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# Hadean isotopic fractionation of xenon retained in deep silicates

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**Our understanding of atmosphere formation essentially relies on noble gases and their isotopes, xenon (Xe) being a key tracer of the early planetary stages. A long standing issue however is the origin of atmospheric depletion in Xe<sup>1</sup> and its light isotopes for the Earth<sup>2</sup> and Mars<sup>3</sup>. Here, we report that feldspar and olivine samples confined at high pressures ( $P$ ) and high temperatures ( $T$ ) with diluted Xe and krypton (Kr) in air or nitrogen are enriched in heavy Xe isotopes by +0.8 to +2.3‰ per a.m.u., and strongly enriched in Xe over Kr. The upper +2.3‰ per a.m.u. value is a minimum since quantitative trapping of unreacted Xe either in bubbles or adsorbed on the samples is likely. In the light of these results, we propose a scenario solving the missing Xe problem involving multiple events of magma ocean stage at the proto-planetary stage combined with atmospheric loss. Each of these events results in trapping Xe at depth and preferential retention of its heavy isotopes. In the case of the Earth, the heavy Xe fraction was later added to the secondary CI chondritic atmosphere through continental erosion and/or recycling of an Hadean felsic crust.**

Atmospheric Xe is elementally depleted by a factor of 24 relative to Kr in CI chondrites (Table 1), and isotopically depleted by 35 ‰ per a.m.u., which is known as the missing Xe problem<sup>1</sup>. The loss of elemental Xe occurred very early on<sup>4</sup> (<100 My). Its isotopic fractionation in the terrestrial atmosphere is recorded continuously throughout the Archean<sup>5</sup>, a situation settled before 4 Gy for

the martian atmosphere. Scenarios have been proposed, but none is exempt of ad-hoc hypothesis so far<sup>6</sup>. Atmospheric escape scenarios<sup>7-9</sup> require strong EUV radiation and/or magnetic field to selectively ionize Xe amongst other noble gases by collision with H<sup>+</sup> ions, a sufficiently large H<sub>2</sub> drag, and eventually an additional Xe-specific process to retain it at depth<sup>7</sup> or in organic aerosols<sup>8</sup>. Atmospheric escape processes should also be related to the mass of the planet, which is not consistent with Mars and Earth having the same missing Xe problem. An alternative scenario to alleviate the need for Xe loss is to have a cometary component in the planetary building blocks<sup>10</sup>. Comets were indeed expected to have much smaller Xe/Kr and Xe/Ar ratios than chondrites based on noble gases trapping experiments on ice, but this has not been confirmed by analyses from comet 67P/Churyumov-Gerasimenko<sup>11</sup>. Comets are in fact even more enriched in light isotopes than chondrites compared to the atmosphere<sup>12</sup>. A 22% comets - 78% chondrites mix matches the U-Xe component from which atmospheric Xe isotopic signature is obtained by mass-dependant fractionation, but that does not explain the mass-dependent fractionation process itself. Last but most importantly, the terrestrial budget of water seems better explained by a mostly enstatite chondritic Earth<sup>13</sup> which satisfies the largest number of geochemical constraints<sup>14,15</sup>, and only a minor late input of carbonaceous chondrites to surficial reservoirs. If the noble gases planetary budget was indeed established as for water very early on, then the continuous depletion of atmospheric Xe light isotopes throughout the Archean might not necessarily trace the isotopic fractionation process but may instead trace the release of a formerly trapped heavy component.

Trapping-at-depth scenarios stem from the effect of high  $P$  to induce Xe chemistry at depth with planetary materials<sup>16</sup>. Xe may covalently bond to oxygen in pure oxides at the  $P$ - $T$  conditions of the lower mantle<sup>17</sup>, it may also bond to nickel at the conditions of the Earth deep outer core<sup>18</sup>. High  $P$  phases however may only be relevant as a trapping scenario if they include Xe at natural levels of abundance, *i.e.* as a trace element, not if they are stoichiometric compounds. That Mars and Earth share the missing Xe problem besides excludes the lower mantle and core as potential reservoirs.

Instead, Xe oxidation by substitution to Si in silicates is a viable mechanism. It occurs at the modest *P-T* conditions of the deep crust and higher, in all types of silicates with tetrahedral silicon from isolated tetrahedra olivine<sup>19</sup> to framework quartz<sup>20,21</sup>, and at trace concentrations of Xe with a storage capacity up to 0.4 at%. Unlike for tetrahedrally coordinated silicates, Xe is not retained within the octahedral coordinated silicates of the lower mantle such as bridgmanite<sup>22</sup>. Therefore unlike crustal, upper mantle, and atmospheric reservoirs, the lower mantle likely does not currently retain Xe in silicates except for zones that could have remained isolated from the convecting mantle. Ingassing through subduction recycles Xe at depth<sup>23</sup> by neutral retention in cyclo-silicates in the altered lithosphere<sup>24</sup>, and its release in the upper mantle along with the aqueous fluid upon plate dehydration.

Table 1 summarises occurrences of heavy noble gases (Xe/Kr/Ar) enrichments in naturally high *P* samples. Bravo Dome fluids<sup>26</sup> and MORB popping rock values<sup>27</sup> enrichments are partially explained by seawater recycling at depth (Xe/Kr enrichment by a factor of 2) with another source of enrichment such as added oceanic sedimentary component<sup>26</sup>, although the latter should give other geochemical imprints that are not observed. Mantle xenoliths<sup>28-30</sup> display a stronger Xe over Ar enrichment of up to 17 times that of air albeit Kr data are not available for those samples<sup>30</sup>. Much stronger Xe enrichments are observed in continental crust samples, by one to two orders of magnitude *vs* Kr, and two to three orders of magnitude *vs* Ar, the strongest values being for impact rocks<sup>31,32</sup>. Similar enrichment values are reported for excavated lunar anorthosites<sup>33</sup>. Relatively to the chondritic noble gas concentration trend, 8 to 12 atmospheric masses of Xe are missing<sup>11</sup>, which translates into <sup>132</sup>Xe concentration of  $1.1 \times 10^{-14} \text{ mol.g}^{-1}$  to  $1.7 \times 10^{-14} \text{ mol.g}^{-1}$  if stored in the crust and upper mantle. This matches the highest concentrations reported in shocked granite<sup>31</sup> ( $1.3 \times 10^{-14} \text{ mol.g}^{-1}$ ) and lunar anorthosite<sup>33</sup> (up to  $1.7 \times 10^{-14} \text{ mol.g}^{-1}$ ), while next highest Xe concentrations are reported for the KTB continental crust drill<sup>34</sup> ( $1.5 \times 10^{-15} \text{ mol.g}^{-1}$ ) and deep fluids<sup>26</sup> ( $2.5 \times 10^{-15} \text{ mol.g}^{-1}$ ). Given that Xe is not preserved in the crystal structure of silicates brought back to surface

conditions and is expected to diffuse out on geological timescales, the natural record only gives a minimum estimation of the relevant Xe content at depth. And indeed, Xe content is highest in shocked rocks, *i.e.* rocks brought back to ambient  $P$  on very short timescales that limit diffusion out. This is also seen in the Xe/Kr ratios that remain higher than chondritic only in rapidly exhumed shocked rocks<sup>31,32</sup>. The next step now is to evaluate what are the consequences of Xe retention in silicates on its isotopic signature.

Here, we report Xe isotopic fractionation of +0.8 to  $+2.3 \pm 0.2\%$  per a.m.u. in feldspar and olivine crystals mixed with Xe and Kr diluted in either air or nitrogen gas, and brought at high  $P$  and  $T$  conditions of 3.5 GPa and 800°C to 1100°C (Fig. 1 and Extended Data Table 1). Xe isotopic fractionations are measured by mass spectrometry on bulk sample fragments fully melted by laser heating (see Methods). This fractionation is observed for both olivine and feldspar, but only in samples undersaturated in Xe, *i.e.* mixed with either 1% or 1‰ Xe and Kr diluted in either air or nitrogen gas. The results do not depend on the dilution gas nature, *i.e.* with or without oxygen (Fig. 2a), nor on the sample fragment mass (Extended Data Fig. 1b) or Xe content (Fig. 2b). Considering that Xe was partitioned between the N<sub>2</sub>-rich fluid phase (*i.e.* the pressurized gas) and crystals at high  $P$  and  $T$ , and that a fraction of the non-oxidised Xe might be retained by adsorption on grains and/or trapped in bubbles, +2.3‰ per a.m.u. is a lower limit. Attempts to isolate the oxidised Xe fraction by step heating show variations in isotopic fractionation by a factor of two depending on  $T$  (Extended Data Fig. 2). Hence the real Xe isotopic fractionation resulting from Xe oxidation in silicates at depth should not exceed +4‰ per a.m.u. After recovery at ambient conditions, the heavy Xe fraction is retained in the sample on the scale of up to 400 days after the experiment (Extended Data Fig. 1a). In contrast, samples saturated in Xe, with Xe exsolution in bubbles observed in quenched samples (Extended Data Fig. 3), do not show any isotopic fractionation (Fig. 2a). For these samples, the signal is controlled by excess Xe that did not react with the silicates at high  $P$  and  $T$  and is not isotopically fractionated (Extended Data Table 1). For undersaturated samples, the Kr

isotopes signal is within the background signal so that isotopic ratios could not be quantitatively measured. Since Xe and Kr are present in equivalent quantities in the diluted gases, it however demonstrates that Kr is strongly depleted compared to Xe by two to four orders of magnitude in the reacted minerals. The observed isotopic fractionation results from Xe partitioning between phases with markedly different oxidation states, *e.g.* reduced  $^0\text{Xe}$  in the fluid phase and oxidised  $^{+3}\text{Xe}$ <sup>19,21</sup> in high  $P$ - $T$  silicates. Xenon oxidation state in compressed magmas has not yet been determined, and we find no isotopic fractionation for feldspar glasses quenched from the molten state at 1400°C and 3.5 GPa (Fig. 2a and Extended Data Table 1), despite being undersaturated in Xe. Combining our results on crystal/ $\text{N}_2$ -rich fluid and melt/ $\text{N}_2$ -rich fluid systems, Xe isotopic fractionation between crystals and melt is expected to be equal to that measured between crystal/ $\text{N}_2$ -rich fluid. The onset of feldspar and olivine crystallization occurred at 0.6 GPa and 3.9 GPa respectively in the lunar magma ocean<sup>35</sup>, which can be considered as a good analogue of magma oceans in planetary embryos. Hence the relevant conditions for Xe trapping at depth and consequent isotopic fractionation are of the order of 1 to several GPa.

We observe the same level of isotopic and elemental enrichment for both feldspar and olivine in our experimental samples while continental crust-like natural samples show the strongest Xe over Kr enrichment. Based on these results, we propose that Xe got trapped and isotopically fractionated on Earth and Mars in tetrahedral silicates (Fig. 3a), preferentially in the primordial felsic crusts as they were formed and reworked upon meteoritic impacts in the early Hadean, and to a lesser extent in the crystallizing mantle unless the poorly sampled sub-lithospheric mantle contains more Xe than lithospheric xenoliths (Table 1). There are evidences of felsic crusts in the inner solar system from the planetesimal stage<sup>36</sup> to the planetary stage. The existence of a primordial felsic crust within the first 100 My is attested by zircons on Mars<sup>37</sup>, and may have massively formed on Earth from 4.5 Gy on<sup>38,39</sup>. While the heavy Xe isotopes fraction was retained in silicates at depth, the light fraction was

let in the atmosphere that was lost by the combination of impacts and XUV-driven hydrodynamic escape within the first 100 My<sup>40</sup> (Fig. 3b).

With an isotopic fractionation of a few ‰ per a.m.u. upon Xe oxidation, the trapping at depth process must have occurred not once but multiple times to explain the observed depletion of +35‰ per a.m.u. In fact, having multiple magma ocean events on the proto-Earth is required to explain the high <sup>3</sup>He/<sup>22</sup>Ne ratio in the MORB mantle source compared to the 6.7-fold lower solar nebula value, and 11-fold lower chondritic value<sup>41</sup>. Using a He/Ne solubility ratio ( $S_{\text{He}}/S_{\text{Ne}}$ ) of  $\sim 2$ <sup>42</sup>, magma ocean ingassing of solar nebula gases followed by at least two degassing processes, *i.e.* two magma ocean stages, raises the <sup>3</sup>He/<sup>22</sup>Ne ratio by a factor of 2x2x2, *i.e.* 8, satisfying the observations<sup>41</sup>. However more recent molecular dynamics calculations on noble gases solubility in magmas<sup>43</sup> including the *P* effect, predict a  $S_{\text{He}}/S_{\text{Ne}}$  solubility ratio converging to 1.3 at 2273 K above 2 GPa. Using this value, the minimum number of degassing events is raised to 7. This is still a minimum number<sup>41</sup> as 1) the <sup>3</sup>He/<sup>22</sup>Ne ratio value of 10 in the MORB source is just a minimum value, 2) atmospheric loss is likely only partial between two successive magma ocean stages, and 3) any deviation from equilibrium degassing or any hydrodynamic escape process at stake would lower the <sup>3</sup>He/<sup>22</sup>Ne ratio. Our results further constrain the number of events between 9 (for  $\delta\text{Xe}^{i+1}/\text{Xe}^i = +4\text{‰}$ ) and 15 (for  $\delta\text{Xe}^{i+1}/\text{Xe}^i = +2.3\text{‰}$ ). The fractionation scenario is therefore a succession of magma oceans and atmospheric loss on proto-planets at the planetary embryo stage while collisions were common<sup>44</sup>, noting that magma oceans and atmospheric loss might not necessarily be concomitant<sup>45</sup>. The similar extent of Xe isotopic fractionation on Earth and Mars implies that Xe isotopic and elemental depletion was settled by the time proto-planets had grown to Mars-size objects. The overall loss of Xe must have been massive as reported for Ar and Ne<sup>46,47</sup>, *i.e.* on the order of 99% to 99.9%, while the ‘missing Xe’ paradox only concerns the relative depletion of Xe compared to Kr and is retained in silicates at depth. [Using a Rayleigh distillation law and a depletion of 99.9%, the total +35 ‰/a.m.u. fractionation gives an instantaneous fractionation factor of +5 ‰/a.m.u. This is very close](#)

to the +4 ‰/a.m.u. upper value proposed here. However, this is just an indication as Xe loss was a combination of continuous hydrodynamic escape processes and erosion impact events, and would therefore require a more complex modelling. Consequently, a lesser mass of late veneer (<0.01% mass Earth) than based on siderophile elements is required as to not re-set the fractionated Xe signature. This would also be more consistent with values proposed on the basis of hydrogen isotopes for water<sup>13</sup>, possibly due to the higher volatility of water and noble gases compared to siderophile elements.

Unlike for Xe, there is no report of *P*-induced oxidation for any other noble gas in crystalline silicates. Oxidation has only been reported for Kr in magmas<sup>48</sup>, with a Kr-O bond length at  $2.5 \pm 0.1$  Å too large to be accommodated by substitution of Kr to Si in the  $[\text{SiO}_4]^{-1}$  tetrahedra, but that can fit into the melt rings structure<sup>49</sup>. In early planetary stages, Kr bonding to oxygen only in magmas might have resulted in isotopically heavier magmas that eventually degassed before loss of the primary atmosphere, and in isotopically lighter crystals consistently with terrestrial Kr being depleted in heavy isotopes by 0.8‰ per a.m.u.<sup>50</sup>. That we measure here a Xe/Kr enrichment of 2 to 4 orders of magnitude confirms the preferential trapping of Xe over lighter noble gases. Literature data on crystal/melt noble gases partitioning is sparse<sup>51</sup>, with values spanning up to 6 orders of magnitude in the case of Xe from highly incompatible to moderately compatible. While great care was taken to avoid any melt nor bubbles in crystal analyses<sup>51</sup>, Xe bubbles are not necessarily artefacts but can instead be produced upon quenching the experiment back to room conditions as observed by *in situ* x-ray diffraction experiments<sup>52</sup>. Therefore, it is not straightforward to estimate the solubility and partitioning behaviour of noble gases and more generally of volatile elements from measurements on quenched samples. *Ab initio* calculations nonetheless confirm the compatibility of Xe in olivine<sup>19</sup>. Consequently, any degassing process from the upper mantle and deep crust is bound to preferentially retain Xe over other noble gases, resulting in the currently observed Xe deficiency in the atmosphere.

CI chondrites contribution to the secondary atmosphere later set up the initial atmospheric composition for Xe for the Earth, that was continuously modified by inputs from continents, through erosion, metamorphic and magmatic processes until CI signature got overprinted by released heavy Xe at the end of the Archean (Fig. 3c). By approximately the same time, the Hadean felsic crust would have been well re-mixed with the mantle as estimated from  $^{142}\text{Nd}$  anomalies<sup>38</sup>. Compared to the early depleted mantle and crust, the enrichment in the light Xe isotopes in the mantle<sup>26,54</sup> reflects either recycling of the more chondritic Archean atmosphere (Extended Data Fig. 4), or input from a slightly less fractionated lower mantle resulting from the last magma ocean stage having affected only the upper mantle due to the lack of reactivity between Xe and bridgmanite<sup>22</sup>. Mantle degassing has been invoked as a mechanism to release Xe-depleted volatiles following noble gases solubility trend in magmas<sup>53</sup>. Mantle degassing only cannot explain atmospheric evolution of Xe isotopes as it occurred on a different timescale with an extensive loss of volatiles within the first 100 My<sup>55</sup>. However, recycling of the felsic crust within the mantle and its further degassing by magmatism could have contributed to the evolution of atmospheric Xe isotopic signature during the Archean<sup>5</sup>.

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**Figure 1. Xenon isotopic spectra.** Feldspar loaded with pure Xe gas (yellow curve, circles), feldspar loaded with 1% Xe and Kr enriched air (orange curve, squares), and olivine loaded with 1‰ Xe and Kr enriched nitrogen (green curve, diamonds); all three samples were brought at 3.5 GPa and 1100°C for 24 h. Coloured areas around data points represent the standard error (SE).

**Figure 2. Full Xe isotopic data set for crystalline feldspar and olivine. a.** Xe fractionation as a function of the synthesis gas used (1% and 1‰ stand respectively for 1 mol% of both Xe and Kr enrichment, and 1 mol‰ of both Xe and Kr enrichment), **b.** Xe fractionation as a function of the sample Xe content. Vertical error bars: SE, horizontal error bars on panel b:  $\pm 30\%$  error on [Xe] determination. Note that the sample fragment weight was not available for a few data points, hence not reported in b (see Extended Data Table 1).

**Figure 3. Xe trapping-at-depth scenario.** Due to successive collisions, multiple events of **a.** equilibrium between reduced Xe in a primary atmosphere and oxidised Xe in the crystallising magma ocean, preferential trapping of heavy Xe isotopes at depth in silicates, and **b.** loss of the light isotopic Xe fraction upon impact-induced atmosphere erosion and hydrodynamic escape; **c.** partial release of the trapped heavy Xe in the CI chondritic secondary atmosphere through magmatism/continental erosion during the Archean resulting in an elementally Xe-depleted and isotopically heavy Xe-enriched atmosphere, and Xe ingassing initiated at subduction zones.

## Methods

**Sample preparation.** Samples are made from mortar-crushed natural mineral powders, namely olivine from a San Carlos peridotite, and two feldspar sanidine samples, one from an unknown location (sanidine 1) and one from Itrongay in Madagascar (sanidine 2). Extended Data Table 2 reports the composition of the three minerals<sup>56,57</sup>. The powder is put into a platinum (Pt) tube enclosed at one side only and gas-loaded<sup>58</sup> with air or nitrogen, enriched in both Xe and Kr. Xe and Kr contents are 1‰ or 1% for under-saturated conditions (Air Liquide gas bottles). For over-saturated conditions, pure Xe is used. The Pt capsules are 5 mm tall and 3 mm wide, and are inserted in pairs in a 10 mm diameter talc-pyrex cell assembly. High  $P$ - $T$  conditions of 3.5 GPa and up to 1400°C are generated by a Depth of the Earth L.L.C. piston cylinder press. Run duration varies from 2 to 72 hours, depending on run  $T$  (Extended Data Table 1).

Starting and recovered samples from high  $P$ - $T$  experiments were embedded in an epoxy resin slab for scanning electronic microscopy (SEM) observations, and electron probe micro-analysis (EPMA). SEM was used with its angle selective detector (AsB). EPMA (Extended Data Table 2) was done using the SX-Five quintuple spectrometer device on the CAMPARIS platform. The beam size is 1  $\mu\text{m}$ . Samples were all gas loaded with a gas pressure of 12 bars. However, the amount of gas effectively loaded in capsules varies due to the capsule sealing process during which part of the loaded gas may escape. SEM images (Extended Data Fig. 3) show the range of textures observed for sanidine 1 samples, from bubble-free (Extended Data Fig. 3a) to bubble-rich (Extended Data Fig. 3b and c), depending on the amount of gas loaded.

**Isotopic ratios measurements.** Isotopic ratios were measured at LP2i (formerly CENBG) on the PIAGARA platform (Interdisciplinary platform for noble gas analysis), and all data are provided in the Supplementary Information file along with Xe isotopes spectra for each analysis. Pieces of

samples from 0.1 mg to 3.3 mg were weighted preferentially using a CAHN/Ventron 21 automatic electro-balance with a ~1% accuracy, or a Mettler-Toledo ME204 balance with a 0.1 mg accuracy. Each piece was then placed in a cavity shaped in a tantalum (Ta) sheet itself supported by a tungsten (W) cylinder. The Ta sheet and W support were previously heated up to ~2100 K to ensure the removal of any eventual trapped gas. The sample and its support were put in a degassing chamber pumped overnight reaching a residual pressure below  $10^{-8}$  mbar. Sample heating was achieved by focussing a high power continuous wave laser<sup>59</sup> while working in a relatively cold environment (chamber walls, base and viewport not exceeding 150°C), and continuously monitored by a camera until full melting was reached as attested by the sample shape changing to a spheroid and the simultaneous release of micro-bubbles of gas. Laser power was held steady for a further 30 seconds, and then shut down. The extracted gases were submitted to a 10 min treatment by hot Ti sponges to remove all non-noble gases. This purification step was completed on the gas fraction brought to the mass spectrometer (MS) by an additional 10 min treatment on a second set of Ti sponges set at 300°C, 400°C, 500°C and 600°C, and a SORB-AC® trap (SAES Getter, Lainate, Italy). A second SORB-AC® trap is also present in the MS volume. The MS employed for the analyses is a magnetic sector, 60° deflection and 12 cm radius instrument (model 1202 of V. G. Micromass 12) incorporating in a small interior volume, a Nier-type source (VG3000) and a (Cu-Be) electron multiplier detector used in integrating mode for ion counting.

The sought isotopic fractionations being expected to be extremely low, extensive care has to be taken to ensure the validity and improve the precision of the determined values. Our magnetic sector mass spectrometer, as all of its kind, has for each isotope  $i$  a sensitivity  $s_i$  that will evolve with time and depends on numerous parameters, most notably gas pressure (total and that of the considered element and isotope). Consequently, we routinely consider  $s_i$  to be known with a 5% error with a recent calibration, which is 2 orders of magnitude more than the precision we need for the present study. Although this error is reduced by one order of magnitude when considering

isotope ratios of a same element, a mass discrimination factor correction with its own error and influencing parameters still needs to be applied as the heavier the isotope, the lower is the sensitivity. Therefore to further lower the intrinsic error on the  ${}^i\text{Xe}/{}^{130}\text{Xe}$  ratios (the  ${}^{130}\text{Xe}$  being arbitrarily selected as the reference isotope), we defined the measured ratio  $R_i$  as follows:

$$R_i = \frac{\left( r_i^{sample} \times \frac{s_i^{sample}}{s_{130}^{sample}} \right)}{\left( r_i^{com.gas} \times \frac{s_i^{com.gas}}{s_{130}^{com.gas}} \right)} \quad (1)$$

with  $r_i = {}^i\text{Xe}/{}^{130}\text{Xe}$ , determined by the time-zero regression of the ratio of the electrical currents measured by the MS detector for the  ${}^i\text{Xe}$  and  ${}^{130}\text{Xe}$  isotopes, and *com.gas* an aliquot of the Air Liquide gas used for the sample synthesis at high  $P$  and  $T$ . Measuring Xe MS intensity ratios from the reference synthesis gas and sequentially later (or earlier) on the same day than that extracted out of the fused sample with optimally less than a 10% difference in the Xe quantities between the two analysed aliquots allows to cancel out sensitivities from Eq.1 ( $s_i^{com.gas} = s_i^{sample}$  and  $s_{130}^{com.gas} = s_{130}^{sample}$ ). This thus naturally simplifies to:

$$R_i = \frac{\left( \frac{r_i^{sample}}{r_{130}^{sample}} \right)}{\left( \frac{r_i^{com.gas}}{r_{130}^{com.gas}} \right)} \quad (2)$$

Each  $r_i^{sample}$  value of a sample fragment is obtained from a sole MS run (except for  $i = 134$  or  $136$ , see Supplementary information file's foreword) and  $r_i^{com.gas}$  is only determined from an also unique *com.gas* measurement made the same day in conditions as close to possible to that of the sample. As such, our data errors originate from in-run standard errors (SE) or  $r_i$  measurements and are propagated to the relevant isotopic fractionation values according to customary error quadratic propagation rules<sup>60</sup>. With this protocol,  $R_i$  uncertainties range from 1‰ to 10‰, with uncertainties levels mostly related to the considered isotope relative abundancy. The individual fractionation  $\delta_i$  are then directly derived from  $R_i$ :  $\delta_i = 1000 \times (R_i - 1)$  with  $\delta_i$  expressed in ‰ per a.m.u. The average

fractionation  $\delta_n$  is finally obtained by linear regression with error weighting done by OriginLab 2016 software. Each  $\delta_i$  of a series weight the linear regression allowing  $\delta_n$  determination proportionally to  $1/\sigma_i^2$  with  $\sigma_i$  the standard error associated to  $\delta_i$  and propagated from the standard error associated to the MS measurements. [All of the  \$r\_i\$ ,  \$R\_i\$ ,  \$\delta\_i\$  and  \$\delta\_n\$  values with associated uncertainties are provided in the Supplementary information file.](#) Given the uncertainties associated with the isotopic ratios measurements, the employed protocol allows us to consider as proof of a real fractionation any  $\delta_n$  value  $\geq 0.5$  ‰ per a.m.u.

**Data Availability Statement** All data generated or analysed during this study are included in this published article and its supplementary information file, and is available on Zenodo repository (DOI: 10.5281/zenodo.6076901).

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**Author Contributions** C.S. and D.H. devised the project, I.R. and C.S. carried out the high  $P$ - $T$  experiments, I.R., D.H. and E.G. carried out analyses on the noble gas spectrometer. C.S. wrote the paper with input from I.R. and D.H.

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**Extended Data Table 1 | Summary of all experimental synthesis runs, Xe contents and average fractionations.** Samples are referred to by their material (O, S1 or S2), their synthesis number (2 digits) and when relevant their fragment number (a single letter). (\*) symbol is used to indicate the results chosen to appear in the main manuscript's Fig. 1. †: For S1-15 synthesis, a failure of the cooling water system automatically stopped the run overnight, thus the exact duration of this run could not be determined. Brown writing refer to experimental conditions that led to the absence of detectable fractionation (100% Xe gas leading to sample

saturation with Xe bubbles ; runs at 1400°C resulting in full melting of the mineral). For a few experiments (N/D in the Xe concentration column), the melted fragments were not weighted because of a long unavailability of the microbalance, thus preventing Xe concentration determination. All 29 mass spectrometry results are detailed in individual Tables (Supplementary Information file). Xe contents errors are 99% confidence intervals (CI). Errors associated to the average fractionations  $\delta_x$  are described with the presentation of individual Tables.

**Extended Data Table 2 | Chemical composition of starting and recovered samples.** EPMA analysis on sanidine 1 over 17 points, sanidine 2 over 15 points<sup>55</sup>, olivine San Carlos over 10 points<sup>56</sup> and on sanidine 1 after gas (air - 1 wt.%Xe and Kr) doping at high *P-T* conditions (sample S1-13, see conditions in

Extended Data Table 1). Abundances are given in wt.%. Errors reported are 2 standard errors.

**Extended Data Figure 1 | a, Xe fractionation as a function of the time spent between the synthesis and the mass spectrometry analysis, and b, Xe fractionation as a function of the sample mass.** Data points for samples characterized, as expected, by an absence of detectable fractionation (runs at 1400°C or with 100% Xe loading gas) were removed from this Figure for the sake of clarity. Vertical error bars represent the SE for isotopic fractionation calculation.

**Extended Data Figure 2 | Summary of measured  $\delta_n$  values in experiments realized with laser heating increasing steps.** Instead of analysing all Xe released after laser melting of the fragments, the tuneable heating laser was first set at lower powers (indicated as the power voltage V applied to the laser source). Each heating plateau was kept for a few minutes and the released Xe were analysed by mass spectrometry using the same general protocol described in the Methods section. A handful attempts were made on olivine and sanidine 1 samples. They all point toward Xe predominantly exiting the material at the fusion point (or close to). Only two experiments with sanidine, S1-11d with 1% Xe gas and S1-19b with 100% Xe gas, led to the successful measurement for all of the heating steps of both  $\delta_n$  and [Xe] values, as reported in the present Figure. Each point area is proportional to the Xe content ([Xe]) extracted at the heating plateau. The stars are  $\delta_n$  values combining all  $\delta_n$  measured and weighted by each [Xe], in other words the  $\delta_n$  we would had measured if the sample fragment had been directly melted. For S1-11d (1% Xe gas), we observe variations of  $\delta_n$  by a roughly 2-fold factor along the heating ramp. For this same sample, an unfractionated component was evidenced

for the lowest laser voltage, but represent a marginal part (5.3% of the total released Xe). Since for similar heating power, ~45% of the total Xe of S1-19b (100% Xe gas) was released, this low  $T$  release is possibly associated to Xe trapped as bubbles. At the highest  $T$ , *i.e.* at the sample melting point, for S1-19b and S1-11d respective  $0.54 \pm 0.12$  ‰/amu and  $0.61 \pm 0.11$  ‰/amu fractionations were measured, which points towards a Xe component with some fractionated Xe, but still with an unfractionated component lowering the overall measured  $\delta_n$ . This indirectly confirms that Xe chemical incorporation and the associated isotopic fractionation occurs in all samples prepared at  $T \leq 1100^\circ\text{C}$ ;  $\delta_n$  close to zero for samples prepared with 100% Xe gas being only due to a disruptive phenomenon whose extent is proportional to Xe partial pressure: oversaturation of the mineral (bubble formation, as seen in Extended Data Fig. 3). Detailed data used to construct this Figure are found in the results Tables for S111d and S1-19b given in Supplementary information file, while synthesis conditions are found in Extended Data Table 1.

**Extended Data Fig. 3 | SEM images in AsB mode. a and b,** Feldspar sanidine 1 loaded with 1 mol% Xe and 1 mol% Kr enriched air (identical to syntheses S1-13 and S1-14). Round dark area in **b** are synthesis gas bubbles revealed and opened by

polishing. **c,** a sanidine 1 loaded with 100 mol% Xe (identical to syntheses S1-17, S1-18 and S1-19). Brighter areas in **c** are Xe bubbles, found in oversaturated samples, *i.e.* loaded with 100 mol% Xe gas.

**Extended Data Figure 4 | Non-radiogenic Xe data reveal the possibility of Archean atmosphere contribution to mantle Xe within the present scenario of an early fractionated silicate Earth.** Xe measured in deep crustal fluids<sup>50</sup> (black and grey circles), MORB popping rock<sup>54</sup> (brown circle), air<sup>25</sup>, Archean atmosphere as trapped in crustal samples (dark blue and black squares) ; and primordial

components (green and maroon circles). All data are shown with associated SE. Alternatively, the deep fluids and MORB popping rock enrichment in Xe light isotopes compared to air could be explained by input from a slightly less fractionated lower mantle resulting from the last magma ocean stage having affected only the upper mantle.

Sample	$^{130}\text{Xe}/^{84}\text{Kr}$	$^{130}\text{Xe}/^{36}\text{Ar}$	$\frac{\left(\frac{^{130}\text{Xe}}{^{84}\text{Kr}}\right)_{\text{sample}}}{\left(\frac{^{130}\text{Xe}}{^{84}\text{Kr}}\right)_{\text{air}}}$	$\frac{\left(\frac{^{130}\text{Xe}}{^{36}\text{Ar}}\right)_{\text{sample}}}{\left(\frac{^{130}\text{Xe}}{^{36}\text{Ar}}\right)_{\text{air}}}$	$\frac{\left(\frac{^{130}\text{Xe}}{^{84}\text{Kr}}\right)_{\text{sample}}}{\left(\frac{^{130}\text{Xe}}{^{84}\text{Kr}}\right)_{\text{EH}}}$
air <sup>25</sup>	5.63x10 <sup>-3</sup>	1.17x10 <sup>-4</sup>	1	1	0.1
CI <sup>6</sup>	0.135	1.49x10 <sup>-3</sup>	24	12.5	2.1
EH <sup>11</sup>	0.1	7.15x10 <sup>-4</sup>	17.8	6.1	1
<b>Mantle samples</b>					
MORB <sup>27</sup>	9.25x10 <sup>-3</sup>	2.2x10 <sup>-4</sup>	1.6	1.9	0.3
Bravo Dome fluids <sup>26</sup>	[1.6-3.0]x10 <sup>-2</sup>	[5.3-7.5]x10 <sup>-4</sup>	<b>[2.8-5.4]</b>	<b>[4.6-6.4]</b>	[0.2-0.3]
xenoliths <sup>28-30</sup>	[0.4-3.8]x10 <sup>-2</sup>	[0.7-19.7]x10 <sup>-4</sup>	<b>[0.7-6.7]</b>	<b>[0.6-16.7]</b>	[0.04-0.38]
<b>Felsic crusts</b>					
KTB drilling project <sup>34</sup>	[1.9-90.0]x10 <sup>-3</sup>	[1-80]x10 <sup>-4</sup>	<b>[0.3-16.0]</b>	<b>[0.8-68.7]</b>	[0.02-0.90]
Red rock impact <sup>31</sup>	0.199	0.163	<b>35.3</b>	<b>1395.7</b>	<b>2.0</b>
tektites <sup>32</sup>	0.529	4.17x10 <sup>-2</sup>	<b>94.0</b>	<b>357.2</b>	<b>6.4</b>
Lunar anorthosite <sup>33</sup>	[1.6-11.9]x10 <sup>-2</sup>	[1.3-25.8]x10 <sup>-3</sup>	<b>[2.9-21.1]</b>	<b>[11.1-220.5]</b>	[0.2-1.2]

**Table 1 Xe/Kr/Ar ratios in natural samples.** Heavy noble gases enrichment compared to air and to potential bulk Earth's noble gas compositions. Ratios are from abundances given in mol.g<sup>-1</sup>. Significant Xe enrichments are given in bold characters.





