

## ■ The xenon isotopic signature of the mantle beneath Massif Central

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### ■ Supplementary Information

The Supplementary Information includes:

- Analytical Procedure
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#### **Analytical Procedure**

Nine aliquots of the gas were analysed. Each aliquot corresponds to a volume of gas of 0.2 cm<sup>3</sup> 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). <sup>3</sup>He is collected on the electron multiplier in pulse counting mode whereas <sup>4</sup>He is analysed on the faraday cup and the signal is amplified using either the 10<sup>11</sup> ohms or the 10<sup>12</sup> 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 <sup>3</sup>He peak, a scan of HD+H<sub>2</sub> is performed before the introduction of helium and a fixed difference of magnetic field is applied to determine the field for <sup>3</sup>He. The scan of <sup>4</sup>He is performed after the introduction of the helium into the instrument to get the magnetic field necessary for <sup>4</sup>He. 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, <sup>20</sup>Ne is measured using a mass-scan instead of setting the magnet on the required field to measure <sup>20</sup>Ne. This method is applied because it turned out that it allows a better determination of <sup>20</sup>Ne during the data processing. Indeed, the partial contributions of <sup>40</sup>Ar<sup>++</sup>, HF<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> on the peak at mass 20 were difficult to estimate using only measurement at a given magnetic field due to hysteresis problems. <sup>21</sup>Ne, <sup>22</sup>Ne, <sup>40</sup>Ar and CO<sub>2</sub> 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. <sup>36</sup>Ar and <sup>38</sup>Ar are collected on the electron multiplier whereas <sup>40</sup>Ar is measured on faraday using the 10<sup>11</sup> 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 <sup>4</sup>He 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  $\mu$ 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  $\text{cm}^3$  and a reservoir volume of 2 litres). The standard was prepared using 10 pipettes of 0.1  $\text{cm}^3$  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  $^3\text{He}/^4\text{He}$  ratio of  $12.56 \pm 0.05$  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  $^{22}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{130}\text{Xe}$  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 $\sigma$	<sup>22</sup> Ne (cps) <sup>2</sup>	<sup>20</sup> Ne/ <sup>22</sup> Ne	1 $\sigma$	<sup>21</sup> Ne/ <sup>22</sup> Ne	1 $\sigma$	<sup>40</sup> Ar (fA) <sup>2</sup>	<sup>38</sup> Ar/ <sup>36</sup> Ar	1 $\sigma$	<sup>40</sup> Ar/ <sup>36</sup> Ar	1 $\sigma$
#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
<b>Mean <math>\pm</math> STD/<math>\sqrt{9}</math></b>	<b>5.51</b>	<b>0.03</b>		<b>10.118</b>	<b>0.009</b>	<b>0.03297</b>	<b>0.00005</b>		<b>0.18833</b>	<b>0.00015</b>	<b>1113</b>	<b>3</b>
AIR	1			9.800		0.02900			0.1880		296	
AIRS measured <sup>1</sup>			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: <sup>22</sup>Ne and <sup>40</sup>Ar 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 CO<sub>2</sub> 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.

	$^{130}\text{Xe}$ introduced (cps)	$^{124}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{126}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{128}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{129}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{131}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{132}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{134}\text{Xe}/$ $^{130}\text{Xe}$	±	$^{136}\text{Xe}/$ $^{130}\text{Xe}$	±
#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
<b>Mean ± STD/√(n)</b>		<b>0.02326</b>	<b>0.00033</b>	<b>0.02177</b>	<b>0.00019</b>	<b>0.4704</b>	<b>0.0012</b>	<b>6.5310</b>	<b>0.0069</b>	<b>5.2045</b>	<b>0.0053</b>	<b>6.6088</b>	<b>0.0077</b>	<b>2.5786</b>	<b>0.0024</b>	<b>2.1897</b>	<b>0.0010</b>
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 <sub>2</sub> 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.
- Kunz, J., Staudacher, T., Allègre, C.J. (1998) Plutonium-Fission Xenon Found in Earth's Mantle. *Science* 280, 877-880.

