The end of the isotopic evolution of atmospheric xenon

L. Ardoin1,2*, M.W. Broadley1, M. Almayrac1, G. Avice3, D.J. Byrne1, A. Tarantola4, A. Lepland5, T. Saito6, T. Komiya7, T. Shibuya6, B. Marty1

Abstract

Noble gases are chemically inert and, as such, act as unique tracers of physical processes over geological timescales. The isotopic composition of atmospheric xenon, the heaviest stable noble gas, evolved following mass-dependent fractionation throughout the Hadean and Archaean aeons. This evolution appears to have ceased between 2.5 and 2.1 Ga, around the time of the Great Oxidation Event (GOE). The coincidental halting of atmospheric Xe evolution may provide further insights into the mechanisms affecting the atmosphere at the Archaean-Proterozoic transition. Here, we investigate the isotopic composition of Xe trapped in hydrothermal quartz from three formations around the GOE time period: Seidorechka and Polisarka (Imandra–Varzuga Greenstone Belt, Kola Craton, Russia) with ages of 2441 ± 1.6 Ma and 2434 ± 6.6 Ma, respectively, and Ongeluk (Kaapvaal Craton, South Africa) dated at 2114 ± 312 Ma (Ar-Ar age) with a host formation age of 2425.6 ± 2.6 Ma (upper bound). From these analyses we show that Xe isotope fractionation appears to have ceased during the time window delimited by the ages of the Seidorechka and Polisarka Formations, which is concomitant with the disappearance of mass-independent fractionation of sulfur isotopes (MIF-S) in the Kola Craton. The disappearance of Xe isotope fractionation in the geological record may be related to the rise in atmospheric oxygen and, thus, can provide new insights into the triggering mechanisms and timing of the GOE.

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Introduction

Due to their chemical inertness, noble gases (He, Ne, Ar, Kr, Xe) constitute powerful geochemical tracers for constraining physical processes occurring in the Earth’s atmosphere. Atmospheric xenon is of particular interest because its isotopic composition is highly mass-dependently fractionated (MDF) by 41.5 ‰ u−1 when compared to its presumed primitive ancestor U-Xe (Pepin, 1991). Studies of palaeo-atmospheric Xe trapped in Archaean rocks (mainly as fluid inclusions in hydrothermal quartz) have shown that the evolution of isotopic fractionation of Xe was a long-term process that took place during the Hadean and the Archaean aeons. This protracted MDF appears to be unique to Xe, with no evidence that the other noble gases underwent progressive fractionation (Pujol et al., 2011; Avice et al., 2018; Almayrac et al., 2021). Such Xe specific evolution has been attributed to preferential, non-thermal escape of xenon from the Earth’s atmosphere to space upon ionisation by solar UV photons (Pujol et al., 2011; Hébrard and Marty, 2014; Avice et al., 2018) and subsequent entrainment by escaping hydrogen ions (Zahnle et al., 2019). Available data indicate that the evolution of the isotopic composition of atmospheric xenon ceased at some point between 2.6 and 1.8 Ga (Avice et al., 2018).

Xenon is the second atmospheric element for which a stable isotope fractionation during the Archaean aeon has been observed, with the mass-independent fractionation of sulfur isotopes (MIF-S) being characteristic for Archaean age samples (Farquhar and Wing, 2003; Philippot et al., 2018). The MIF-S signature was likely produced by interactions between volcanic sulfur species and ultraviolet radiation, and shows a sharp transition and collapse during the Great Oxidation Event (GOE) (Farquhar and Wing, 2003). Conversely, the Xe isotope evolution was a gradual and cumulative process, causing atmospheric Xe to become increasingly fractionated with time. Furthermore, the GOE is understood to have stopped the generation of MIF-S, as ozone from free oxygen in the atmosphere shielded solar UV photons. For Xe, it is not clear if the GOE was also responsible for stopping Xe+ escape, and which environmental parameters (e.g., atmospheric composition, hydrogen escape, solar activity) may have changed to prevent Xe from escaping the Earth’s atmosphere.
In order to investigate the end of atmospheric MDF-Xe and to assess if it was coincidental with the GOE, we have analysed noble gases extracted from fluid inclusions from well-characterised hydrothermal quartz with ages encompassing that of the GOE. Using a new cumulative crushing technique, adapted from the procedure first used by Péron and Moreira (2018), allows the extraction of gas from much larger sample quantities, resulting in smaller analytical uncertainties (Supplementary Information). This is required to detect the low levels of Xe fractionation relative to the modern atmosphere that are observed close to the GOE. The samples measured in this study are, from oldest to youngest, Seidorechka (FD1A) and Polisarka (FD3A) Sedimentary Formations (Imandra-Varzuga Greenstone Belt, Kola Craton, Russia), and from the Ongeluk Formation (Kaapvaal Craton, South Africa). Depositional ages of FD1A and FD3A have been constrained between 2501.5 ± 1.7 Ma and 2441 ± 1.6 Ma (Amelin et al., 1995), and 2441 ± 1.6 Ma and 2434 ± 6.6 Ma (Brasier et al., 2013), respectively. The lower bounds of these time intervals are defined by the ages of overlying volcanic formations that are considered contemporaneous with quartz veining in underlying sediments.

Preservation of Ancient Atmospheric Xe

Fluid inclusions can potentially preserve the noble gas signature of the ancient atmosphere (Pujol et al., 2011). The petrographical study of the inclusions of the Ongeluk Formation performed by Saito et al. (2018) and our study of samples from the Kola Craton (FD1A and FD3A) indicate that a majority of the fluid inclusions have been trapped during quartz growth (Supplementary Information). The Ar and Xe content of the quartz fluid inclusions were measured using a Thermofisher Helix MC Plus© mass spectrometer at CRPG. The new extraction method was performed on FD1A and FD3A and consists of accumulating the extracted gases after crushing steps in an empty and previously evacuated steel bottle (Péron and Moreira, 2018; Péron et al., 2021).

Figure 1  Isotopic spectrum of Xe released from fluid inclusions in (a) sample FD1A and (b) sample FD3A. The grey line and its associated envelope (2σ) correspond to the isotopic trend of the $^{124,126,128,130}\text{Xe}$. (a) Mantle excesses of $^{131,132,134,136}\text{Xe}$ are estimated using the $^{129}\text{Xe}$ excess (Supplementary Information). Individual error bars are at 2σ.
Table 1 Isotopic ratio of the noble gases released by crushing and Xe fractionation. The fractionation was calculated from the 124Xe/128Xe ratios. The ratios are the weighted average of several replicates (Table S-3).

<table>
<thead>
<tr>
<th>Samples</th>
<th>124Xe</th>
<th>126Xe</th>
<th>128Xe</th>
<th>129Xe</th>
<th>131Xe</th>
<th>132Xe</th>
<th>133Xe</th>
<th>134Xe</th>
<th>136Xe</th>
<th>40Ar/36Ar</th>
<th>Xe Fractionation (‰ u⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.0234</td>
<td>0.0218</td>
<td>0.4715</td>
<td>6.496</td>
<td>5.213</td>
<td>6.607</td>
<td>2.563</td>
<td>2.176</td>
<td>298</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozima and Podosek (2002)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>±0.0005 ±0.0004 ±0.0004 ±0.0040 ±0.0066 ±0.0050 ±0.0640 ±0.0220 ±0.0200 ±1488 ±2.4</td>
<td></td>
</tr>
<tr>
<td>Ongeluk fm</td>
<td>0.0233</td>
<td>0.0220</td>
<td>0.4707</td>
<td>6.540</td>
<td>5.188</td>
<td>6.632</td>
<td>2.603</td>
<td>2.229</td>
<td>4570</td>
<td>−0.3</td>
<td></td>
</tr>
<tr>
<td>errors (2σ)</td>
<td>±0.0005</td>
<td>±0.0004</td>
<td>±0.0004</td>
<td>±0.0040</td>
<td>±0.0066</td>
<td>±0.0050</td>
<td>±0.0640</td>
<td>±0.0220</td>
<td>±0.0200</td>
<td>±1488</td>
<td>±2.4</td>
</tr>
<tr>
<td>FD1A</td>
<td>0.0235</td>
<td>0.0220</td>
<td>0.4745</td>
<td>6.578</td>
<td>5.235</td>
<td>6.669</td>
<td>2.666</td>
<td>2.284</td>
<td>3010</td>
<td>−2.0</td>
<td></td>
</tr>
<tr>
<td>errors (2σ)</td>
<td>±0.0004</td>
<td>±0.0004</td>
<td>±0.0034</td>
<td>±0.0026</td>
<td>±0.0686</td>
<td>±0.0044</td>
<td>±0.0192</td>
<td>±0.0106</td>
<td>±1504</td>
<td>±1.8</td>
<td></td>
</tr>
<tr>
<td>FD3A</td>
<td>0.0235</td>
<td>0.0216</td>
<td>0.4684</td>
<td>6.554</td>
<td>5.243</td>
<td>6.778</td>
<td>2.801</td>
<td>2.458</td>
<td>3639</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>errors (2σ)</td>
<td>±0.0006</td>
<td>±0.0006</td>
<td>±0.0054</td>
<td>±0.0056</td>
<td>±0.0444</td>
<td>±0.0566</td>
<td>±0.0284</td>
<td>±0.0224</td>
<td>±610</td>
<td>±3.0</td>
<td></td>
</tr>
</tbody>
</table>

All our analyses present an excess of 40Ar relative to modern atmospheric Ar with a minimum 40Ar/36Ar ratio of 1760 ± 18, from one crush of the Ongeluk Formation (Table S-4), attesting to limited exchange, if any, with modern atmospheric Ar. The 131,132,134,136Xe excesses detected for all our samples correspond to a contribution from the spontaneous fission of 238U (Fig. 1). We computed linear regressions on 124,126,129Xe/130Xe isotope ratios using the IsoplotR software (Vermeesch, 2018). The oldest sample, FD1A, presents a fractionation of 2.0 ± 1.8 ‰ u⁻¹ (2σ; Fig. 1a) compared to the present day atmosphere. The FD3A (0.7 ± 3.3 ‰ u⁻¹, Fig. 1b) and Ongeluk quartz (−0.3 ± 2.4 ‰ u⁻¹, Fig. S-2), the youngest samples, do not display a resolvable MDF-Xe signature beyond uncertainty at 2σ (Table 1). Compared to modern atmospheric Xe (129Xe/130Xe = 6.50; Ozima and Podosek, 2002), the samples preserve small excesses of radiogenic 129Xe (129Xe/130Xe of 6.58 ± 0.04, 6.55 ± 0.06 and 6.54 ± 0.07 for FD1A, FD3A and Ongeluk Formation samples, respectively). It is the opposite of what is usually observed in samples from the Archaean aon (Avice et al., 2017; Bekkaert et al., 2018). The mono-isotopic depletion in 129Xe within the Archaean atmosphere is thought to have been compensated by the progressive release of 131Xe from the mantle throughout the Archaean aon (Marty et al., 2019). The 129Xe excess in the oldest sample, FD1A, is therefore likely to be due to a local input of mantle-derived Xe in the hydrothermal fluids from which the quartz precipitated. A mantle Xe input could potentially account for the light Xe isotope excesses measured in the samples, especially when considering Xe in the Archaean mantle was likely primordial (chondritic; Broadley et al., 2020). We ruled out this possibility because the 129Xe/130Xe of FD1A is inconsistent with mixing between the primordial mantle and modern atmosphere (Fig. S-4), and atmospheric regassing of the mantle was likely to be inefficient during the Archaean aon (Péron and Moreira, 2018). Mantle contributions are then negligible (Table S-1; Supplementary Information) and excesses of 124,126,129Xe in FD1A are considered to reflect the ancient atmospheric composition.

**Link between Xe Fractionation and MIF-S**

From our analyses we have shown, for the first time, that MDF-Xe signals disappear between two well-characterised Kola Craton sedimentary formations, implying that the fractionation process stopped between 2441 ± 1.6 Ma and 2434 ± 6.6 Ma (Fig. 2). Previous data from Avice et al. (2018) indicated that MDF-Xe was observabe throughout the Archaean and into the Palaeoproterozoic era until 2 Ga. The difference between these previous data and our new results can be explained by (i) the age of the fluid inclusions containing the atmospheric Xe, and (ii) the precision required to distinguish between the present day atmosphere and the small extent of isotope fractionation of Xe present in fluid inclusion formed close to the cessation of Xe evolution. The fluid inclusion inventory reflects the atmospheric composition at the last equilibration with the atmosphere, which may be different from the age of quartz precipitation. Thus, the 6.5 ± 1.5 ‰ u⁻¹ recorded in the 3.7 Ga Isua rocks that was attributed to a resetting metamorphic event at 2.3 Ga (Avice et al., 2018) may, in fact, reflect an older atmospheric composition. Because the gas accumulation method is more precise than those used previously (Avice et al., 2018), we could identify a slight MDF-Xe for sample FD1A at the 2σ precision level. Considering the 2σ error range for the fractionation of Xe in previously studied 2.1 ± 0.1 Ga Gaoua (Burkina Faso) and the 2.0 ± 0.1 Ga Carnaiba (Brazil) samples gives values of 2.6 ± 4.2 and 1.8 ± 4.4 ‰ u⁻¹ for the fractionation of atmospheric Xe (Avice et al., 2018). These values are both within uncertainty of modern atmosphere, and therefore it is not clear whether they, in fact, contained a fractionated atmospheric Xe signature.

The MDF-Xe evolution results from a poorly understood cumulative process, which took place during the Hadean and Archaean periods. Storage of Xe in an organic haze and the contemporary loss of the residual Xe from space could explain the observed fractionation (Hébrard and Marty, 2014). This process would stop in an O₂-rich atmosphere that would halt the production of the haze. However, this possibility would still necessitate the escape of non-trapped Xe and therefore an additional, not yet identified, process is required. The escape of hydrogen ions to space entraining Xe has been also previously suggested to account for both the oxidation of the atmosphere and the unique fractionation of Xe isotopes (Zahnle et al., 2019). Consequently, this model leads to the oxidation of the surface reservoirs, including the crust, to the point where O₂ became stable enough to compete with atmospheric reduced gases, such as H₂ and CH₄ (Zahnle et al., 2019). According to our data, the MDF-Xe signal disappears and the present day composition is reached between ~2441 and ~2434 Ma (Fig. 2). Sustaining a continuous escape of ionised hydrogen from the Earth formation until the GOE depends on many parameters including the strength of the Earth’s magnetic field, the level of solar extreme ultraviolet (EUV) irradiation and the amount of hydrogen present in the atmosphere (Zahnle et al., 2019). In the case of discrete escape episodes rather than a constant rate of atmospheric Xe-loss, our results imply a final burst occurring simultaneously with the initiation of the GOE.
The end of MDF-Xe between FD1A and FD3A is coincident with the disappearance of MIF-S as recorded in the sedimentary rocks hosting the quartz veins (Warke et al., 2020). Sulfur isotopes represent an instantaneous record of the oxidation states of the atmosphere, at a local scale. MDF-Xe is the result of a cumulative process at global scale so it is likely that these geochemical markers would not be exactly simultaneous in their cessation. In light of the S-Xe relationship, it appears that the atmospheric process traced by Xe isotopes is linked with the oxidation state of the terrestrial atmosphere (Avice et al., 2018).

The formation of the ozone layer as a consequence of O₂ rise in the atmosphere accounts for the end of the MIF-S signature (Farquhar and Wing, 2003; Lyons et al., 2014). However, MIF-S signals could be preserved under oxidative weathering and then obscure the MIF/MDF transition due to a memory effect (Philippot et al., 2018). This leads to a delay between the rise of oxygen and the disappearance of MIF-S signals of about 2.32 Ga (Gumsley et al., 2017; Poulton et al., 2021). Moreover, some environments may require more time to adapt and become permanently oxygenated after the end of hydrogen escape (Lyons et al., 2014). Contrary to the MIF-S, hydrodynamic escape is not affected by the ozone formation (Zahnle et al., 2019), and may be more sensitive to O₂ availability. Thus, the end of MDF-Xe fractionation could mark the time when atmospheric escape of hydrogen ceased, and ceased to contribute to the change of the redox ratio of Earth’s surface reservoirs. It is important to underline the fact that Xe fractionation is a cumulative process: local variation of the signal cannot occur, unlike sulfur (Philippot et al., 2018). In light of this, Xe is a reliable tracer and may better constrain the rise of oxygen levels within the atmosphere.

Conclusion

We have measured an isotopically fractionated Xe composition of 2.0 ± 1.8 ‰ relative to modern atmosphere at 2441 ± 1.6 Ma. A slightly younger sample of 2434 ± 6.6 Ma does not record any such fractionation, and is indistinguishable from the modern atmospheric composition. The disappearance of isotopically fractionated Xe signals could be a consequence of O₂ accumulation in the atmosphere. A temporal link between the disappearance of the Xe isotope fractionation and the MIF-S signature at the Archaean-Proterozoic transition is clearly established for the Kola Craton. The mass-dependent evolution of Xe isotopes is the indication of a cumulative atmospheric process that may have played an important role in the oxidation of the Earth’s surface (Zahnle et al., 2019), independently of biogenic O₂ production that started long before the permanent rise of O₂ in the atmosphere (Lyons et al., 2014).

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Additional Information

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References


