

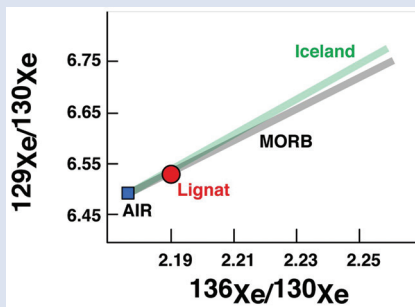
The xenon isotopic signature of the mantle beneath Massif Central

M. Moreira^{1*}, V. Rouchon², E. Muller¹, S. Noirez²



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Abstract



The origin of the Central European Volcanic Province, which includes the Massif Central and the Eifel regions, is currently debated. Several different causes have been proposed to account for the volcanism observed in the area. Namely, both the presence of one or more mantle plumes under Europe, and the upwelling and melting of upper mantle related to the formation of the Alps, have been suggested as possible drivers of volcanism. In order to distinguish between these possibilities, we have analysed noble gases in the Lignat Spring to constrain the nature of the mantle source below the Massif Central. The gas has a $^3\text{He}/^4\text{He}$ ratio of 5.51 Ra, whereas its neon isotopic signature is identical to that of MORB source. The gas has an $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 1113 ± 3 , far in excess of the atmospheric ratio. The xenon isotopic pattern is explained by 95 % atmospheric contamination of a MORB-like gas. The noble gases clearly show that the mantle beneath Massif

Central has a geochemical signature similar to MORB source mantle, with the exception of helium, which more closely corresponds to SCLM signatures, and thus removes the need for the presence of a mantle plume in the region.

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Introduction

Noble gases are excellent records of interactions between the mantle and the atmosphere over geological history, and provide important information on the origin and evolution of volatiles on Earth. Helium and neon are clear markers of the layered structure of the mantle, because their isotopic ratios are less radiogenic in most Oceanic Island Basalts (OIB) than in Mid Ocean Ridge Basalts (MORB), which is interpreted as reflecting the existence of a deep undegassed mantle, the source of mantle plumes (Kurz *et al.*, 1982; Honda *et al.*, 1991; Moreira and Allègre, 1998). Xenon in oceanic basalts also places strong constraints on the degassing history of the mantle and on the origin and evolution of volatiles (Ozima *et al.*, 1985; Kunz *et al.*, 1998; Mukhopadhyay, 2012). Radiogenic/fissionogenic isotopic ratios ($^{129}, ^{131-136}\text{Xe}/^{130}\text{Xe}$) are well constrained in the sources of MORB and OIB using neon as a proxy for the degree of contamination by air (Moreira *et al.*, 1998; Mukhopadhyay, 2012). However, due to their low abundances, non-radiogenic isotopes ($^{124-128}, ^{130}\text{Xe}$) are difficult to analyse, and hence only a few gas-rich samples, such as CO_2 -well gases, can be accurately measured. These samples therefore provide fundamental constraints on the origin and evolution of terrestrial noble gases (Caffee *et al.*, 1999; Holland and Ballentine, 2006). Existing evidence shows that the primitive mantle had a chondritic xenon isotope composition

(Holland and Ballentine, 2006; Holland *et al.*, 2009), and that the xenon of the Hadean atmosphere was a mixture of chondritic and cometary xenon (Marty *et al.*, 2017). Since the Hadean, the atmosphere has progressively lost Xe, such that <10 % remains today. The physical mechanism for such loss is unknown, however it has caused considerable isotopic fractionation and resulted in the present-day atmospheric isotopic composition (Pujol *et al.*, 2011). Furthermore, subduction of atmospheric xenon has modified the non-radiogenic xenon isotopic ratios of the mantle from a chondritic ratio down to the present-day mantle composition (Holland and Ballentine, 2006).

If subduction of atmospheric xenon is possible, then the homogeneity of the xenon isotopic composition in different mantle sources is an enigma. One might expect significant variations in all xenon isotopic ratios. However, xenon analysis in oceanic basalts remains difficult because of its low abundance, in addition to the presence of a ubiquitous atmospheric contaminant that masks the mantle signature (Ballentine and Barfod, 2000). In order to circumvent this difficulty, gases from thermal springs, where CO_2 degasses naturally, are analysed, as they carry also mantle-derived noble gases. Indeed, mantle-derived noble gas signatures are observed at Victoriaquelle in the Eifel volcanic region, Germany (Brauer *et al.*, 2013). Recently, this spring has been studied for xenon, providing constraints on the xenon composition of the mantle

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and on the nature of volcanism in the Eifel region (Caracausi *et al.*, 2016). Interestingly, the authors observed a xenon signature that does not fall on the MORB-OIB line in the $^{129}\text{Xe}/^{130}\text{Xe}$ - $^{136}\text{Xe}/^{130}\text{Xe}$ diagram, although the He and Ne clearly have signatures consistent with their derivation from MORB- or Sub Continental Lithospheric Mantle (SCLM)-sources (Brauer *et al.*, 2013). More surprisingly, they report $^{124-128}\text{Xe}$ anomalies for a sample with more than 90 % atmospheric contamination, which is interpreted as reflecting the chondritic signature of the Eifel mantle source for these isotopes. In order to determine whether this is a widespread feature of the European mantle or whether it is specific to the Eifel region, we have analysed the isotopic ratios of each of the noble gases in the Lignat thermal spring, Massif Central. The Massif Central, like the Eifel, belongs to the Central European Volcanic Province (CEVP), in which the cause of volcanism is a matter of debate. Several scenarios have been proposed to account for the widespread volcanism in the region: an asthenospheric upwelling resulting from the formation of a deep lithospheric root under the Alps (Merle and Michon, 2001), the melting of the Sub-Continental Lithospheric Mantle (SCLM) (Gautheron *et al.*, 2005) or a deep-seated mantle plume (*e.g.*, Buikin *et al.*, 2005). Our results show that noble gases have signatures consistent with those expected from a mantle source similar to that of MORB, obviating the need for a deep mantle plume.

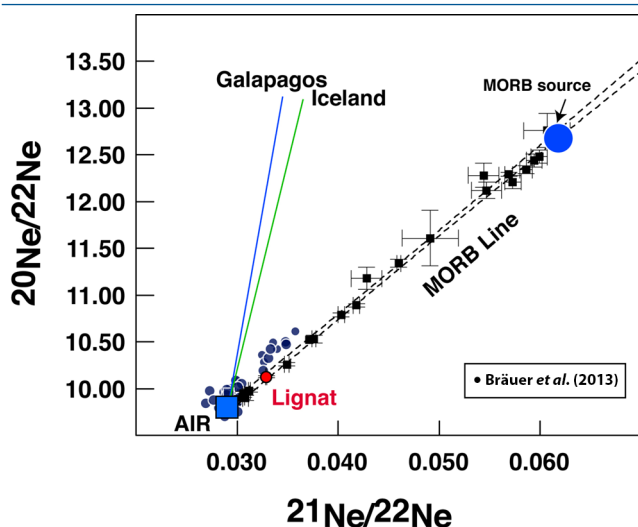


Figure 1 Three-neon isotope diagram. MORB data are from Moreira *et al.* (1998) and define the MORB-AIR mixing line (Sarda *et al.*, 1988), which has a different slope than the OIB mixing lines (Honda *et al.*, 1991; Moreira *et al.*, 2001). The OIB mixing lines are from Mukhopadhyay (2012) and Peron *et al.* (2016). The MORB source has a $^{20}\text{Ne}/^{22}\text{Ne}$ ~12.5. The neon in Lignat spring comes from the mixture of mantle-derived (~12 %) and atmospheric neon (~88 %). Data from the Eifel area are also reported (Brauer *et al.*, 2013).

Sample Location, Sampling, Analytical Procedure and Results

The Lignat spring ("La Gargouillère") is located in the Massif Central, ~15 km from Clermont Ferrand, France (45°42'23" N, 3°15'42" E). This source was selected because of its vigorous eruptive activity that liberates pure CO₂. The gas was collected in January 2017 in a 5 litre stainless-steel reservoir. The gas was analysed at IPEN for abundances of major gases and noble gases. It contains 100 % CO₂, 38 ppm helium, 6 ppb neon, 53 ppm argon and 0.8 ppb xenon. The CO₂ δ¹³C is -3.6 ‰ and the CO₂/³He is 3.7 × 10⁹. Noble gas isotopic compositions were

analysed at IPGP following the analytical procedure described in the Supplementary Information.

Results for the Lignat gas are given in Tables S-1 and S-2. In the discussion that follows, the mean compositions of the aliquots are used. The $^3\text{He}/^4\text{He}$ ratio is 5.51 ± 0.03 Ra (1σ) (Ra is the atmospheric ratio = 1.384×10^{-6}). The $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ isotopic ratios are 10.118 ± 0.009 and 0.03297 ± 0.00005 , respectively (air: 9.8 and 0.0290). In the three-neon isotope diagram, the Lignat gas falls on the MORB line (Fig. 1). The $^{38}\text{Ar}/^{36}\text{Ar}$ ratio is atmospheric (0.18833 ± 0.00015), within uncertainty. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is higher (1113 ± 3) than the atmospheric ratio (295.5). Krypton isotopes are not reported because all measured isotopic ratios are atmospheric within uncertainty. Xenon isotopes are given in Table S-2. The $^{129}\text{Xe}/^{130}\text{Xe}$, $^{134}\text{Xe}/^{130}\text{Xe}$ and $^{136}\text{Xe}/^{130}\text{Xe}$ isotopic ratios of the Lignat gas are reported in Figure 2 and compared with those of MORB (Kunz *et al.*, 1998; Parai *et al.*, 2012; Tucker *et al.*, 2012), Iceland (Mukhopadhyay, 2012) and Eifel (Caracausi *et al.*, 2016). Although the excesses are small, the gas contains a detectable contribution of mantle-derived xenon. The Lignat gas falls on the MORB/Iceland line and is clearly different from the Eifel gas value in a $^{129}\text{Xe}/^{130}\text{Xe}$ - $^{136}\text{Xe}/^{130}\text{Xe}$ diagram. The non-radiogenic isotopic ratios $^{124}\text{Xe}/^{130}\text{Xe}$, $^{126}\text{Xe}/^{130}\text{Xe}$ and $^{128}\text{Xe}/^{130}\text{Xe}$ are atmospheric within uncertainty.

Discussion

Helium, neon, $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{129-136}\text{Xe}/^{130}\text{Xe}$ isotopic ratios suggest the contribution of mantle-derived gas in the Lignat spring, consistent with the CO₂/³He and δ¹³C values measured. Helium is more radiogenic than the mean MORB ratio of 8 ± 1 Ra (Allègre *et al.*, 1995), and within uncertainty of the mean SCLM ratio of 6.1 ± 0.9 Ra (Gautheron and Moreira, 2002). Neon isotopes suggest a simple binary mixing between air/water and a MORB-like derived gas. A simple calculation indicates that ~12 % of the neon is derived from the mantle, assuming a $^{20}\text{Ne}/^{22}\text{Ne}$ for the MORB source of 12.5 (Ballentine, 1997; Moreira *et al.*, 1998). Xenon isotope systematics also suggest binary mixing between air and a MORB-like gas. However, because MORB and OIB fall on the same mixing line, a plume-like contribution cannot be excluded based on xenon alone. Nevertheless, the neon isotope systematics, which are sensitive to the contribution of primitive mantle (Moreira and Allègre, 1998; Hopp *et al.*, 2004), appear to preclude the contribution of deep mantle material in the source of the Lignat spring. Trends of simple binary mixing between atmospheric- and mantle-derived Xe are illustrated in Figure 3. Here, the isotopic composition of the mixture between 5 % of a MORB-like gas and 95 % of an atmospheric gas is shown. The MORB signature is estimated using both MORB data from Kunz *et al.* (1998) and CO₂-well gases by Holland and Ballentine (2006). The final composition is insensitive to this choice, as both calculated compositions are similar (Table S-2; Fig. 3). On the basis of this model, the Xe isotope composition of Lignat spring can be satisfactorily explained by binary mixing. It also accounts for the absence of any $^{124-128}\text{Xe}$ excesses in the spring. In detail, because the gas contains ~95 % air-derived xenon, this atmospheric contribution completely masks the present-day mantle composition for these isotopes, which could not be chondritic because the mantle was "contaminated" by subducted atmospheric xenon (Holland and Ballentine, 2006).

The $^{131-136}\text{Xe}/^{130}\text{Xe}$ isotopic signature of gases from the Eifel region determined by Caracausi *et al.* (2016) is identical to that of the Lignat gas (Fig. 3). However, the cause of excesses in $^{124-129}\text{Xe}$ isotopes in the Eifel springs remains unclear. The significant air contribution (95 %) needed to explain the heavy xenon isotopic compositions in both gases should not produce

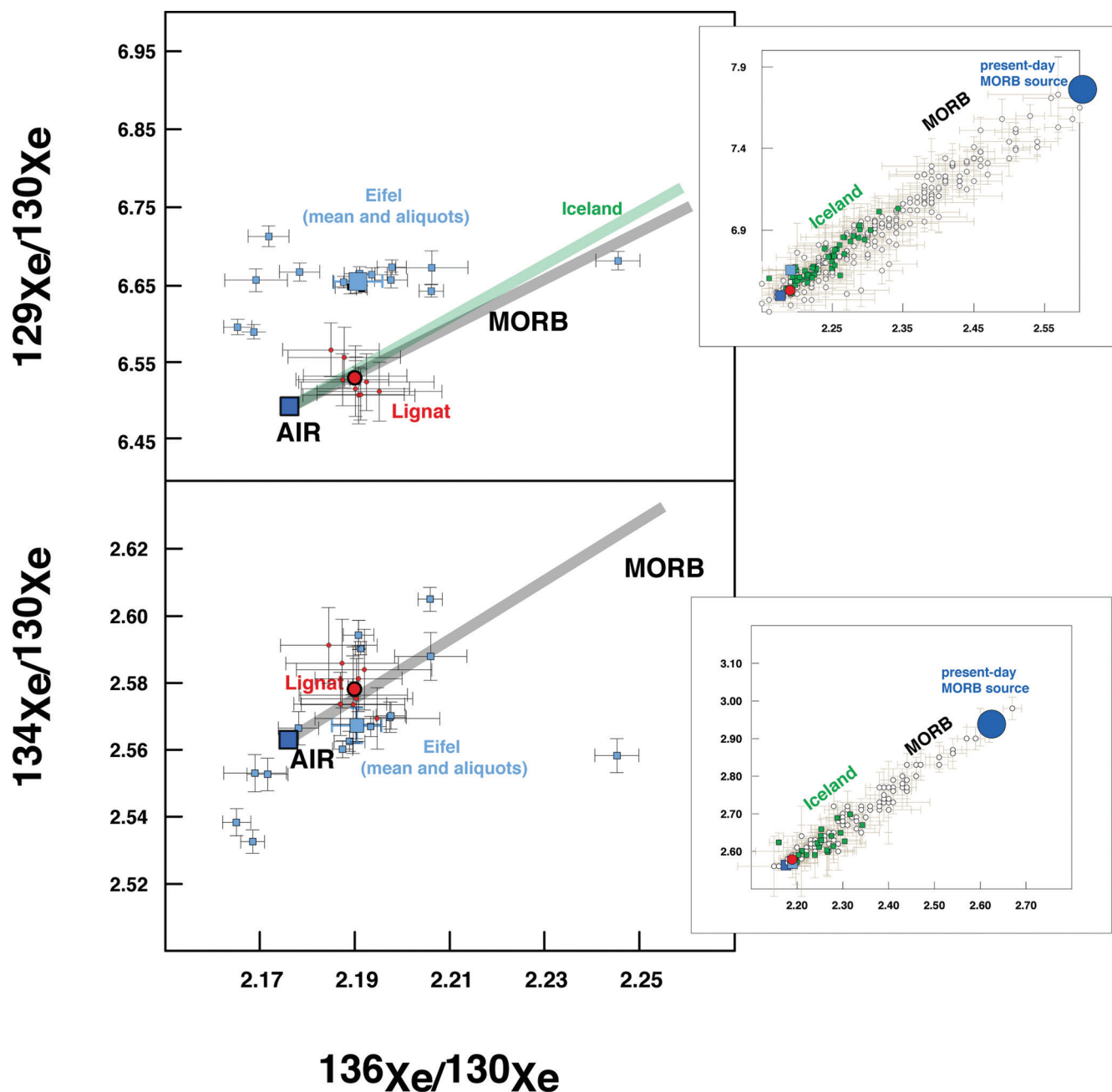


Figure 2 Xenon isotopes in the Lignat gas (aliquots: small red dots; mean: large red dot), compared to MORB (Kunz *et al.*, 1998; Parai *et al.*, 2012; Tucker *et al.*, 2012) and Iceland basalts (Mukhopadhyay, 2012). The Eifel gas is shown for comparison (small blue squares: aliquots, large blue square: mean) (Caracausi *et al.*, 2016). The inserts represent the global scale of variation in mantle-derived samples.

a detectable excess of non-radiogenic isotopes when using the observed present-day mantle composition. Even if the present-day mantle had a chondritic composition in these isotopes, given 95 % contamination by air, then an excess of only 3 ‰ should be observed for the $^{128}\text{Xe}/^{130}\text{Xe}$ ratio, rather than the 15–25 ‰ reported by Caracausi *et al.* (2016). Moreover, a mantle source with a solely chondritic non-radiogenic xenon isotope composition for has not been observed in mantle-derived samples. Certainly, in MORB or CO₂-well gas sources, there is no hint of such a signature (Kunz *et al.*, 1998; Holland and Ballentine, 2006), and the same is true for OIB. The $^{128}\text{Xe}/^{130}\text{Xe}$ ratios measured in Iceland basalts are close to the atmospheric value, and are distinct from chondritic $^{128}\text{Xe}/^{130}\text{Xe}$ value in high $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{129}\text{Xe}/^{130}\text{Xe}$ crushing steps (Mukhopadhyay, 2012).

Based on our study, a plume origin is not required to cause the volcanism observed in the Massif Central. By contrast, a plume scenario is still permissible in the Eifel region. Based on neon isotopes measured on xenoliths, Buikin *et al.* (2005) suggest that there is a mantle plume contributing to the European intraplate magmatism, an interpretation challenged by other authors who argue that the source was restricted to the upper mantle (Gautheron *et al.*, 2005; Brauer *et al.*, 2013). A deep mantle plume origin was also suggested based on xenon isotopes by Caracausi *et al.* (2016) on the basis of the $^{129}\text{Xe}/^{136}\text{Xe}$ ratio, which appears to be close to that of Icelandic basalts (Mukhopadhyay, 2012). However, for the aforementioned reasons, other explanations are required to account for the high $^{124-129}\text{Xe}/^{130}\text{Xe}$ ratios in these air-contaminated gases (Fig. 3). For the Eifel, a simple MORB-AIR mixing scenario

would not be able to satisfy both the $^{131-136}\text{Xe}/^{130}\text{Xe}$, He, Ne isotopic ratios and the $^{124-129}\text{Xe}/^{130}\text{Xe}$ ratios. A deep mantle plume origin for the volcanism in Eifel therefore remains questionable and further work is clearly required to understand the signatures observed in springs in both the Massif Central and the Eifel.

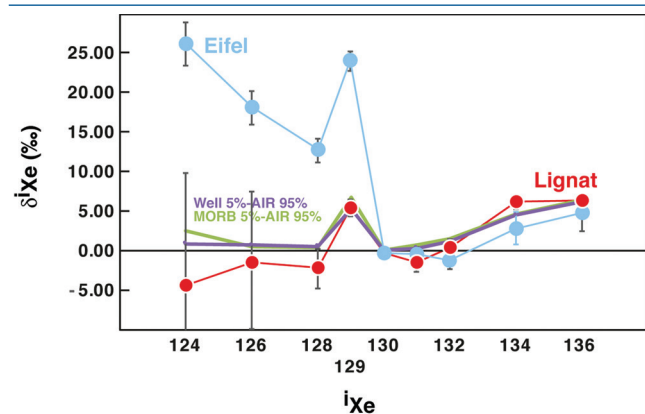


Figure 3 Xenon isotopic ratios in the Lignat gas expressed in % deviation relative to the atmospheric composition. Assuming the xenon composition reflects mixing between air and MORB (or CO_2 -well gas; Holland and Ballentine, 2006), one can estimate the proportion of atmospheric xenon. Using the $^{136}\text{Xe}/^{130}\text{Xe}$ ratio, 95 % of the ^{130}Xe in the Lignat source is sourced from the air. The other isotopic ratios can be estimated using this mixing proportion. Two patterns are given for the result of this mixing: violet using CO_2 -well gas and green using the mean MORB-source ratios (Table S-2). The Lignat gas satisfies a simple binary mixture between air and MORB. Although the Eifel gas (blue circles) shows the same pattern for fissiogenic isotopes, it exhibits notable excesses in light Xe isotopes that are unaccounted for by the MORB-AIR mixing model.

Conclusions

We have analysed noble gases in the Lignat thermal spring (Massif Central) in order to characterise the noble gas isotopic composition of the mantle under the CEVP. The sample shows extensive atmospheric contamination, but measurable mantle-derived noble gases. The $^3\text{He}/^4\text{He}$ ratio is 5.51 ± 0.03 Ra. The neon isotopic composition falls exactly on the MORB line in the three-neon isotope diagram. The $^{124-128}\text{Xe}/^{130}\text{Xe}$ ratios are atmospheric within uncertainties whereas $^{129-136}\text{Xe}/^{130}\text{Xe}$ ratios show evidence for the contribution of a typical MORB signature, in agreement with the neon isotope systematics. The isotopic spectrum of xenon is well explained by a mixture between atmospheric and present-day MORB-source xenon. The mantle under Massif Central thus appears distinct from the mantle beneath Eifel.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1805>.



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■ The xenon isotopic signature of the mantle beneath Massif Central

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■ Supplementary Information

The Supplementary Information includes:

- Analytical Procedure
- Tables S-1 to S-2
- Supplementary Information References

Analytical Procedure

Nine aliquots of the gas were analysed. Each aliquot corresponds to a volume of gas of 0.2 cm³ equilibrated with the 5-litre sampling reservoir. A first stage of gas purification using a Bulk Getter (SAES) was performed during 5 minutes at 400 °C and the heating system was then turned off to decrease the temperature of the getter to ~25 °C. After 15 minutes, the gas was purified a second time using titanium sponge at 800 °C for 5 minutes, and then the heating system was turned off. After 10 minutes a third purification was completed with a second titanium sponge getter at 800 °C for 5 minutes. After 10 minutes the noble gases, except helium, were adsorbed during 15 minutes on activated charcoal at 30 K. Helium is introduced into the Helix-SFT mass spectrometer (Thermo Instruments ©) and analysed using peak jumping (due to hysteresis problems when analysing the five noble gases, we have preferred using this method in spite the Helix-SFT allows multi collection for helium). ³He is collected on the electron multiplier in pulse counting mode whereas ⁴He is analysed on the faraday cup and the signal is amplified using either the 10¹¹ ohms or the 10¹² ohms resistance depending of the signal. The gain between the two resistances is systematically measured after the helium analysis. Over three years, the gain is very constant and the value is 11.09. To obtain the position of the ³He peak, a scan of HD+H₂ is performed before the introduction of helium and a fixed difference of magnetic field is applied to determine the field for ³He. The scan of ⁴He is performed after the introduction of the helium into the instrument to get the magnetic field necessary for ⁴He. After helium measurement, neon is released from the cold trap at 70 K. Two cycles of neon isotope measurement are performed before neon introduction to stabilize the magnet. For each cycle, ²⁰Ne is measured using a mass-scan instead of setting the magnet on the required field to measure ²⁰Ne. This method is applied because it turned out that it allows a better determination of ²⁰Ne during the data processing. Indeed, the partial contributions of ⁴⁰Ar⁺⁺, HF⁺ and H₂O⁺ on the peak at mass 20 were difficult to estimate using only measurement at a given magnetic field due to hysteresis problems. ²¹Ne, ²²Ne, ⁴⁰Ar and CO₂ were measured during 10 seconds each using peak switching. Argon is partially desorbed at 130 K and transferred to charcoal at a temperature of liquid nitrogen for 15 minutes. After desorption of argon at room temperature from the charcoal trap, dilution(s) using a 1 litre balloon is used to decrease the amount of argon introduced into the mass spectrometer. ³⁶Ar and ³⁸Ar are collected on the electron multiplier whereas ⁴⁰Ar is measured on faraday using the 10¹¹ ohms resistance. Krypton is partially desorbed at 160 K and transferred to charcoal at a temperature of liquid nitrogen for 15 minutes. All krypton isotopes are analysed using the electron multiplier. Xenon is desorbed at 320 K and introduced into the mass spectrometer after 5 minutes purification with a cold SAES getter for analyse using the electron multiplier. The dead time of the electron multiplier and its pulse counting system was determined at 35 ns using alternative measurements of ⁴He on faraday and on electron multiplier. He, Ne, Ar and Kr were

analysed using an acceleration voltage of 4.5 kV. Xenon is analysed using an acceleration voltage of 3 kV. The acquisition software is home-made and written in C#© in order to be used together with the software of the extraction and purification line written in Labview©. Each gas has its own tuning in order to get the better sensitivity for each. For all gases, except helium, the trap current is at 250 μ A (helium is at 400). Data processing is performed using our home-made software written in Matlab©. Each isotope is interpolated to the time of the reference isotope and isotopic ratios are calculated for each cycle at the time of the reference isotopes. Linear or polynomial fittings are used to extrapolate to the introduction time. These extrapolated ratios are then corrected for mass discrimination and blank corrections to produce the final isotopic ratios given in Tables S-1 and S-2. For the error propagation, we use the following strategy. For samples, blanks and standards, the uncertainty on one isotopic ratio corresponds to $STD/n^{1/2}$ where n is the number of cycles (15 or 20) and STD is the standard deviation of the extrapolated ratio. The mass discrimination of the mass spectrometer is estimated using the mean of standards measured during a given period of time. The uncertainty on the mass discrimination is the standard deviation of all standards. Final uncertainties for the isotopic ratios in samples correspond to the error propagation of the measured uncertainty, of the blank correction, and of the correction for mass discrimination. For Ne, Ar, Kr and Xe, the standard is the atmosphere (pipette 0.1 cm³ and a reservoir volume of 2 litres). The standard was prepared using 10 pipettes of 0.1 cm³ at atmospheric pressure introduced in the reservoir previously in ultra-high vacuum. The helium standard is a gas collected at the Irene thermal spring (Reunion island) with a ³He/⁴He ratio of 12.56 ± 0.05 Ra. For the present study, blank corrections were negligible. Because Nier sources are known to fractionate isotopic ratios with the gas pressure, we have paid attention to have similar ²²Ne, ⁴⁰Ar, ¹³⁰Xe introduced into the mass spectrometer for aliquots and air standards (Tables S-1 and S-2).

We use for the discussion the mean of all aliquots (Tables S-1 and S-2). The uncertainty on this mean is the standard deviation divided by $n^{1/2}$ where n=9.



Supplementary Tables

Table S-1 He-Ne-Ar isotopic compositions of gas aliquots from the Lignat source. We give also in the last line the mean measured values and standard deviations of our air standards.

	R/Ra	1 σ	²² Ne (cps) ²	²⁰ Ne/ ²² Ne	1 σ	²¹ Ne/ ²² Ne	1 σ	⁴⁰ Ar (fA) ²	³⁸ Ar/ ³⁶ Ar	1 σ	⁴⁰ Ar/ ³⁶ Ar	1 σ
#1	5.44	0.13	7443	10.100	0.027	0.03288	0.00020	329.7	0.18803	0.00073	1124	8
#2	5.68	0.13	7824	10.114	0.027	0.03296	0.00023	335.7	0.18758	0.00075	1105	8
#3	5.58	0.12	6430	10.107	0.028	0.03290	0.00020	287.2	0.18822	0.00079	1107	8
#4	5.46	0.12	6457	10.136	0.025	0.03267	0.00019	287.0	0.18877	0.00069	1097	7
#5	5.52	0.12	6516	10.070	0.029	0.03289	0.00023	288.0	0.18788	0.00083	1109	8
#6	5.46	0.12	6424	10.153	0.027	0.03310	0.00019	284.7	0.18870	0.00079	1122	8
#7	5.48	0.12	6388	10.124	0.032	0.03312	0.00022	284.2	0.18824	0.00074	1110	8
#8	5.46	0.12	6422	10.105	0.028	0.03307	0.00020	277.7	0.18857	0.00076	1124	8
#9	5.44	0.12	6207	10.148	0.026	0.03315	0.00019	275.7	0.18899	0.00077	1122	8
Mean \pm STD/$\sqrt{9}$	5.51	0.03		10.118	0.009	0.03297	0.00005		0.18833	0.00015	1113	3
AIR	1			9.800		0.02900			0.1880		296	
AIRS measured ¹			7587 \pm 192	10.195	0.023	0.02934	0.00012	244.0 \pm 3.1	0.19519	0.00068		

1: uncertainties are 1 standard deviation of all standards.

2: ²²Ne and ⁴⁰Ar introduced into the mass spectrometer in cps and fA.



Table S-2 Xe isotopic compositions of gas from the Lignat source (Massif Central). The MORB compositions are derived from Kunz *et al.* (1998) using the mean of MORB with $^{129}\text{Xe}/^{130}\text{Xe}$ above 7.3 to minimise air contamination. We use also the CO₂ well gas WBD04-B samples from Holland and Ballentine (2006) as a possible MORB composition. Both compositions are similar. We also provide in the last line the mean *measured* value and the standard deviation of our standards.

	^{130}Xe introduced (cps)	$^{124}\text{Xe}/$ ^{130}Xe	±	$^{126}\text{Xe}/$ ^{130}Xe	±	$^{128}\text{Xe}/$ ^{130}Xe	±	$^{129}\text{Xe}/$ ^{130}Xe	±	$^{131}\text{Xe}/$ ^{130}Xe	±	$^{132}\text{Xe}/$ ^{130}Xe	±	$^{134}\text{Xe}/$ ^{130}Xe	±	$^{136}\text{Xe}/$ ^{130}Xe	±
#1	1140	0.02368	0.00095	0.02127	0.00087	0.4713	0.0025	6.511	0.036	5.206	0.023	6.610	0.042	2.575	0.012	2.191	0.012
#2	1631	0.02300	0.00090	0.02184	0.00079	0.4688	0.0016	6.512	0.033	5.196	0.022	6.621	0.033	2.581	0.010	2.191	0.009
#3	1046	0.02392	0.00108	0.02221	0.00084	0.4765	0.0036	6.528	0.037	5.224	0.026	6.610	0.039	2.584	0.012	2.192	0.014
#4	1044	0.02379	0.00100	0.02310	0.00093	0.4731	0.0021	6.531	0.033	5.202	0.022	6.595	0.035	2.573	0.009	2.187	0.010
#5	1076	0.02432	0.00099	0.02135	0.00080	0.4663	0.0027	6.515	0.038	5.201	0.025	6.577	0.032	2.569	0.009	2.195	0.013
#6	1035	0.02313	0.00100	0.02158	0.00085	0.4739	0.0030	6.519	0.036	5.182	0.024	6.573	0.040	2.576	0.014	2.190	0.011
#7	1003	0.02205	0.00093	0.02159	0.00083	0.4658	0.0022	6.535	0.038	5.220	0.027	6.641	0.040	2.573	0.015	2.190	0.011
#8	1007	0.02416	0.00096	0.02144	0.00079	0.4691	0.0016	6.569	0.035	5.224	0.022	6.628	0.035	2.591	0.011	2.185	0.010
#9	979	0.02134	0.00086	0.02159	0.00084	0.4693	0.0034	6.559	0.039	5.184	0.026	6.624	0.041	2.585	0.013	2.188	0.012
Mean ± STD/√(n)		0.02326	0.00033	0.02177	0.00019	0.4704	0.0012	6.5310	0.0069	5.2045	0.0053	6.6088	0.0077	2.5786	0.0024	2.1897	0.0010
MORB: KUNZ Mean		0.0245	0.0003	0.0220	0.0003	0.4748	0.0019	7.37	0.02	5.29	0.01	6.80	0.01	2.80	0.01	2.46	0.01
MORB: CO ₂ well gases		0.0238	0.0002	0.0221	0.0003	0.4767	0.0016	7.18	0.02	5.24	0.01	6.76	0.01	2.79	0.01	2.44	0.01
mean AIR measured Uncertainty are 1 standard deviation of standards	911±29	0.02225	0.00084	0.02194	0.00076	0.4690	0.0008	6.681	0.030	5.270	0.018	6.703	0.029	2.601	0.003	2.220	0.006



Supplementary Information References

- Holland, G., Ballentine, C.J. (2006) Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* 441, 186-191.
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