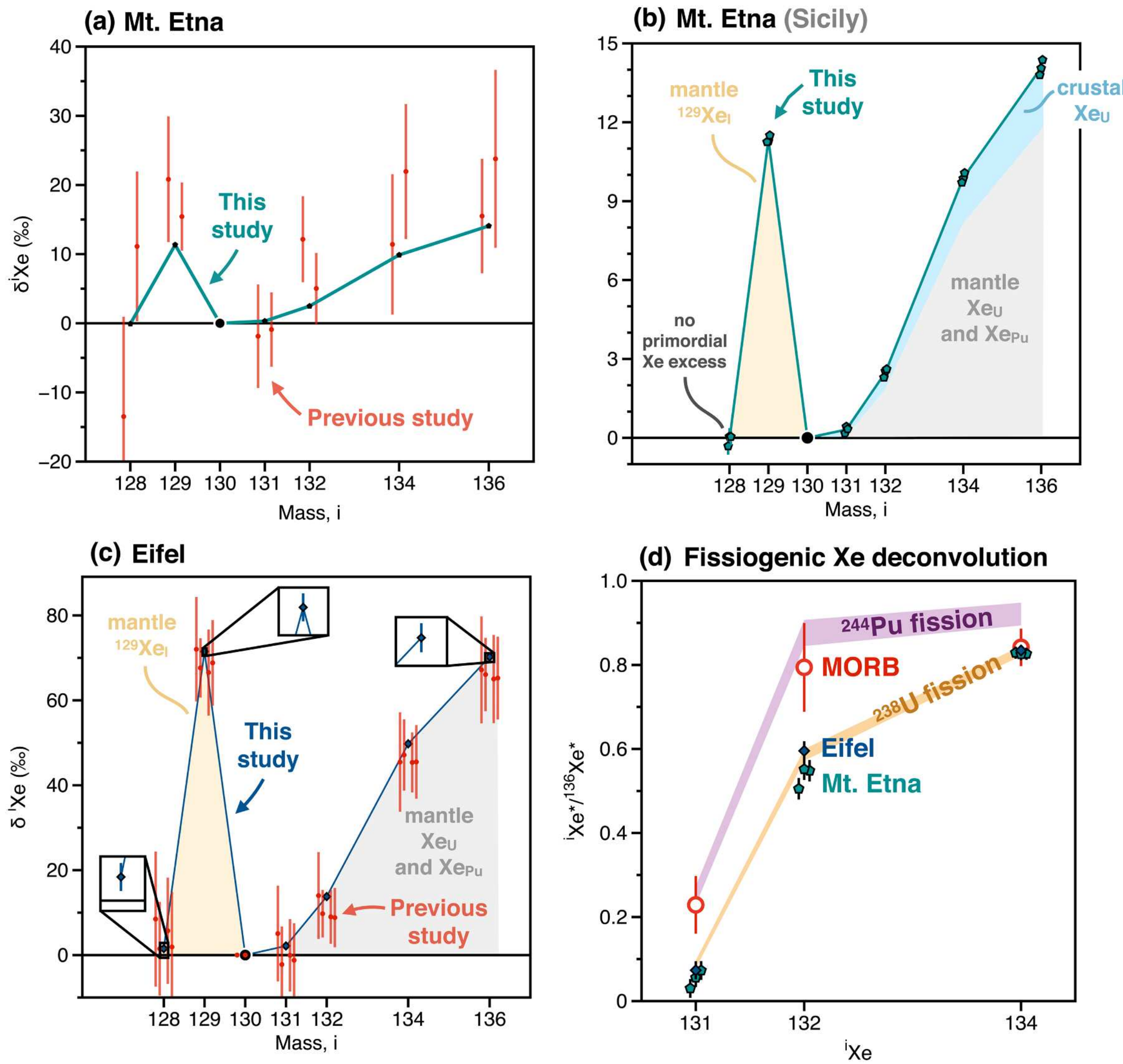


**Fig. 1.** Xenon isotope systematics of Mt. Etna and Eifel volcanic gas. (a) Comparison of Naftia well gas Xe isotope compositions measured by static-vacuum (Nakai et al., 1997) and dynamic (this study) mass spectrometry. (b) Ultrahigh precision Xe isotopic spectrum of Mt. Etna volcanic gas with $^{129}$Xe excess from $^{129}$I radiogenic decay ($^{129}Xe_I$) and $^{131-136}$Xe excesses from $^{238}$U ($Xe_U$) and $^{244}$Pu ($Xe_{Pu}$) fission. The crustal fissiogenic contribution derived by assuming a $^{129}$Xe/$^{136}$Xe of MORB (Péron and Moreira, 2018) is shown in light blue and labeled "crustal $Xe_U$". (c) Ultrahigh precision Xe isotopic spectrum of Eifel gas (this study) and comparison with literature data (Bekaert et al., 2019). (d) Spectra of fissiogenic Xe isotopes in Mt. Etna and Eifel gas (this study) compared with the fission spectra for fission of $^{238}$U (orange area) and $^{244}$Pu (purple area). The spectrum of fissiogenic Xe isotopes in popping rock 2$\pi$D43 from Péron and Moreira (2018) is also shown for comparison. Uncertainties are 1σ.

$^{129}$I-derived $^{129}$Xe/fissiogenic $^{136}$Xe ratio of the convecting mantle is close to that of the atmosphere (Pepin and Porcelli, 2006). However at a finer scale, some disparities exist between the Xe composition of Eifel, measured in this study, and previous determination of Xe in MORB samples (Péron and Moreira, 2018), particularly for δ$^{131}$Xe/$^{130}$Xe and δ$^{132}$Xe/$^{130}$Xe (Fig. 3).

Extrapolating the measured Xe isotope compositions of Mt. Etna to the δ$^{129}$Xe/$^{130}$Xe of the MORB source (Parai and Mukhopadhyay, 2021; Péron and Moreira, 2018) yields an extrapolated δ$^{136}$Xe/$^{130}$Xe greater than that of the MORB mantle source or extrapolated Eifel compositions (Fig. 3b). If Eifel, Mt. Etna and MORBs were to tap a common convecting mantle reservoir, then they should exhibit comparable excesses of radiogenic $^{129}$Xe and fissiogenic $^{136}$Xe relative to air. Comparing the Eifel Xe isotope composition with MORBs indicates that only a minimal fraction (4 ± 3 %) of the fissiogenic $^{136}$Xe excesses in Eifel may reflect an addition of crustal $^{238}$U-derived Xe. For Mt. Etna, ~19 % of fissiogenic $^{136}$Xe excesses could correspond to an addition of crustal $^{238}$U-derived Xe (Figs. 1–3). The amount of crustal $^{238}$U-derived $^{86}$Kr is estimated by using the average $^{136}$Xe/$^{86}$Kr production ratio (6.45) for the spontaneous fission of $^{238}$U (Ballentine and Burnard, 2002), thus allowing for the amount of crustal $^{238}$U-derived $^{84}$Kr to be derived from the $^{84}$Kr/$^{86}$Kr fission production ratios (Ballentine and Burnard, 2002). The proportions of fissiogenic $^{86}$Kr estimated for our samples with this approach are minor, resulting in small corrections to the measured $^{86}$Kr/$^{84}$Kr (Fig. 4).

### 3.2. *Lack of significant primordial Kr and Xe signatures*

DMS data for Eifel gas reveal a Kr isotope signature that is indistinguishable from air within the sub-per mil analytical uncertainty (Fig. 4). While the elevated $^{40}$Ar/$^{36}$Ar and δ$^{129}$Xe/$^{130}$Xe of this Eifel sample suggest that ≥25 % of Ar and ~50 % of Xe in the measured gas is directly sourced from the mantle (Bekaert et al., 2019), its air-like Kr isotope signature (Fig. 4) implies an absence of detectable chondritic Kr component, within uncertainty, in the Eifel mantle source. Note that the final uncertainties on the Eifel Kr data are larger than for Etna, due to

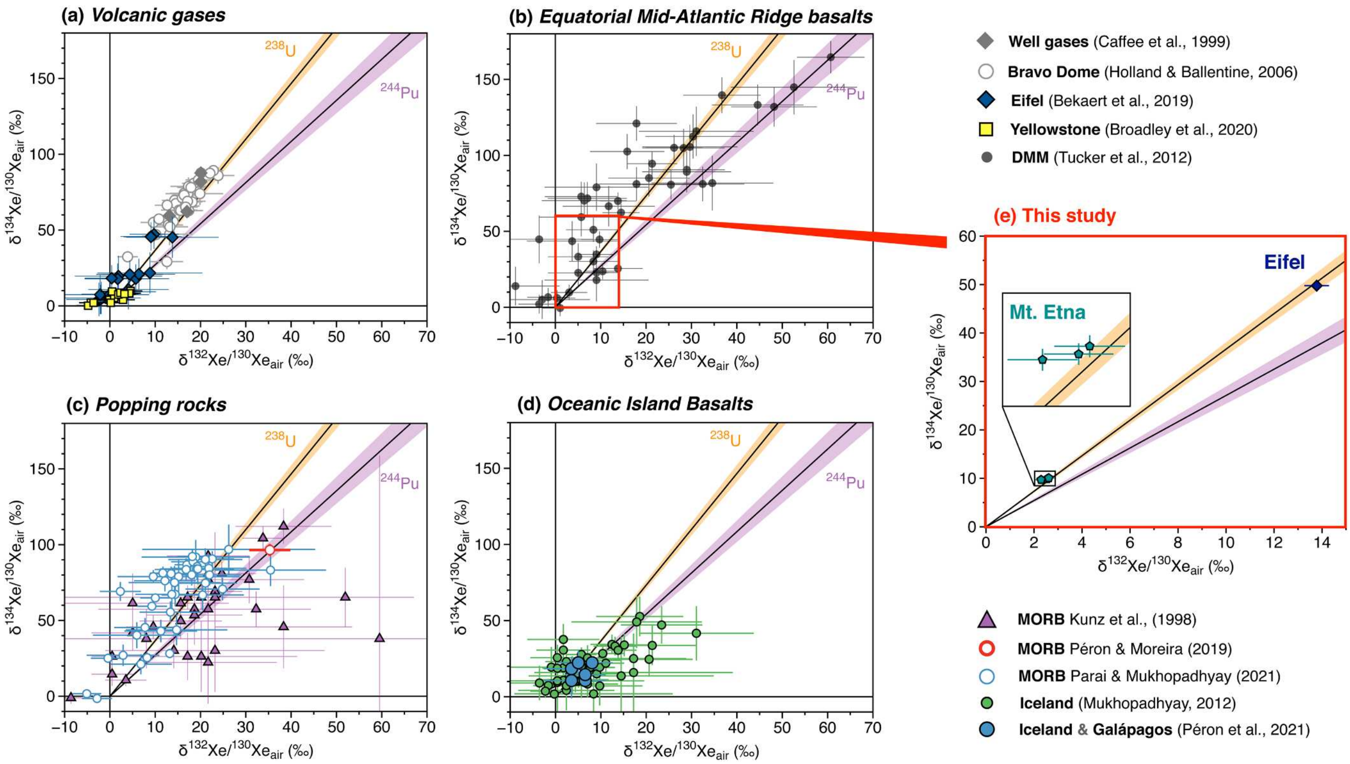


**Fig. 2.** Compilation of $\delta^{134}Xe/^{130}Xe_{air}$ vs. $\delta^{132}Xe/^{130}Xe_{air}$ systematics for previously published (static mass spectrometry) mantle noble gas data and Mt. Etna (dynamic mass spectrometry, this study) data. Also shown is a comparison with the isotopic trends for $^{238}U$ and $^{244}Pu$ fission, which highlights the vast improvement in precision and accuracy, compared to traditional static techniques. Uncertainties are 1σ (Tucker et al., 2012).

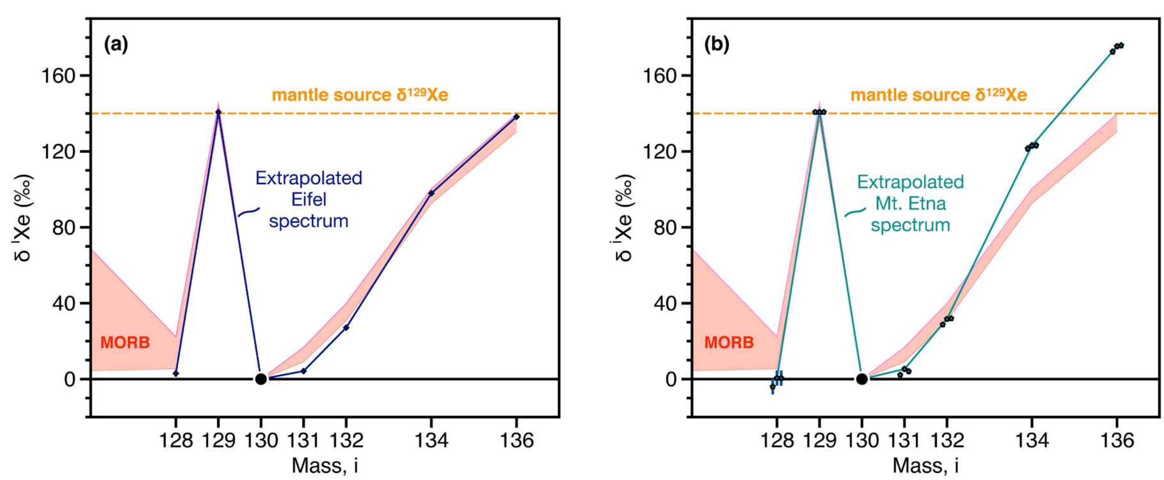


**Fig. 3.** Xenon isotope composition of the Eifel (a) and Mt. Etna (b) mantle sources obtained by extrapolation of the measured Xe isotopes to the $\delta^{129}Xe/^{130}Xe$ of the upper mantle ($^{129}Xe/^{130}Xe = 7.41$, corresponding to $\delta^{129}Xe/^{130}Xe = 141$ ‰; Parai and Mukhopadhyay, 2021; Péron and Moreira, 2018) (orange dashed line). The MORB mantle source Xe composition derived from popping rock analysis (Péron and Moreira 2018) is shown for comparison (red area). Uncertainties are 1σ.

intrinsic characteristics of the analytical approach. In particular, due to the pressure balancing of reference and sample gas on $^{40}Ar$ beams, samples with high $^{40}Ar/^{36}Ar$ (i.e., high $^{40}Ar/Kr$ and $^{40}Ar/Xe$) are analyzed with proportionally lower Kr and Xe beams, therefore invariably reducing counting statistics for Kr and Xe isotope determination. Thus, samples with high $^{40}Ar/^{36}Ar$ tend to have comparatively larger uncertainties on heavy noble gas isotope measurements.

For Mt. Etna, our DMS analyses reveal only slight heavy Kr isotope enrichments, potentially compatible with either (i) a minor contribution from primordial, AVCC-like Kr, or (ii) gravitational enrichment of the atmospheric (groundwater-derived) Kr fraction (Fig. 4). This latter process relates to isotopic fractionation via gravitational settling in the unsaturated zone above groundwater systems, whereby physical heavy-isotope enrichment of ~0.004‰ $u^{-1}$ $m^{-1}$ are transferred to groundwater by equilibrium dissolution at the water table (Seltzer et al., 2019). Given the small magnitude of the resulting isotope fractionation, this process is typically not considered in classical studies of volcanic gas emissions by SMS. However, such a process rises well above analytical noise at the level of precision of DMS. Here, heavy Kr isotope enrichments in Mt. Etna volcanic gas relative to air-equilibrated water (AEW) are broadly consistent with a signal of gravitational settling at a depth of ~30 m (with minor contributions from thermal diffusion and diffusion against constant fluxes of other gas species (Severinghaus et al., 1996)), potentially consistent with observations of water table levels in the

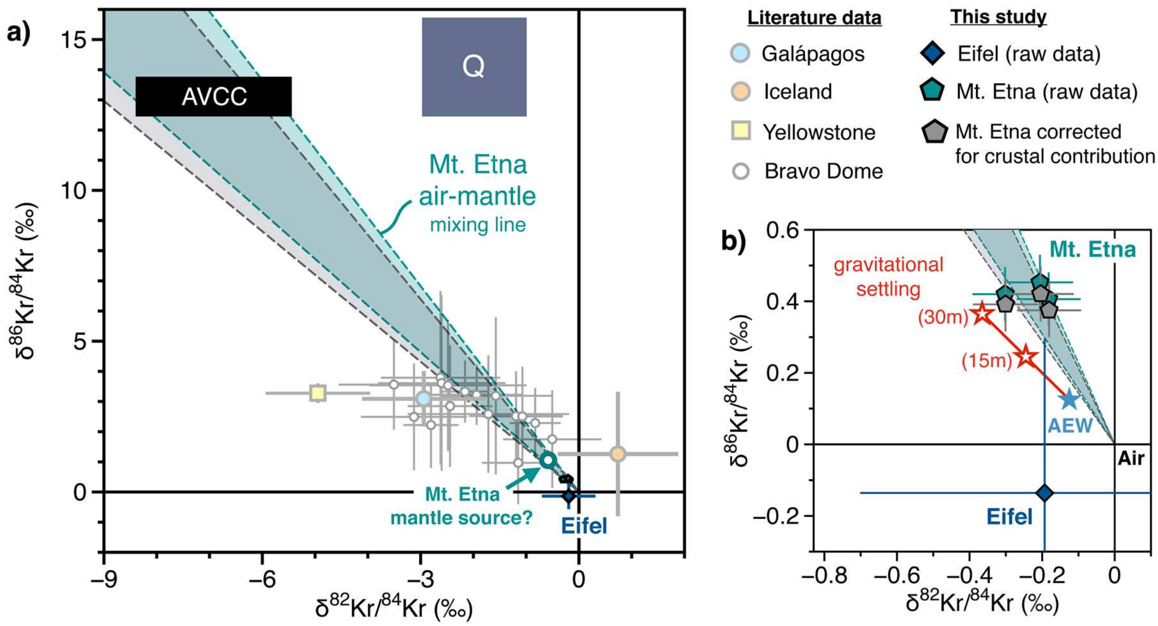


**Fig. 4.** $\delta^{86}Kr/^{84}Kr$ vs. $\delta^{82}Kr/^{84}Kr$ systematics of mantle-derived samples. (a) Extrapolation of Mt. Etna Kr isotope data towards the mantle end-member (green envelope) is potentially consistent with the occurrence of an AVCC-Kr component (rather than the chondritic Q signature; Busemann et al., 2000). Literature data for upper mantle-derived samples ($CO_2$ well gases; Holland et al., 2009) and plume source samples (Iceland and Galapagos basaltic glasses Péron et al., 2021, volcanic gas from Yellowstone; Broadley et al., 2020) are shown for comparison. The Mt. Etna mantle source composition is estimated by assuming that 40 % of the measured Kr is directly sourced from the mantle source (intermediate between estimates from $^{40}Ar/^{36}Ar$ ($\geq$25 %) and $\delta^{129}Xe/^{130}Xe$ ($\sim$50 %) systematics). (b) Mt. Etna and Eifel Kr isotope compositions (this study) are shown altogether with air-equilibrated water (AEW) composition and depth-proportional signals (between 0 and 30 m) set by gravitational settling in soil air at the time of recharge. Correction of Mt. Etna data for crustal Kr contribution (grey envelope) is carried out by combining the 19 $\pm$ 2 % crustal $Xe_U$ contribution to $Xe_{TF}$ (Fig. 1) with $^{238}U$ fission yield estimates (see Section 3.3.). Uncertainties are 1σ.

region (Fan et al., 2013) (Fig. 4). Assuming that deep groundwater-derived noble gases were degassed into a volcanic gas phase via $CO_2$ stripping (Bekaert et al., 2023), most of the non-radiogenic heavy noble gas isotope signals detected in Mt. Etna volcanic gas could thus correspond to a deep groundwater signal. Ar-Kr-Xe elemental ratios indeed suggest limited (if any) contributions from unfractionated air (Fig. S1).

Although $\delta^{124}Xe/^{130}Xe$ and $\delta^{126}Xe/^{130}Xe$ determination by DMS is not yet available (due to analytical challenges associated with low signal sizes), our data consistently show only minor $^{128}Xe$ excesses relative to the atmospheric composition (Figs. 1, 3): the average $\delta^{128}Xe/^{130}Xe$ of Mt. Etna samples (-0.08 $\pm$ 0.21‰; 1σ) is indistinguishable from air at the sub-permil level, and the $\delta^{128}Xe/^{130}Xe$ (+1.52 $\pm$ 0.90‰; 1σ) of the Eifel sample is only slightly positive. Importantly, the occurrence of heavy isotope enrichment due to gravitational settling would tend to slightly lower $\delta^{128}Xe/^{130}Xe$ values, potentially masking primordial signals. However, when translating the inferred gravitational settling Kr isotope signal (i.e., $\sim$0.12‰ amu$^{-1}$ for a water table depth of 30 m) to Xe isotopes, the $\delta^{128}Xe/^{130}Xe$ corrected for gravitational settling remain within error of the atmospheric composition (Fig. S2). This supports the absence of a detectable primordial Xe component in Mt. Etna volcanic gases, regardless of any assumption about the potential effect of gravitational settling. For Eifel, the lack of resolvable heavy Kr isotope enrichments relative to air precludes potential identification of a gravitational settling signal.

### 3.3. Subsurface fractionation in hydrothermal systems

Subsurface isotope fractionation is a globally pervasive process that can cause significant (per mil-level) light noble gas isotope enrichments (i.e., positive $\delta^{128}Xe/^{130}Xe$) within hydrothermal systems (Bekaert et al., 2023). Here, we cannot exclude the possibility that the Eifel gas sample measured in this study was marginally affected by subsurface isotope fractionation (as previously observed for other Eifel samples (Bekaert et al., 2023)), hence producing the slightly positive $\delta^{128}Xe/^{130}Xe$ relative to Mt. Etna samples. Thus, the estimated proportion of primordial Xe in the Eifel mantle source is a maximum value. Because Mt. Etna gas samples were directly collected from a well, they likely avoided the processes of subsurface isotope fractionation (Bekaert et al., 2023) potentially affecting Eifel data.

For the sake of clarity and transparency, we emphasize that attributing the slightly positive $\delta^{128}Xe/^{130}Xe$ observed for Eifel to subsurface isotope fractionation would affect Kr isotope systematics for this sample. For illustrative purposes, we carried out a correction of Eifel Kr isotope data for potential subsurface isotope fractionation following the approach of Bekaert et al. (2023), assuming an extreme scenario whereby the positive $\delta^{128}Xe/^{130}Xe$ observed for Eifel arises from diffusive transport fractionation (DTF) (i.e., complete absence of a chondritic Xe component in Eifel gas). We find that, in this case, the Kr isotope composition of Eifel (corrected for potential DTF, propagating all potential sources of uncertainty) is in agreement with previous mantle-derived data (including Bravo Dome samples BD07 and BD04, with $^{40}Ar/^{36}Ar$ akin to that of the Eifel sample analyzed in this study; Fig. S3), suggesting a potential contribution from an AVCC-like Kr component within Earth's mantle. However, the occurrence of this chondritic Kr component only arises when the $\delta^{128}Xe/^{130}Xe$ of the Eifel sample is assumed to be $\sim$0‰ (i.e., complete overprinting of mantle Xe by recycling of atmosphere-derived components), thus necessitating the original (chondritic) Kr isotope composition of the upper mantle to have been far less extensively overprinted by subduction than Xe isotopes. Such an extreme scenario is considered highly unlikely. Therefore, while we cannot exclude the possibility that the heavy Kr isotope compositions of Mt. Etna and DTF-corrected Eifel samples reflect slight contributions from a chondritic, AVCC-like component, our data require a smaller contribution of primordial (chondritic or solar) Xe within Earth's convecting mantle than was identified in previous analyses of upper mantle-derived Xe by SMS (Holland and Ballentine, 2006; Péron and Moreira, 2018; Bekaert et al., 2019; Caffee et al., 1999).

### 3.4. Mantle source composition estimates

A correction for surficial contamination by atmosphere-derived components is carried out for both site locations by extrapolating the measured Xe isotope spectra to the surmised mantle source $\delta^{129}Xe/^{130}Xe$ (Parai and Mukhopadhyay, 2021; Péron and Moreira, 2018) (Figs. 3, 5). For Mt. Etna, the extrapolated $\delta^{128}Xe/^{130}Xe$ ($\delta^{128}Xe/^{130}Xe_{EXTP}$) are so close to air that they encompass negative values that should only be regarded as indicating that the mantle source $\delta^{128}Xe/^{130}Xe$ of Mt. Etna is essentially air-like. At face value (i.e., not considering the potential for light Xe isotope enrichment due to secondary processes), the $\delta^{128}Xe/^{130}Xe_{EXTP}$ of Eifel gas appears slightly positive, being potentially greater than the air-like $\delta^{128}Xe/^{130}Xe_{EXTP}$ of Mt. Etna. This positive $\delta^{128}Xe/^{130}Xe_{EXTP}$ of Eifel gas indicates that the fraction of non-radiogenic, non-fissiogenic upper mantle Xe from a chondritic source is $\leq 7$ %. Interestingly, trace element and radiogenic isotope data for MORBs show the convecting mantle has been heterogeneously overprinted by subduction of surface-derived materials (e.g., Hofmann 2003), which appears supported by the suggestion that $^{40}Ar/^{36}Ar$ variations across different mantle domains reflect variable extents of overprinting by subduction-derived (atmospheric) argon (e.g., Parai et al. 2012, Péron et al. 2019, Bekaert et al. 2024). Given that Xe is likely to be more efficiently recycled to the mantle than Ar, one may expect even greater heterogeneity in the extent of Xe recycling across the convecting mantle than presently observed from Ar isotope systematics. Thus, we cannot exclude the possibility that slight differences in $\delta^{128}Xe/^{130}Xe_{EXTP}$ exist between the different convecting mantle reservoirs sampled at mid-ocean ridges, Eifel, Mt. Etna, and other well gases (Parai and Mukhopadhyay, 2021; Holland and Ballentine, 2006; Péron and Moreira, 2018; Bekaert et al., 2019; Caffee et al., 1999). We also cannot exclude the possibility of an even greater extent of Xe overprinting by recycled atmospheric gases in the mantle source of Mt. Etna compared to Eifel, potentially related to the addition of recycled atmospheric volatiles from nearby subduction (Supplementary Information). Recent alkaline magmas indeed suggest an increase in $H_2O/CO_2$ of the mantle source of Mt. Etna through time (Bragagni et al., 2022), potentially related to a greater contribution of water-rich subducting fluids that partially overprint the older, carbonatite-like signature. However, because the $\delta^{128}Xe/^{130}Xe_{EXTP}$ of Eifel and Mt. Etna remain indistinguishable from one another within uncertainty, these Xe isotope data are discussed together to provide a best estimate for the upper mantle's composition based on DMS analyses. In doing so, our data suggest that the fraction of primordial Xe within the upper mantle is $\leq 3$ % (Fig. 5), in contrast with previous suggestions of primordial Xe contributions on the order of ~20 % (Parai and Mukhopadhyay, 2021).

The fissiogenic Xe budgets of Eifel and Mt. Etna mantle sources appear largely dominated by $^{238}U$-fission. In order to more precisely estimate the proportion of $^{244}Pu$-derived Xe in both mantle sources, we carry out Monte Carlo linear least square deconvolutions of extrapolated Xe isotope data (Parai and Mukhopadhyay, 2015) (Supplementary

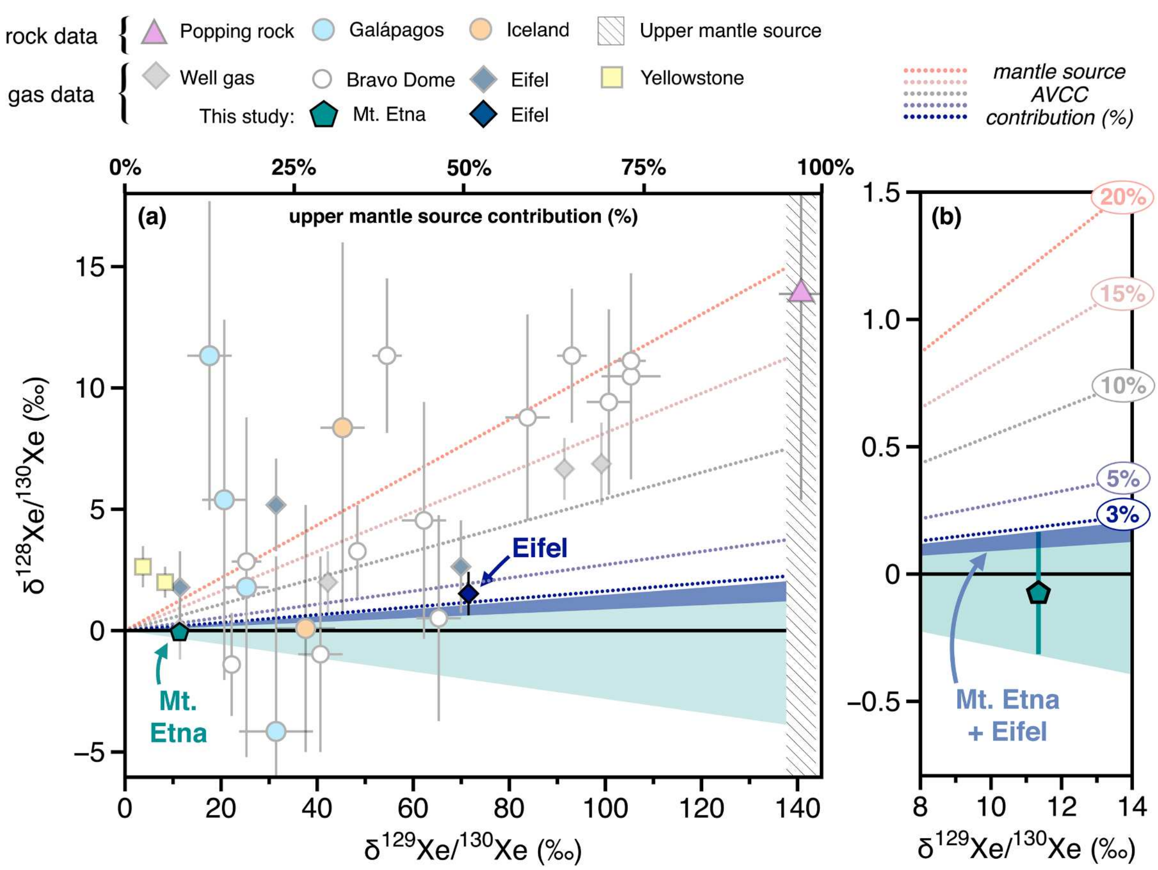


**Fig. 5.** $\delta^{128}Xe/^{130}Xe$ vs. $\delta^{129}Xe/^{130}Xe$ systematics of mantle-derived samples. The green and purple envelopes show the extrapolation of Mt. Etna and Eifel $^{128}Xe/^{130}Xe$ data, respectively, towards the MORB source $^{129}Xe/^{130}Xe$. Although different upper mantle reservoirs may have different proportions of recycled versus primordial components (Parai et al., 2019), Mt. Etna and Eifel Xe isotope data may be combined together to derive a best estimate for the upper mantle's composition from DMS analyses (blue envelope, representing the field where this green envelope overlaps with the extrapolation of Eifel data). Dashed lines represent mixing trends between air and mantle source compositions with MORB-like $^{129}Xe/^{130}Xe$ and variable proportions of air and AVCC-Xe (shown as percentages on panel b). Literature data for convecting, upper-mantle-derived samples ($CO_2$ well gases; Holland and Ballentine, 2006; Caffee et al., 1999), Mid-Atlantic Ridge popping rock (Péron and Moreira, 2018), volcanic gas from Eifel (Bekaert et al., 2019), and plume-source samples (blue and orange circles: Galapagos and Iceland basaltic glasses from Péron et al. 2021; green hexagon: Iceland basaltic glass from Parai 2023, volcanic gas from Yellowstone Broadley et al., 2020) are shown for comparison. Uncertainties are 1σ.

Information). Crucially, the exact proportions of primordial (in this case AVCC), atmospheric, $^{238}$U-fission Xe and $^{244}$Pu-Xe in Mt. Etna and Eifel mantle sources may still vary depending on the choice of the mantle source $^{129}$Xe/$^{130}$Xe and inclusion or not of $^{128}$Xe in the calculation (Tables S1 and S2). However, they are generally consistent with only a minimal contribution from $^{136}Xe_{Pu}$, corresponding to $^{136}Xe_{Pu}/^{136}Xe_{TF}$ lower than previously-derived estimates for convecting (31 ± 11 %) and lower (~97 %) mantle sources (Parai et al., 2019) (Fig. 6; Table S3). Considering a mantle source $^{129}$Xe/$^{130}$Xe of 7.41 and excluding $^{128}$Xe suggests that the upper mantle $^{136}Xe_{Pu}/^{136}Xe_{TF}$ derived from Eifel data is between 4 and 17%, with a mean value of 9 % (Fig. 6; Table S1). For Mt. Etna, including $^{128}$Xe in the Monte Carlo linear least square deconvolution generates even lower $^{136}Xe_{Pu}/^{136}Xe_{TF}$ values close to 0 (i.e., virtually no $Xe_{Pu}$; Table S2), in line with the direct comparison of fissiogenic Xe isotopes excesses and fission spectra for fission of $^{238}$U and $^{244}$Pu (Fig. 1d). These $^{136}Xe_{Pu}/^{136}Xe_{TF}$ should however only represent minimal values due to the surmised addition of fissiogenic Xe from crustal $^{238}$U (Fig. 1b). The occurrence of this crustal component in Mt. Etna volcanic gas could potentially relate to (i) fissiogenic Xe production in the crust beneath Mt. Etna, or (ii) the occurrence of subduction-derived material in the Mt. Etna mantle source (e.g., Tonarini et al. 2001). The latter point may also reflect the occurrence of a long-lived recycled component, potentially consistent with the proposed affinity of Mt. Etna volcanic products with both HIMU- ((“high-μ”; $\mu = {}^{238}U/{}^{204}Pb$) and depleted "upper" mantle-type end-members (Correale et al., 2014). Note that N isotope systematics have been used to suggest that the Eifel mantle could have been metasomatized by subducted volatiles (Labidi et al. 2020), but we see no evidence for the occurrence of such a component (i.e., no absolute excess of fissiogenic Xe relative to MORBs) based on Xe isotope systematics in this study.

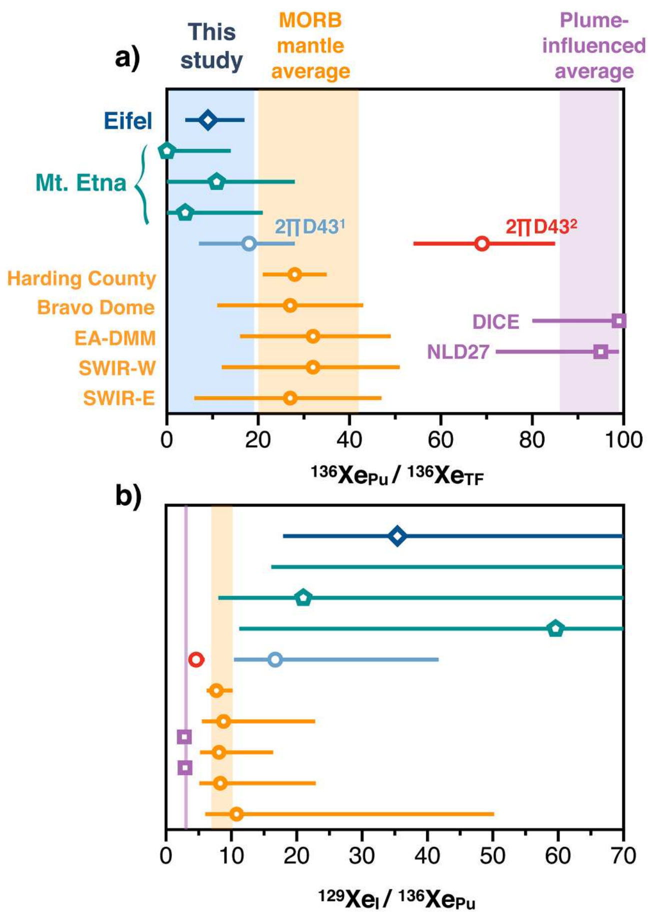


**Fig. 6.** $^{136}Xe_{Pu}/^{136}Xe_{TF}$ (a) and $^{129}Xe_{I}/^{136}Xe_{Pu}$ (b) variations for Mt. Etna and Eifel mantle sources (this study), popping rock 2∏D43 (Parai and Mukhopadhyay, 2021 (1, in blue); Péron and Moreira, 2018 (2, in red)), and comparison with MORB mantle and plume-influenced averages (Parai et al., 2019). Our samples were corrected for surficial atmospheric Xe contribution by extrapolation of the measured Xe isotope data towards the upper mantle source $^{129}$Xe/$^{130}$Xe of 7.41 (Fig. 2). For comparison with previous studies, the initial (primordial) Xe isotope composition of the mantle is AVCC, the recycled atmosphere component is taken to have a modern-like isotopic composition, and $^{128}$Xe is excluded. Changing one or several of these assumptions (e.g., upper mantle source $^{129}$Xe/$^{130}$Xe or including $^{128}$Xe) would affect the face value of these Monte Carlo outputs (Tables S1 and S2) without changing our conclusions.

For such low $^{136}Xe_{Pu}$ samples, difficulties in resolving the $Xe_{Pu}$ component can generate spuriously high $^{129}Xe_{I}/^{136}Xe_{Pu}$ that may not be representative of the mantle source composition (Parai and Mukhopadhyay, 2015). Nonetheless, our data consistently point towards greater mantle source $^{129}Xe_{I}/^{136}Xe_{Pu}$ than previously determined values (Fig.6). Monte Carlo linear least square deconvolutions also support our previous conclusion of minimal contributions from the primordial (AVCC) component, confirming that the non-radiogenic and non-fissiogenic Xe isotopes within the mantle sources of Eifel and Mt. Etna vastly derive from recycled atmosphere (Tables S1 and S2). Considering a mantle source $^{129}$Xe/$^{130}$Xe of 7.41, excluding $^{128}$Xe, and considering the average composition of our three Mt. Etna gas measurements indicates that only 3.3 ± 1.1 % of non-radiogenic, non--fissiogenic Xe in the upper mantle derives from AVCC, with the remaining fraction (96.7 ± 1.1 %) deriving from recycled atmosphere. Remarkably, Monte Carlo linear least square deconvolutions of Eifel data excluding $^{128}$Xe consistently yield negligible (~0 %) contribution from AVCC, regardless of the assumed mantle source $^{129}$Xe/$^{130}$Xe (Table S1). Including $^{128}$Xe yields slightly higher (several percent) proportions of AVCC, which should only be regarded as maximum values given the potential for light Xe isotope enrichments to have emerged as a result of sub-surface isotope fractionation.

### 3.5. *Implications and open questions*

The low primordial heavy noble gas (accounting for ≤3 % of non-radiogenic, non-fissiogenic Xe) and low $^{244}$Pu-derived Xe ($^{136}Xe_{Pu}/^{136}Xe_{TF}$ ~ 9.8 ± 9.3 %) contents of Earth’s convecting mantle sampled at Eifel and Etna, have important implications for our understanding of terrestrial volatile evolution, therefore warranting detailed discussion and careful comparison with previously published mantle noble gas data.

#### 3.5.1. *Early planetary volatile loss*

Our study indicates that the fraction of primordial Xe within the mantle sources of Eifel and Mt. Etna (~3.3 ± 1.1 % of non-radiogenic, non-fissiogenic Xe) may be too low to allow for an identification of terrestrial Xe’s precursor(s). The possibility that Mt. Etna and DTF-corrected Eifel data point to an apparent chondritic Kr component within Earth’s mantle cannot be completely discarded. Crucially, the Kr AVCC composition was recently redefined using the average and standard error of Kr isotope compositions from a subset of carbonaceous chondrites (Péron et al., 2021), leading to a more precise estimate of the AVCC composition than was previously proposed (Pepin, 2000) (Fig. S3). The authors argued that small deviations from an AVCC end-member should represent mantle Kr nucleosynthetic anomalies, with far reaching implications for the accretionary history of our planet (Péron et al., 2021). In light of the fact that there is large variability in bulk carbonaceous chondrite Kr isotope data (Fig. S3), we caution against overinterpreting Kr isotope deviations from this precisely defined AVCC end-member as truly reflecting mantle source Kr nucleosynthetic anomalies (Péron et al., 2021).

The low $^{136}Xe_{Pu}/^{136}Xe_{TF}$ of the upper mantle can be regarded as resulting from the extensive, long-term degassing of the upper mantle. However, the occurrence of $^{129}$Xe from short-lived $^{129}$I ($t_{1/2}$=16 Myr) within Eifel and Mt. Etna mantle sources implies that the apparent lack of chondritic Xe cannot be ascribed to a complete loss of mantle volatiles through long-term degassing. One possibility is that accretionary heavy noble gases were mostly lost from planetary building blocks, prior to the main stage of terrestrial accretion and $^{129}$Xe build-up via $^{129}$I radioactive decay. As suggested by the absence of significant trapped "planetary" noble gas components in the 4,565-My-old andesitic meteorite Erg Chech 002 (Barrat et al., 2021), primordial heavy noble gases could have been lost during degassing of early-formed planetesimals that accreted to form our planet. Such a scenario has recently been proposed for water (Newcombe et al., 2023), suggesting that substantial amounts of water (and, by extension, primordial heavy noble gases) could only have been delivered to Earth by means of unmelted material, rather than differentiated (and efficiently degassed) planetesimals. The undisputable occurrence of primordial light noble gases (He, Ne) within Earth's mantle (Mukhopadhyay and Parai, 2019), however, precludes the possibility that Earth initially accreted devoid of primordial volatiles, and rather calls for a pervasive overprinting of primordial heavy noble gases (in particular Xe) by subduction of surface-derived components. Such a scenario appears compatible with the present-day global mass balance of volatile element transport between Earth's surface and interior, pointing to a net ingassing regime of heavy noble gases – as opposed to a net outgassing regime for light noble gases (Bekaert et al., 2021).

### 3.5.2. *Pu/U systematics of the early Earth and the potential role of the hadean crust*

Our data suggest that the total fissiogenic $^{136}$Xe from $^{244}$Pu-Xe (9.8 ± 9.3 %) in the convecting mantle sampled at Eifel and Mt. Etna may be lower than previous estimates suggest (31 ± 11 %; Parai et al., 2019) (Fig. 6), supporting the interpretation of a greater extent of upper mantle long-term degassing relative to the plume mantle (Pepin and Porcelli, 2006; Parai and Mukhopadhyay, 2021). As discussed by Mukhopadhyay (2012), the exact $^{136}Xe_{Pu}/^{136}Xe_{TF}$ of a given mantle reservoir is however difficult to quantify and may also depend on the assumptions underlining the extrapolation of measured data towards the mantle source composition (Tables S1 and S2). Estimates of the total amount of long term degassing based on $^{136}Xe_{Pu}/^{136}Xe_{TF}$ systematics also depend on the initial Pu/U of Earth's mantle, which remains a critical yet poorly constrained parameter, widely taken as the accepted chondritic value of 0.0068 (Hudson et al., 1989). There is a strong case for revising this value, which was inferred from two samples of the LL6 St Severin meteorite (Hudson et al., 1989) by combining temperature steps exhibiting a factor 4 variation in Pu/U, and then applying decay corrections based on whole-rock I–Xe ages (Turner et al., 2007). Other estimates of the initial chondritic Pu/U have yielded lower values (in the range 0.004-0.005) (Jones, 1982) than commonly assumed. Lowering this parameter would directly reduce the amount of Pu expected to have decayed within Earth's mantle.

In addition, most models of terrestrial Xe evolution have considered that the progressive extraction of U and Pu from the mantle to shallow crustal reservoirs occurred over the Archean and Proterozoic eons (Parai and Mukhopadhyay, 2018), i.e., after mantle Pu had gone extinct. Evidence for a primordial ($4.40^{+0.03}_{-0.02}$ Gyr-old; Morino et al., 2017) and large-scale mantle-crust differentiation event is yet provided by the ubiquitous presence of both positive and negative $^{142}$Nd anomalies in the Archean rock record (Liou et al., 2024). Coupled $^{142,143}$Nd chronometry demonstrates a virtually synchronous differentiation of the terrestrial and lunar mantle Morino et al. (2017), suggesting that early crust formation was driven by magma ocean crystallization following the giant impact (Korenaga, 2021; Liou et al., 2024). In line with the detection of $Xe_{Pu}$ in Hadean zircons (Turner et al., 2007), we speculate that a sizeable fraction of Pu decay on Earth could have occurred within the Hadean crust, rather than in the mantle (potentially consistent with some of the latest scenarios explored by Zhang et al. (2023). Extensive reworking of the Hadean crust via bombardments, thermal processing, and early geodynamics would have caused the degassing of crustal $Xe_{Pu}$ to the atmosphere, in line with the fissiogenic component of atmospheric Xe's precursor being almost exclusively derived from Pu (Pepin and Porcelli, 2006; Bekaert et al., 2020). How much Pu (and U) would have been extracted from the mantle to the Hadean crust is however unknown. Although comparisons between meteorite (Hudson et al., 1989) and Hadean zircon (Turner et al., 2007) Xe data generally suggest that Pu/U fractionation during aqueous and magmatic processes associated with Earth's formation and early evolution was likely limited (i.e., within a factor 2), the exact geochemical behavior of Pu on the early Earth remains highly uncertain (see literature review on this topic in Supplementary Information).

Our knowledge of the global volume and composition of the Hadean crust is extremely limited.

In general, the Hadean crust is assumed to form from the residual melt of magma ocean crystallization. Magmatic-thermomechanical models of Hadean geodynamics (Fischer and Gerya, 2016) suggest a crustal thickness of up to 40 km (i.e., total volume of $\sim 2.03 \times 10^{19}$ m$^3$), lying on top of the asthenospheric mantle. This early crust would have been less dense than the average mantle composition (Jordan, 1988), thus forming a buoyant, long-lasting lithosphere, in the form of a stagnant lid (Caro et al., 2017) (Debaille et al., 2013). In order to tentatively evaluate the amount of mantle U (and, by extension, Pu) potentially extracted to the Hadean crust during magma ocean crystallization, we used a model of U partitioning adapted from previous work by Morino et al. (2018) and Caracas et al. (2019) (*see model description in* Supplementary Information). These models show that the amount of mantle U ultimately extracted to the Hadean crust depends on a series of parameters including (i) the amount of Ca-perovskite at pressures >22 GPa, and (ii) the fraction of entrapped melt in cumulates. However, these simple calculations show that the Hadean crust and basal magma ocean (BMO) potentially contained up to ~50 % and ~40 % of U in the Bulk Silicate Earth (BSE), respectively. In this case, the convecting mantle (i.e., 78 vol.% of the BSE) would have been left with only 8–27 % of its U budget (and, by extension, a similar fraction of its Pu budget) after crustal extraction (see Supplementary Information for additional discussion). The preservation of depleted Nd signatures (i.e., positive $^{142}$Nd anomalies) in the mantle until the Neo-Archean (Debaille et al., 2013) and widespread observation of negative $^{142}$Nd anomalies in Archean crust samples worldwide (Caro et al., 2017; Guitreau et al., 2019; Reimink et al., 2018; O'Neil et al., 2008; Schneider et al., 2018) further indicate preservation of the Hadean crust on the timescale of ~1 Gyr. Over that period, the reintroduction of crustal components into the mantle via crustal recycling would have been inefficient due to the widespread melting of the early crust, laden with heat-producing elements, such that a sizeable fraction of Pu decay on Earth would indeed have occurred within the crust, rather than in the mantle. The possibility that substantial incompatible element extraction to the crust occurred within the lifetime of $^{244}$Pu thus suggests that differences between the $^{136}Xe_{Pu}/^{136}Xe_{TF}$ and $^{129}Xe_{I}/^{136}Xe_{Pu}$ of deep and convecting mantle reservoirs do not solely reflect the outcomes of accretionary and long-term degassing processes, as has been conventionally assumed. Furthermore, the occurrence of significant $^{129}$I-derived $^{129}$Xe but not $^{244}$Pu-derived $^{136}$Xe suggests that either I is less incompatible than Pu during melting, or $^{129}$I was largely exhausted prior to the major extraction event into the crust (compatible with a $4.40^{+0.03}_{-0.02}$ Gyr-old, large-scale mantle-crust differentiation event (Morino et al., 2017)).

### 3.5.3. *Pervasive overprinting of the upper mantle by subduction*

The fact that the fractions of recycled atmospheric Xe (and potentially Kr) within the Eifel and Mt. Etna mantle sources are larger (~97 %) than previously considered (~80 %) suggests potential local enhancements of mantle volatile overprinting by subduction, reinforcing the prominent role of subduction in overprinting the global mantle volatile budget (Holland and Ballentine, 2006). Furthermore, the modern-like composition of the recycled atmospheric Xe component implies that efficient transport of surface-derived Xe into the mantle by subduction started over the past 2.5 Gyr (Parai and Mukhopadhyay, 2018), i.e., once the atmosphere had reached its present-day Xe isotope composition (Avice et al., 2017). Around the same time as efficient volatile recycling to the mantle started to occur, the large-scale oxidation of Earth's surface likely caused a significant change in the predominant surface oxidation state of U, which became soluble within oxidizing environments at the Earth's surface (Nielsen, 2010). This could have facilitated its transport from continents to the altered oceanic crust and ultimately back into the mantle, potentially causing the U content of the depleted mantle to have increased over Earth's history because of U subduction and convective mixing. Such a scenario would be consistent with the present-day influx of subducted U in oceanic crust ($\sim 3.1 \times 10^7$ mol/yr; Nielsen, 2010) being greater than the outflux of U emitted at mid ocean ridges ($\sim 1.1 \times 10^7$ mol/yr; computed by considering that about 20 $km^3$ of oceanic crust with 50 ppb U is emitted at mid-ocean ridges every year). This first-order mass balance calculation suggests that the total amount of U in the convecting mantle could be increasing through time, at a present-day rate of $\sim 2 \times 10^7$ mol of U per year. Assuming this flux has remained constant over the 3 billion years of subduction would indicate that up to $5.9 \times 10^{16}$ mol of U could have been added to the mantle since the onset of modern-style subduction. When compared to the total mass of the convecting upper mantle ($3.1 \times 10^{27}$ g), this amount of U ($1.4 \times 10^{19}$ g) would correspond to 4.5 ppb U, compatible with the actual U content of the depleted mantle (5.4 ± 1.3ppb; Arevalo et al., 2009) (Supplementary Information). Importantly, we do not argue here that all of the U in the present-day upper mantle is recycled, as independent constraints from U stable isotopes and radiogenic Pb isotopes suggest it is unlikely that the majority of upper mantle U originates from subduction (Andersen et al., 2015). Instead, we suggest that the total amount of U introduced within the solid Earth of the last 3 billion years of subduction could have, at least to some extent, impacted the general U budget of the convecting mantle. How the combination of early and quantitative incompatible element (U and Pu) extraction to the Hadean crust and subsequent reintroduction of U (after Pu decay) via subduction (Fig. 7) modified (i.e., lowered) the ultimate $^{136}Xe_{Pu}/^{136}Xe_{TF}$ of the upper mantle is currently unknown and unaccounted for in state-of-the-art models of mantle Xe isotope evolution.

### *3.5.4. Discrepancy with previously published data?*

At face value, the observation of marked light Xe isotope enrichments in several upper mantle-derived samples analyzed previously by SMS appears incompatible with the lack of significant primordial isotope signature in Eifel and Mt. Etna mantle sources. For free gas samples, there is a possibility that some of the light Xe isotope enrichments reported in the literature could – at least in part – result from analytical artifacts (i.e., mass-dependent isotope fractionation during sample preparation, Xe separation from Ar, purification, and/or analysis) and/or subsurface isotope fractionation in natural systems (Bekaert et al., 2023). As displayed on Fig. 5, previous analyses of mantle-derived heavy noble gases do not plot along a single mantle line in $\delta^{128}Xe/^{130}Xe$ versus $\delta^{129}Xe/^{130}Xe$ space, suggesting that some of the observed variability could also arise from physical processes of fractionation. However, it is clear that light Xe isotope enrichments paired with heavy Kr isotope enrichments, as observed in well gases Bravo Dome (Holland and Ballentine, 2006), cannot easily be explained by mass dependent fractionation. These data require a contribution from a chondritic-like component that is enriched in light Xe isotopes and heavy Kr isotopes. Why distinct portions of the convecting mantle would retain such variable fractions of primordial components remains to be explained. One possibility is that the observed differences between the proportions of primordial heavy noble gases across different convecting mantle reservoirs (as sampled at mid-ocean ridges, Eifel, Mt. Etna, and other well gases; Fig. 5) primarily reflect mantle source heterogeneities due to the heterogeneous overprinting of mantle volatiles by subduction.

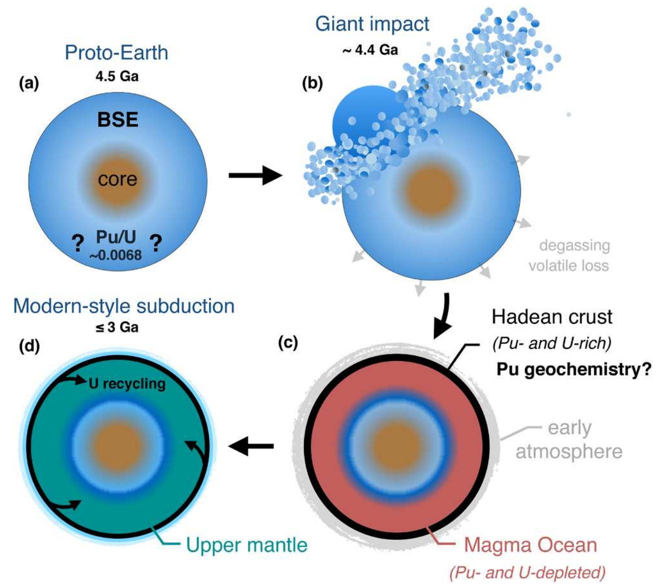


**Fig. 7.** Conceptual cartoon summarizing the main sources of uncertainty regarding Pu/U systematics of the Hadean mantle, emphasizing the possibility that a sizeable fraction of Pu decay on Earth occurred within shallow, crustal levels, rather than in the mantle. (a) At 4.5 Gyr ago, the proto-Earth would have primarily formed from extensively degassed planetesimals (with highly uncertain Pu/U), and initiated its differentiation. (b) The Moon-forming impact then caused extensive mantle degassing and volatile loss. (c) Following the giant impact, a Hadean crust would have formed rapidly, thereby concentrating a significant fraction of incompatible elements at Earth's surface for up to ~1 Gyr. (d) Around 3 Gyr ago, the emergence of modern-style subduction would have led to the onset of efficient incompatible element recycling within the solid Earth, long after Pu had gone extinct. The protracted oxidation of Earth's surface caused a significant change in the predominant surface oxidation state of U, which became soluble within oxidizing environments at the Earth's surface, facilitating its transport from continents to the altered oceanic crust and ultimately, by subduction, back into the mantle.

For mantle-derived rock samples, it is worth mentioning that, within uncertainty, the extrapolated Xe isotope spectrum of the popping rock mantle source (Péron and Moreira, 2018) is not incompatible with a low primordial Xe contribution, as suggested by our study (Fig. 3). In fact, Xe isotope data for mantle-derived rock samples (as well as volcanic gas data presented here) would be consistent with an absence of a chondritic components in Earth's upper mantle at the 2-sigma level. Notably, re-analyses of the same rock sample (e.g., popping rock 2∏D43) in different laboratories have yielded inconsistent $^{136}Xe_{Pu}/^{136}Xe_{TF}$ estimates (Parai and Mukhopadhyay, 2021; Péron and Moreira, 2018). Interestingly, the occurrence of Xe isotopic fractionation in favor of the light isotopes would tend to both (i) bias the deconvolution of $^{238}U$- and $^{244}Pu$-derived Xe towards the $^{244}Pu$-Xe end-member (Bekaert et al., 2019), and (ii) overestimate the contribution of primordial components in the mantle source reservoir.

The recent finding that popping rock 2∏D43 (MORB) and Oceanic Island Basalts (OIBs) are indistinguishable in $\delta^{129}Xe/^{136}Xe_{air}$ vs. $\delta^{130}Xe/^{136}Xe_{air}$ space (Parai and Mukhopadhyay, 2021) (Fig. 8) has important implications for our understanding of Earth's volatile evolution. Namely, this isotope space was historically used to suggest that small Xe isotopic differences between OIB and MORB mantle sources cannot be related solely through recycling atmospheric Xe or by adding fissiogenic $^{136}Xe$ to MORB Xe (Mukhopadhyay, 2012). To have OIB and MORB reservoirs now overlapping in this isotope space may call into question the reliability of Xe isotopes as a means to document the contrasted evolutionary histories of volatile elements in the upper (depleted) and deep (primitive) mantle reservoirs. In $\delta^{129}Xe/^{136}Xe_{air}$ vs.

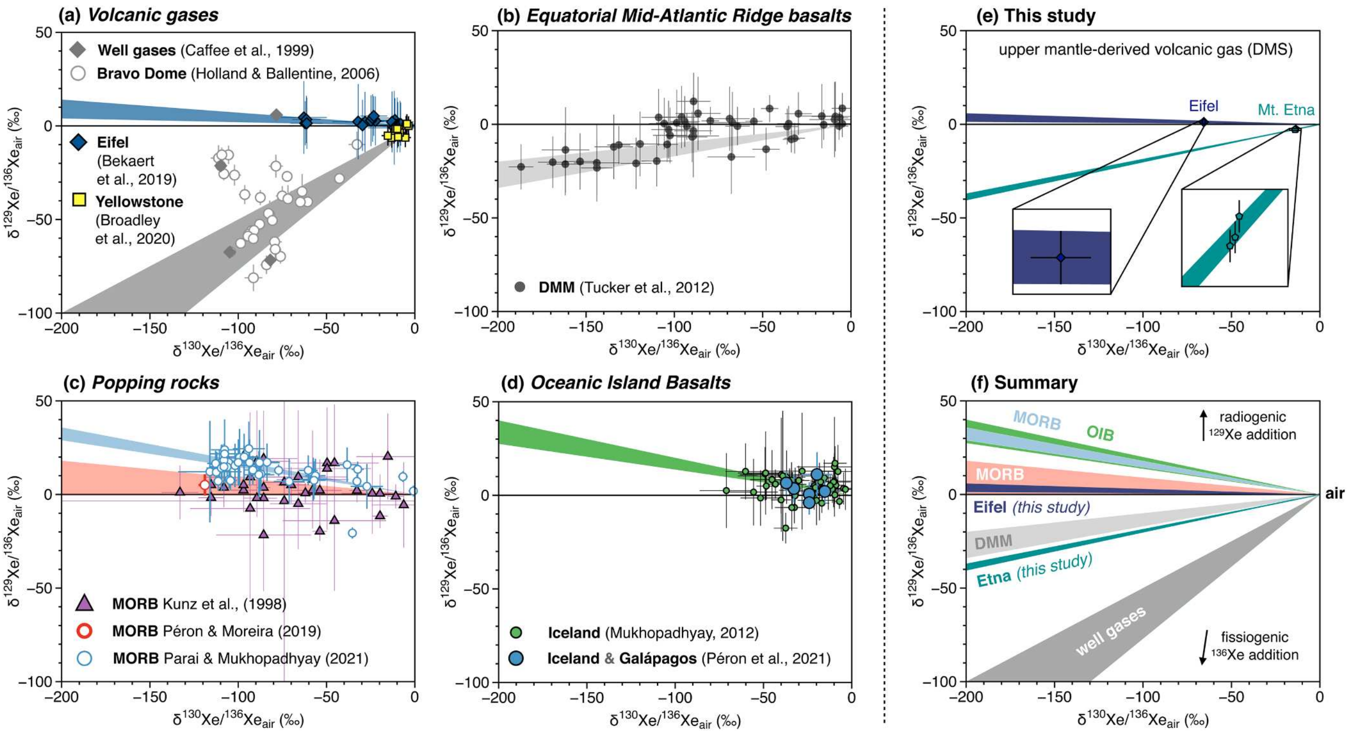


**Fig. 8.** Compilation of $\delta^{129}Xe/^{136}Xe_{air}$ vs. $\delta^{130}Xe/^{136}Xe_{air}$ systematics for previously published mantle noble gas (static mass spectrometry) data and Mt. Etna (dynamic mass spectrometry, this study) data. This classical plot has been used to argue that small Xe isotopic differences between OIB and MORB mantle sources cannot be related solely through recycling atmospheric Xe or by adding fissiogenic $^{136}$Xe to MORB Xe. However, the recent finding that popping rock and Iceland plume data overlap in this isotopic space (Parai and Mukhopadhyay, 2021) may cast doubt on the interpretation that these small differences truly reflect primordial heterogeneities. Uncertainties are 1σ.

$\delta^{130}Xe/^{136}Xe_{air}$ space, Eifel data reported in this study are compatible with previous analyses of Eifel gas (Bekaert et al., 2019) and popping rock 2∏D43 (Péron and Moreira, 2018), but inconsistent with a recent, careful re-analysis of this MORB sample (Parai and Mukhopadhyay, 2021). Whether these disparities truly reflect upper mantle source heterogeneities (Parai and Mukhopadhyay, 2021), some extent of isotope fractionation associated with sample processing, or both, remains uncertain.

## 4. Conclusions and perspectives

The analysis of Ar-Kr-Xe isotopes by ultrahigh precision DMS in mantle-derived gas collected from Mt. Etna (Italy) and Eifel (Germany) reveals lower fractions of primordial Kr-Xe from accretionary sources ($\leq$ 7 % of non-radiogenic, non-fissiogenic isotopes) and $^{244}$Pu-derived Xe ($\leq 9.8 \pm 9.3$ % of total fissiogenic $^{136}$Xe) than previously estimated for the convecting mantle, from which they are yet considered to primarily derive. These observations require early and extensive volatile loss during terrestrial accretion, followed by long-term degassing and pervasive overprinting of primordial heavy noble gases by subduction recycling. Quantitative incompatible element (including Pu, U) extraction to the Hadean crust and subsequent reintroduction of U via subduction could also have contributed to further lowering the ultimate fraction of $^{244}$Pu-derived $^{136}$Xe in the upper mantle.

In essence, the observed discrepancies with previously published upper mantle results could primarily reflect upper mantle source heterogeneities (e.g. due to the heterogeneous overprinting of mantle volatiles by subduction). Some of the literature data could also have suffered from analytical inconsistencies and/or subsurface isotope fractionation in natural systems. Future studies (e.g., analysis of Bravo Dome well gas by DMS) are required to gain insight into the origin of these different results. As of today, the analysis of the two rarest Xe isotopes ($^{124}$Xe and $^{126}$Xe) by DMS is not yet available. The analysis of these isotopes by DMS will represent a critical analytical development to help us better quantify the fractions of primordial heavy noble gases within Earth's mantle reservoirs.

Despite a clear variability within each category, the plume and MORB mantle Xe signatures have been established as distinct, with plume mantle-derived rock samples exhibiting a higher proportion of $^{244}$Pu fission-derived Xe consistent with less processing by partial melting over Earth's history relative to the upper mantle (Parai, 2022). The advent of volcanic gas analysis by DMS offers a promising avenue to evaluate current mantle noble gas models underpinning our understanding of how planetary processes (e.g., giant impact-induced degassing, core-mantle segregation, mantle convection and subduction) have shaped the heterogeneous nature of terrestrial volatiles. These developments go hand in hand with current, gradual analytical developments to improve the quality and reliability of noble gas analyses by multi collector SMS.

## CRediT authorship contribution statement

**D.V. Bekaert:** Writing – original draft, Writing – review & editing, Resources, Methodology, Formal analysis, Visualization, Conceptualization. **A. Caracausi:** Writing – review & editing, Methodology, Resources. **B. Marty:** Writing – review & editing, Resources. **D.J. Byrne:** Writing – review & editing. **M.W. Broadley:** Writing – review & editing, Methodology, Resources. **G. Caro:** Writing – review & editing, Validation. **P.H. Barry:** Visualization, Writing – review & editing. **A.M. Seltzer:** Writing – review & editing, Validation, Visualization, Methodology, Formal analysis, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2024.118886.

## References

Andersen, M.B., Elliott, T., Freymuth, H., Sims, K.W.W., Niu, Y., Kelley, K.A., 2015. The terrestrial uranium isotope cycle. Nature 517, 356–359. https://doi.org/10.1038/nature14062.

Arevalo, R., McDonough, W.F., Luong, M., 2009. The K/U ratio of the silicate Earth: Insights into mantle composition, structure and thermal evolution. Earth Planet. Sci. Lett. 278, 361–369. https://doi.org/10.1016/j.epsl.2008.12.023.

Avice, G., Marty, B., Burgess, R., 2017. The origin and degassing history of the Earth's atmosphere revealed by Archean xenon. Nat. Commun. 8, 1–9. https://doi.org/10.1038/ncomms15455.

Ballentine, C.J., Burnard, P.G., 2002. Production, release and transport of noble gases in the continental crust. Rev. Mineral. Geochem. 47, 481–538.

Barrat, J.A., Chaussidon, M., Yamaguchi, A., Beck, P., Villeneuve, J., Byrne, D.J., Broadley, M.W., Marty, B., 2021. A 4,565-My-old andesite from an extinct chondritic protoplanet. Proc. Natl. Acad. Sci. U. S. A. 118, 1–7. https://doi.org/10.1073/pnas.2026129118.

Bekaert, D.V., Broadley, M.W., Caracausi, A., Marty, B., 2019. Novel insights into the degassing history of Earth's mantle from high precision noble gas analysis of magmatic gas. Earth Planet. Sci. Lett. 525 https://doi.org/10.1016/j.epsl.2019.115766.

Bekaert, D.V., Broadley, M.W., Marty, B., 2020. The origin and fate of volatile elements on Earth revisited in light of noble gas data obtained from comet 67P/Churyumov-Gerasimenko. Sci. Rep. 10 https://doi.org/10.1038/s41598-020-62650-3.

Bekaert, D.V., Turner, S.J., Broadley, M.W., Barnes, J.D., Halldórsson, S.A., Labidi, J., Wade, J., Walowski, K.J., Barry, P.H., 2021. Subduction-driven volatile recycling: a global mass balance. Annu. Rev. Earth Planet. Sci. 70 (49), 37. https://doi.org/10.1146/annurev-earth-071620-055024.

Bekaert, D.V, Barry, P.H., Broadley, M.W., Byrne, D.J., Marty, B., Moor, J.M.De, Rodriguez, A., Hudak, M.R., Subhas, A.V, Caracausi, A., Lloyd, K.G., Giovannelli, D., Seltzer, A.M., 2023. Ultra-high precision noble gas isotope analyses reveal pervasive subsurface fractionation in hydrothermal systems. Sci. Adv. 328, 136–149.

Bekaert, D.V., Barry, P.H., Curtice, J., Blusztajn, J., Hudak, M., Seltzer, A., Broadley, M. W., Krantz, J.A., Wanless, V.D., Soule, S.A., Mittelstaedt, E., Kurz, M.D., 2024. A carbon, nitrogen, and multi-isotope study of basalt glasses near 14° N on the Mid-Atlantic Ridge. Part B: Mantle source heterogeneities. Geochim. Cosmochim. Acta 369, 179–195.

Bragagni, A., Mastroianni, F., Münker, C., Conticelli, S., Avanzinelli, R., Köln, U., Strasse, Z., 2022. A carbon-rich lithospheric mantle as a source for the large CO2 emissions of Etna volcano (Italy). Geology 50 (4), 486–490.

Bräuer, K., Kämpf, H., Niedermann, S., Strauch, G., 2013. Indications for the existence of different magmatic reservoirs beneath the Eifel area (Germany): a multi-isotope (C, N, He, Ne, Ar) approach. Chem. Geol. 356, 193–208.

Broadley, M.W., Barry, P.H., Bekaert, D.V., Byrne, D.J., Caracausi, A., Ballentine, C.J., Marty, B., 2020. Identification of chondritic krypton and xenon in Yellowstone gases and the timing of terrestrial volatile accretion. Proc. Natl. Acad. Sci 117, 13997–14004. https://doi.org/10.1073/pnas.2003907117.

Busemann, H., Baur, H., Wieler, R., 2000. Primordial noble gases in "phase Q" in carbonaceous and ordinary chondrites studied by closed-system stepped etching. Meteorit. Planet. Sci. 35, 949–973. https://doi.org/10.1111/j.1945-5100.2000.tb01485.x.

Caffee, M.W., Hudson, G.B., Velsko, C., Huss, G.R., Alexander Jr., E.C., Chivas, A.R., 1999. Primordial noble gases from Earth's mantle: identification of a primitive volatile component. Science 285, 2115–2118.

Caracas, R., Hirose, K., Nomura, R., Ballmer, M.D., 2019. Melt–crystal density crossover in a deep magma ocean. Earth Planet. Sci. Lett. 516, 202–211. https://doi.org/10.1016/j.epsl.2019.03.031.

Caracausi, A., Avice, G., Burnard, P.G., Füri, E., Marty, B., 2016. Chondritic xenon in the Earth' s mantle. Nature 1–13. https://doi.org/10.1038/nature17434.

Caracausi, A., Favara, R., Giammanco, S., Italiano, F., Paonita, A., Pecoraino, G., Rizzo, A., Nuccio, P.M., 2003. Mount Etna: geochemical signals of magma ascent and unusually extensive plumbing system. Geophys. Res. Lett. 30, 1057. https://doi.org/10.1029/2002GL015463.

Caro, G., Morino, P., Mojzsis, S.J., Cates, N.L., Bleeker, W., 2017. Sluggish Hadean geodynamics: evidence from coupled 146,147Sm–142,143Nd systematics in Eoarchean supracrustal rocks of the Inukjuak domain (Québec). Earth Planet. Sci. Lett. 457, 23–37. https://doi.org/10.1016/j.epsl.2016.09.051.

Clay, P.L., Burgess, R., Busemann, H., Ruzié-Hamilton, L., Joachim, B., Day, J.M.D., Ballentine, C.J., 2017. Halogens in chondritic meteorites and terrestrial accretion. Nature 551, 614–618. https://doi.org/10.1038/nature24625.

Correale, A., Paonita, A., Martelli, M., Rizzo, A., Rotolo, S.G., Corsaro, R.A., Di Renzo, V., 2014. A two-component mantle source feeding Mt. Etna magmatism: Insights from the geochemistry of primitive magmas. Lithos 184–187, 243–258. https://doi.org/10.1016/j.lithos.2013.10.038.

Debaille, V., O'Neill, C., Brandon, A.D., Haenecour, P., Yin, Q.Z., Mattielli, N., Treiman, A.H., 2013. Stagnant-lid tectonics in early Earth revealed by 142Nd variations in late Archean rocks. Earth Planet. Sci. Lett. 373, 83–92. https://doi.org/10.1016/j.epsl.2013.04.016.

Fan, Y., Li, H., Miguez-Macho, G., 2013. Global patterns of groundwater table depth. Science 339, 940–943. https://doi.org/10.1126/science.1229881.

Fischer, R., Gerya, T., 2016. Early Earth plume-lid tectonics: a high-resolution 3D numerical modelling approach. J. Geodyn. 100, 198–214. https://doi.org/10.1016/j.jog.2016.03.004.

Giggenbach, W.F., 1975. A simple method for the collection and analysis of volcanic gas samples. Bull. Volcanol. 39, 132–145. https://doi.org/10.1007/BF02596953.

Guitreau, M., Boyet, M., Paquette, J.L., Gannoun, A., Konc, Z., Benbakkar, M., Suchorski, K., Hénot, J.M., 2019. Hadean protocrust reworking at the origin of the Archean Napier Complex (Antarctica). Geochem. Perspect. Lett. 12, 7–11. https://doi.org/10.7185/GEOCHEMLET.1927.

Hofmann, A.W. (2003). Sampling mantle heterogeneity through oceanic basalts: isotopes and trace elements. Treatise on geochemistry, 2, 568.

Gvirtzman, Z., Nur, A., 1999. The formation of Mount Etna as the consequence of slab rollback. Nature 401 (6755), 782–785.

Holland, G., Ballentine, C.J., 2006. Seawater subduction controls the heavy noble gas composition of the mantle. Nature 441, 186–191. https://doi.org/10.1038/nature04761.

Holland, G., Cassidy, M., Ballentine, C., 2009. Meteorite Kr in Earth's mantle suggests a late accretionary source for the atmosphere. Science 326, 1522–1526.

Hudson, G.B., Kennedy, B.M., Podosek, F.A., Hohenberg, C.M., 1989. The early solar system abundance of 244Pu as inferred from the St. Severin chondrite. In: Proceedings of the 19th Lunar and Planetary Science Conference. Lunar and Planetary Institute, pp. 547–557.

Jackson, C.R.M., Bennett, N.R., Du, Z., Cottrell, E., Fei, Y., 2018. Early episodes of high-pressure core formation preserved in plume mantle. Nature 553, 491–494. https://doi.org/10.1038/nature25446.

Jones, J.H., 1982. The geochemical coherence of Pu and Nd and the 244Pu238U ratio of the early solar system. Geochim. Cosmochim. Acta 46, 1793–1804. https://doi.org/10.1016/0016-7037(82)90118-1.

Jordan, T.H., 1988. Structure and formation of the continental tectosphere. J. Petrol. Special_Volume, 11–37. https://doi.org/10.1093/petrology/Special_Volume.1.11.

Korenaga, J., 2021. Hadean geodynamics and the nature of early continental crust. Precambr. Res 359, 106178. https://doi.org/10.1016/j.precamres.2021.106178.

Labidi, J., Barry, P.H., Bekaert, D.V., Broadley, M.W., Marty, B., Giunta, T., Warr, O., Sherwood Lollar, B., Fischer, T.P., Avice, G., Caracausi, A., Ballentine, C.J., Halldorsson, S.A., Stefansson, A., Kurz, M.D., Kohl, I.E., Young, E.D., 2020. Hydrothermal $^{15}N^{15}N$ abundances constrain the origins of mantle nitrogen. Nature 580 (7803), 367–371.

Lee, J.Y., Marti, K., Severinghaus, J.P., Kawamura, K., Yoo, H.S., Lee, J.B., Kim, J.S., 2006. A redetermination of the isotopic abundances of atmospheric Ar. Geochim. Cosmochim. Acta 70, 4507–4512. https://doi.org/10.1016/j.gca.2006.06.1563.

Liou, P., Caro, G., Cui, X., Li, C., Peng, P., Guo, J., Zhai, M., 2024. Long-term isolation of Hadean mantle domains revealed from coupled $^{147\text{-}146}$Sm-$^{143\text{-}142}$Nd systematics in the eastern North China Craton. Earth Planet. Sci. Lett. 638, 118761.

Liu, W., Zhang, Y., Tissot, F.L.H., Avice, G., Ye, Z., Yin, Q.Z., 2023. I/Pu reveals Earth mainly accreted from volatile-poor differentiated planetesimals. Sci. Adv. 9 https://doi.org/10.1126/sciadv.adg9213.

McKinney, C.R., McCrea, J.M., Epstein, S., Allen, H.A., Urey, H.C., 1950. Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios. Rev. Sci. Instrum. 21, 724–730. https://doi.org/10.1063/1.1745698.

Meshik, A., Pravdivtseva, O., Burnett, D., 2020. Refined composition of Solar Wind xenon delivered by Genesis NASA mission: comparison with xenon captured by extraterrestrial regolith soils. Geochim. Cosmochim. Acta 276, 289–298. https://doi.org/10.1016/j.gca.2020.03.001.

Morino, P., Caro, G., Reisberg, L., 2018. Differentiation mechanisms of the early Hadean mantle: Insights from combined 176Hf-142,143Nd signatures of Archean rocks from the Saglek Block. Geochim. Cosmochim. Acta 240, 43–63. https://doi.org/10.1016/j.gca.2018.08.026.

Morino, P., Caro, G., Reisberg, L., Schumacher, A., 2017. Chemical stratification in the post-magma ocean Earth inferred from coupled 146,147Sm–142,143Nd systematics

in ultramafic rocks of the Saglek block (3.25–3.9 Ga; northern Labrador, Canada). Earth Planet. Sci. Lett. 463, 136–150. https://doi.org/10.1016/j.epsl.2017.01.044.
Mukhopadhyay, S., 2012. Early differentiation and volatile accretion recorded in deep-mantle neon and xenon. Nature 486, 101–104. https://doi.org/10.1038/nature11141.
Mukhopadhyay, S., Parai, R., 2019. Noble gases: A record of earth's evolution and mantle dynamics. Annu. Rev. Earth Planet. Sci. 47, 389–419. https://doi.org/10.1146/annurev-earth-053018-060238.
Nakai, S., Wakita, H., Nuccio, M.P., Italiano, F., 1997. MORB-type neon in an enriched mantle beneath Etna, Sicily. Earth Planet. Sci. Lett. 153, 57–66. https://doi.org/10.1016/s0012-821x(97)00161-1.
Newcombe, M.E., Nielsen, S.G., Peterson, L.D., Wang, J., Alexander, C.M.O.D., Sarafian, A.R., Shimizu, K., Nittler, L.R., Irving, A.J., 2023. Degassing of early-formed planetesimals restricted water delivery to Earth. Nature 615, 854–857. https://doi.org/10.1038/s41586-023-05721-5.
Nielsen, S.G., 2010. Potassium and uranium in the upper mantle controlled by Archean oceanic crust recycling. Geology 38, 683–686. https://doi.org/10.1130/G30852.1.
O'Neil, J., Carlson, R.W., Francis, D., Stevenson, R.K., 2008. Neodymium-142 evidence for Hadean Mafic Crust. Science 321, 1828–1831.
Ozima, M., Podosek, F.A., 2002. Noble gas geochemistry, 2nd edition. Cambridge University Press, p. 286.
Paonita, A., Liuzzo, M., Salerno, G., Federico, C., Bonfanti, P., Caracausi, A., Giuffrida, G., La Spina, A., Caltabiano, T., Gurrieri, S., Giudice, G., 2021. Intense overpressurization at basaltic open-conduit volcanoes as inferred by geochemical signals: the case of the Mt. Etna December 2018 eruption. Sci. Adv 7, eabg6297. https://doi.org/10.1126/sciadv.abg6297.
Parai, R., Mukhopadhyay, S., Standish, J.J., 2012. Heterogeneous upper mantle Ne, Ar and Xe isotopic compositions and a possible Dupal noble gas signature recorded in basalts from the Southwest Indian Ridge. Earth Planet. Sci. Lett. 359, 227–239.
Parai, R., 2023. Primordial noble gas isotopes from immoderate crushing of an Icelandic basalt glass. Geochem. Perspect. Lett. 27, 32–37. https://doi.org/10.7185/GEOCHEMLET.2331.
Parai, R., 2022. A dry ancient plume mantle from noble gas isotopes. Proc. Natl. Acad. Sci. 119 (29), e2201815119.
Parai, R., Mukhopadhyay, S., 2021. Heavy noble gas signatures of the North Atlantic Popping Rock 2ΠD43: Implications for mantle noble gas heterogeneity. Geochim. Cosmochim. Acta 294, 89–105. https://doi.org/10.1016/j.gca.2020.11.011.
Parai, R., Mukhopadhyay, S., 2018. Xenon isotopic constraints on the history of volatile recycling into the mantle. Nature 560, 223–227. https://doi.org/10.1038/s41586-018-0388-4.
Parai, R., Mukhopadhyay, S., 2015. The evolution of MORB and plume mantle volatile budgets: constraints from fission Xe isotopes in Southwest Indian Ridge basalts. Geochem. Geophys. Geosyst. 16, 719–735.
Parai, R., Mukhopadhyay, S., Tucker, J.M., Pető, M.K., 2019. The emerging portrait of an ancient, heterogeneous and continuously evolving mantle plume source. Lithos 346–347. https://doi.org/10.1016/j.lithos.2019.105153.
Pepin, R.O., 2000. On the isotopic composition of primordial xenon in terrestrial planet atmospheres. Space Sci. Rev. 92, 371–395. https://doi.org/10.1023/a:1005236405730.
Pepin, R.O., Porcelli, D., 2006. Xenon isotope systematics, giant impacts, and mantle degassing on the early Earth. Earth Planet. Sci. Lett. 250, 470–485. https://doi.org/10.1016/j.epsl.2006.08.014.
Péron, S., Moreira, M., 2018. Onset of volatile recycling into the mantle determined by xenon anomalies. Geochem. Perspect. Lett. 9, 21–25. https://doi.org/10.7185/geochemlet.1833.
Péron, S., Moreira, M.A., Kurz, M.D., Curtice, J., Blusztajn, J.S., Putlitz, B., Wanless, V.D., Jones, M.P., Soule, S.A., Mittelstaedt, E., 2019. Noble gas systematics in new popping rocks from the Mid-Atlantic Ridge (14° N): evidence for small-scale upper mantle heterogeneities. Earth Planet. Sci. Lett. 519, 70–82.
Péron, S., Mukhopadhyay, S., Kurz, M.D., Graham, D.W., 2021. Deep-mantle krypton reveals Earth's early accretion of carbonaceous matter. Nature 600, 462–467. https://doi.org/10.1038/s41586-021-04092-z.
Reimink, J.R., Chacko, T., Carlson, R.W., Shirey, S.B., Liu, J., Stern, R.A., Bauer, A.M., Pearson, D.G., Heaman, L.M., 2018. Petrogenesis and tectonics of the Acasta Gneiss Complex derived from integrated petrology and 142Nd and 182W extinct nuclide-geochemistry. Earth Planet. Sci. Lett. 494, 12–22. https://doi.org/10.1016/j.epsl.2018.04.047.
Schneider, K.P., Hoffmann, J.E., Boyet, M., Münker, C., Kröner, A., 2018. Coexistence of enriched and modern-like 142 Nd signatures in Archean igneous rocks of the eastern Kaapvaal Craton, Southern Africa. Earth Planet. Sci. Lett. 487, 54–66. https://doi.org/10.1016/j.epsl.2018.01.022.
Seltzer, A.M., Bekaert, D.V., 2022. A unified method for measuring noble gas isotope ratios in air, water, and volcanic gases via dynamic mass spectrometry. Int. J. Mass Spectrom. 478, 116873 https://doi.org/10.1016/j.ijms.2022.116873.
Seltzer, A.M., Ng, J., Danskin, W.R., Kulongoski, J.T., Gannon, R.S., Stute, M., Severinghaus, J.P., 2019. Deglacial water-table decline in Southern California recorded by noble gas isotopes. Nat. Commun. 10, 1–6. https://doi.org/10.1038/s41467-019-13693-2.
Seltzer, A.M., Shackleton, S.A., Bourg, I.C., 2023. Solubility equilibrium isotope effects of noble gases in water: theory and observations. J. Phys. Chem. B 127 (45), 9802–9812.
Severinghaus, J.P., Bender, M.L., Keeling, R.F., Broecker, W.S., 1996. Fractionation of soil gases by diffusion of water vapor, gravitational settling, and thermal diffusion. Geochim. Cosmochim. Acta 60, 1005–1018.
Tonarini, S., Armienti, P., D'Orazio, M., Innocenti, F, 2001. Subduction-like fluids in the genesis of Mt. Etna magmas: evidence from boron isotopes and fluid mobile elements. Earth Planet. Sci. Lett. 192 (4), 471–483.
Tucker, J.M., Mukhopadhyay, S., Schilling, J.G., 2012. The heavy noble gas composition of the depleted MORB mantle (DMM) and its implications for the preservation of heterogeneities in the mantle. Earth Planet. Sci. Lett 355–356, 244–254. https://doi.org/10.1016/j.epsl.2012.08.025.
Turner, G., Busfield, A., Crowther, S.A., Harrison, M., Mojzsis, S.J., Gilmour, J., 2007. Pu-Xe, U-Xe, U-Pb chronology and isotope systematics of ancient zircons from Western Australia. Earth Planet. Sci. Lett. 261, 491–499. https://doi.org/10.1016/j.epsl.2007.07.014.
Zhang, X.J., Avice, G., Parai, R., 2023. Noble gas insights into early impact delivery and volcanic outgassing to Earth's atmosphere: a limited role for the continental crust. Earth Planet. Sci. Lett. 609, 118083 https://doi.org/10.1016/j.epsl.2023.118083.