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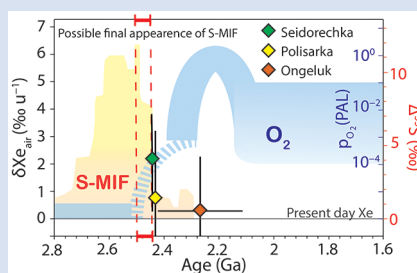
The end of the isotopic evolution of atmospheric xenon

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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.

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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.

The Ongeluk Formation has been dated at 2114 ± 312 Ma (Ar-Ar age; Saito *et al.*, 2018) with an upper bound defined by the host formation age of 2425.6 ± 2.6 Ma (Gumsley *et al.*, 2017).

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).

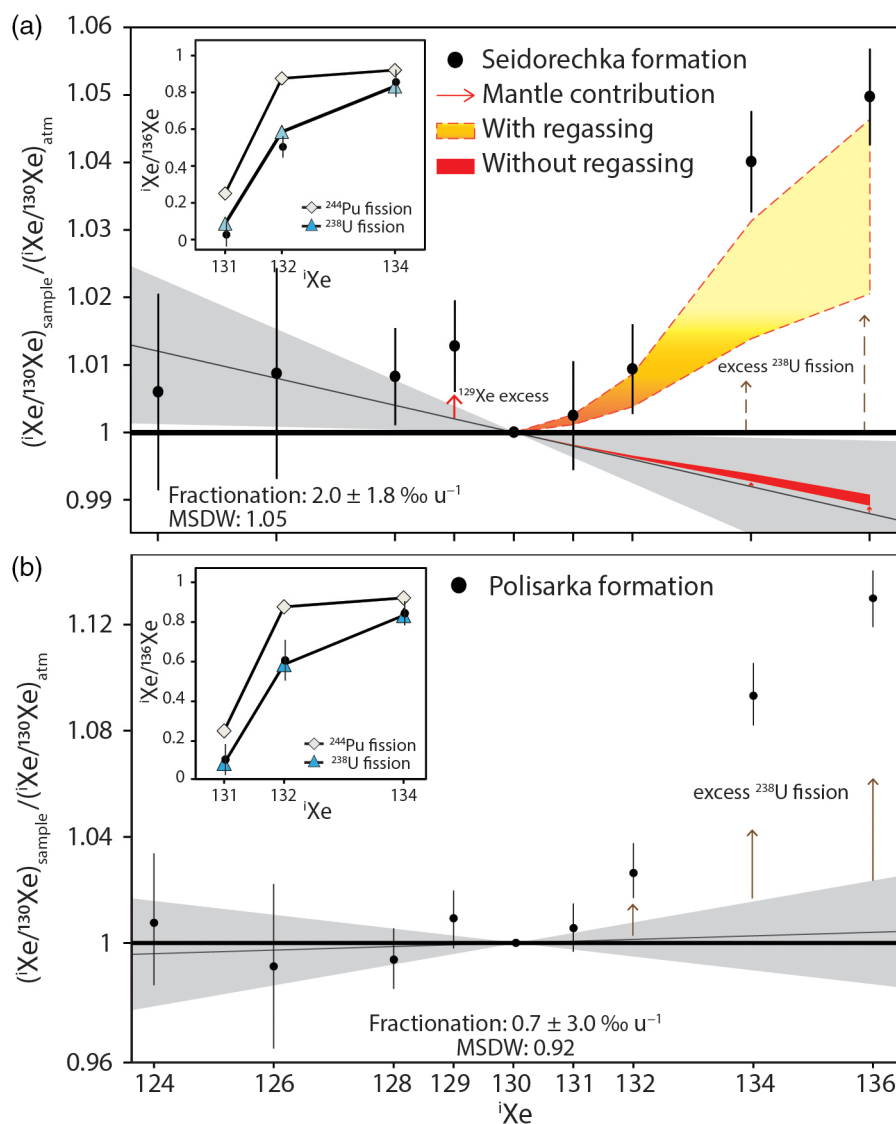


Figure 1 Isotopic spectrum of Xe released from fluid inclusions in (a) sample FD1A and (b) sample FD3A. The grey line and its associated envelope (2σ) correspond to the isotopic trend of the $^{124,126,128,130}\text{Xe}$. (a) Mantle excesses of $^{131,132,134,136}\text{Xe}$ are estimated using the ^{129}Xe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

Samples	^{124}Xe	^{126}Xe	^{128}Xe	^{129}Xe	^{131}Xe	^{132}Xe	^{134}Xe	^{136}Xe	$^{40}\text{Ar}/^{36}\text{Ar}$	Xe Fractionation (% u^{-1})
	$^{130}\text{Xe} = 1$									
Air Ozima and Podosek (2002)	0.0234	0.0218	0.4715	6.496	5.213	6.607	2.563	2.176	298	
Ongeluk fm errors (2σ)	0.0233 ± 0.0005	0.0220 ± 0.0004	0.4707 ± 0.0040	6.540 ± 0.066	5.188 ± 0.050	6.632 ± 0.640	2.603 ± 0.220	2.229 ± 0.020	4570 ± 1488	-0.3 ± 2.4
FD1A errors (2σ)	0.0235 ± 0.0004	0.0220 ± 0.0004	0.4745 ± 0.0034	6.578 ± 0.026	5.235 ± 0.068	6.669 ± 0.044	2.666 ± 0.0192	2.284 ± 0.016	3010 ± 504	-2.0 ± 1.8
FD3A errors (2σ)	0.0235 ± 0.0006	0.0216 ± 0.0006	0.4684 ± 0.0054	6.554 ± 0.056	5.243 ± 0.044	6.778 ± 0.056	2.801 ± 0.028	2.458 ± 0.024	3639 ± 610	0.7 ± 3.0

All our analyses present an excess of ^{40}Ar relative to modern atmospheric Ar with a minimum $^{40}\text{Ar}/^{36}\text{Ar}$ 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 $^{131,132,134,136}\text{Xe}$ excesses detected for all our samples correspond to a contribution from the spontaneous fission of ^{238}U (Fig. 1). We computed linear regressions on $^{124,126,128}\text{Xe}/^{130}\text{Xe}$ 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 ($^{129}\text{Xe}/^{130}\text{Xe} = 6.50$; Ozima and Podosek, 2002), the samples preserve small excesses of radiogenic ^{129}Xe ($^{129}\text{Xe}/^{130}\text{Xe}$ 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 aeon (Avice et al., 2017; Bekaert et al., 2018). The mono-isotopic depletion in ^{129}Xe within the Archaean atmosphere is thought to have been compensated by the progressive release of ^{129}Xe from the mantle throughout the Archaean aeon (Marty et al., 2019). The ^{129}Xe 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 $^{128}\text{Xe}/^{130}\text{Xe}$ 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 aeon (Péron and Moreira, 2018). Mantle contributions are then negligible (Table S-1; Supplementary Information) and excesses of $^{124,126,128}\text{Xe}$ 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 observable 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^+ into 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 O_2 -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 O_2 became stable enough to compete with atmospheric reduced gases, such as H_2 and CH_4 (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.

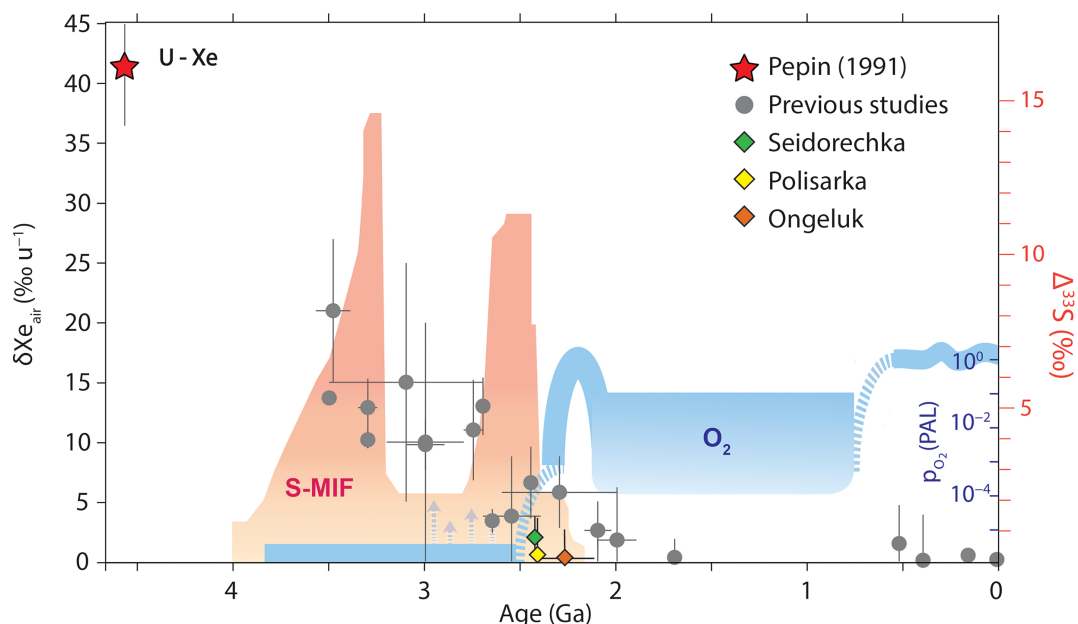


Figure 2 Records of atmospheric oxygen (O_2 , blue; Lyons *et al.*, 2014), mass-independent fractionation of sulfur isotopes (MIF-S, orange; data from Killingsworth *et al.*, 2019) and mass dependent fractionation of xenon isotopes throughout Earth's history (Pepin, 1991; Avice *et al.*, 2018; Almayrac *et al.*, 2021), uncertainties are at 2σ .

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 O_2 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 O_2 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 $2.0 \pm 1.8 \text{ ‰ u}^{-1}$ relative to modern atmosphere at $2441 \pm 1.6 \text{ Ma}$. A slightly younger sample of $2434 \pm 6.6 \text{ Ma}$ 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 O_2 accumulation in the atmosphere. A temporal link between the disappearance of the Xe isotopes 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 O_2 production that started long before the permanent rise of O_2 in the atmosphere (Lyons *et al.*, 2014).

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2207>.



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Supplementary Information

The Supplementary Information includes:

- Geological Context
- Materials and Methods
- Fluid Inclusions Study
- Fissiogenic and Mantle Contribution
- Tables S-1 to S-4
- Figures S-1 to S-4
- Supplementary Information References

Geological Context

Hydrothermal quartz samples were selected from two different cratons based on their ages of formation, between 2.3 and 2.5 Ga, encompassing the GOE (Holland, 2006; Lyons *et al.*, 2014; Gumsley *et al.*, 2017). The Ongeluk Formation is a succession of pillowed and sheeted andesitic basalts that has undergone alteration with temperatures not exceeding 200 °C and metamorphism up to prehnite-pumpellyite facies (Cornell *et al.*, 1996; Gutzmer *et al.*, 2001, 2003). This formation is intercalated with the Makganyene glaciation deposits formed during one of the Paleoproterozoic snowball earth events (Evans *et al.*, 1997). Pods of quartz formed within the open spaces of the pillows soon after the eruption as indicated by the lack of deformation in the cavities (Gutzmer *et al.*, 2003; Saito *et al.*, 2016). The pillow-lavas are considered to have formed 2425.6 ± 2.6 Ma (2σ ; Gumsley *et al.*, 2017) and give an upper bound to the sample. Saito *et al.*, (2018) performed Ar-Ar dating on three distinct quartz pods to estimate when the quartz crystals precipitated. They

found a maximum age of 2701 ± 43 Ma (1σ) and a minimum age of 2114 ± 312 (1σ) Ma. The difference is likely due to the difficulties in estimating the initial amount of K in the fluid. The age of ≈ 2701 Ma is unlikely given the age of the host rock. The petrographic description of the fluid inclusion indicates a predominantly primary origin (Saito *et al.*, 2018). Thus, the minimum age of the trapped atmospheric noble gases within the inclusions is relative to the quartz pods formed at 2114 ± 312 Ma, consistent with the upper bound of the pillow lava formation.

The Seidorechka (sample FD1A) and Polisarka (sample FD3A) sedimentary formations are part of the Imandra-Varzuga Greenstone Belt. These formations were targeted by the Fennoscandian Arctic Russia – Drilling Early Earth Project (FAR-DEEP; Melezhik *et al.*, 2013) of the International Continental Scientific Drilling Program. The Imandra-Varzuga Greenstone Belt consist of several successions of alternating thin sedimentary and thick volcanic formations overlying the Archean basement (Melezhik and Sturt, 1994; Warke *et al.*, 2020). Hydrothermal quartz was collected from veins cross-cutting solely these sedimentary formations, in the shale member for FD1A and in the diamictite-greywacke member for FD3A. Depositional ages of Seidorechka and Polisarka sedimentary formations 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. We assumed that minerals contained in quartz veins formed contemporaneously with the overlying volcanic formations that define the minimum age of these sedimentary formations and thus yield ages of 2441 ± 1.6 Ma for the quartz veins crossing Seidorechka Sedimentary Formation (FD1A ; Amelin *et al.*, 1995) and at 2434 ± 6.6 Ma for the quartz veins crossing Polisarka Sedimentary Formation (FD3A ; Brasier *et al.*, 2013).

Materials and Methods

For noble gas analyses, quartz grains of 2 to 4 mm in size were handpicked under a binocular microscope and loaded into hand-activated crushers under vacuum. Gases were extracted using a 3.5 Nm torque wrench to activate each crusher. Purified Ar and Xe gas fractions were measured using a ThermoFisher Helix MC Plus© mass spectrometer at CRPG. A total of 9 Ar and Xe analyses were performed on the Ongeluk quartz using the method of Avice *et al.* (2018) that consisted of replicated analyses on distinct crushes of 1 to 3 g of quartz. The Ar isotopic ratios were systematically analysed after each crush to check for the absence of atmospheric contamination. A new technique was used to study samples from the Kola Craton (Péron and Moreira, 2018). It consists of accumulating the extracted gases after crushing steps in an empty and previously evacuated steel bottle immersed in liquid nitrogen (77 K) during 10 minutes before purification and analysis. This method allowed the crushers to be recharged multiple times with fresh quartz grains and therefore enables the Ar and Xe gas fractions to be concentrated within the bottle. By using this method, we prepared 3 bottles for analyses: two bottles by crushing 16.70 g (FD1A-B1) and 10.08 g (FD1A-B2) of sample FD1A in 4 and 3 crusher loads respectively, and one bottle by crushing 18.16 g of sample FD3A in 4 separate crusher loads. The two



different bottles of FD1A extracted gases (FD1A – B1 and FD1A – B2) permitted the analysis of 4 and 5 aliquots of gas, respectively, to ensure reproducibility of the measurements. One bottle of extracted gases from FD3A permitted the analyses of 4 aliquots (Table S-3). The Ar abundance and isotopes were analysed only in the first gas aliquot for each bottle by multicollection. Isotopic ratios of Xe presented in Table 1 are weighted averages of the replicated analyses for each sample. For each sample, we estimated the potential mass-dependent fractionation of Xe (MDF-X, in permille per atomic mass unit $\text{‰}\cdot\text{u}^{-1}$, where a value of 0 indicates no MDF-Xe relative to modern atmospheric Xe) by computing linear regressions on $^{124,126,128}\text{Xe}/^{130}\text{Xe}$ isotope ratios using the IsoplotR software (Vermeesch, 2018). Data are given with uncertainties at 2σ .

Fluid inclusions Study

Petrography

Rocks of Seidorechka and Polisarka sedimentary formations are respectively crossed by 3 pluri-centimetric (5 to 10 cm) hydrothermal quartz veins. These veins are restricted to each sedimentary formation and formed after sedimentation. In these volcano-sedimentary deposits (Melezhik *et al.*, 2013), it is likely that the main fluid circulations are linked to the deposit of volcanic units overlying the sedimentary units. Thus, it is assumed that hydrothermal circulations are linked to the accumulation of Seidorechka and Polisarka volcanic formations overlying both sedimentary formations. Fluid inclusions were studied using 200- μm doubly polished thick sections.

Sample FD1A from Seidorechka sedimentary formations does not present obvious quartz recrystallisation but shows a general pattern of parallel trails of fluid inclusions confined within individual grains. At the grain scale, inclusions are either isolated or organised within parallel trails that do not cross grain boundaries (Fig. S-1). The boundaries between grains are decorated by fluid inclusions of less than 5 μm . The interior of the grains contains bigger inclusions, up to 20 μm , that allowed microthermometry and Raman analyses. The inclusions are thus considered primary in origin if they are isolated or pseudo-secondary when organised in trails within the grain structure, in any case trapped during quartz growth (Roedder, 1984). All the inclusions in FD1A are biphasic with the fraction of the bubble in the range 10–20 % of the total volume. Between 5 and 10 % of the inclusions are characterised by the typical CO_2 double bubble feature at room temperature (*e.g.*, Diamond, 2003).

Petrography of fluid inclusions in FD3A from Polisarka sedimentary formation is complex due to quartz deformation and recrystallisation, which resulted in (i) undulose extinction under microscope and (ii) formation of newly recrystallised grains, over ~15 % of the studied thin-section, depleted in fluid inclusions (Fig S-1; Kerrich, 1976). Given the scarcity of 1 to 5 μm fluid inclusions within recrystallised quartz, the recrystallisation has a negligible effect on noble gas analyses compared to non-recrystallised quartz grains where most of fluid inclusions are observed. In the



latter, inclusions can be isolated, organised as trails confined within grains or as decorating quartz sub-grain boundaries. These observations are coherent with a continuous fluid entrapment contemporaneous with formation and deformation of host quartz (Eglinger *et al.*, 2014). No evidence of secondary fluid inclusions was observed. Liquid monophasic and biphasic inclusions about 10 to 20 μm may coexist within the same grain (Fig. S-1). The volume of the vapour bubbles in biphasic inclusions varies from 80 to 20 % of the volume.

Methods

Microthermometry was performed on fluid inclusions from samples FD1A and FD3A using a Linkam MDS600 heating-cooling stage at GeoRessources laboratory (Nancy, France). The following phase transition temperatures were measured when possible: final melting of the carbonic phase ($T_{\text{m car}}$), apparent first melting of the aqueous phase (T_{fm}), ice melting ($T_{\text{m ice}}$), clathrate dissociation ($T_{\text{m cla}}$), partial homogenisation of the carbon-dominated phase ($T_{\text{h car}}$) and bulk homogenisation of the entire inclusion (T_{h}). Microthermometry experiments were made between $-150\text{ }^{\circ}\text{C}$ and not above $200\text{ }^{\circ}\text{C}$ to avoid decrepitation. The microthermometric stage was calibrated daily using natural pure CO_2 ($-56.6\text{ }^{\circ}\text{C}$) and synthetic pure H_2O fluid inclusions with known transition temperatures. Precisions of the phase transition temperature measurements are about $\pm 2\text{ }^{\circ}\text{C}$ for T_{fm} , $\pm 0.1\text{ }^{\circ}\text{C}$ for $T_{\text{m car}}$, $T_{\text{m ice}}$, T_{fm} , and $T_{\text{m cla}}$, and $\pm 1\text{ }^{\circ}\text{C}$ for T_{h} .

Raman spectra were acquired at room temperature using a LabRAM HR spectrometer (Horiba Jobin Yvon) equipped with an $1,800\text{ gr.mm}^{-1}$ grating and an edge filter at GeoRessources laboratory (Nancy, France). Excitation was provided by an Ar^+ laser operating at a wavelength of 514.53 nm focussed through a $\times 50$ objective (Olympus). The aperture of the focal hole and the slit were $500\text{ }\mu\text{m}$ and $100\text{ }\mu\text{m}$ respectively. A total of 3 acquisitions were accumulated for each spectrum and acquisition time was variable between 60 and 10 s depending on the quality of the signal and the mobility of the bubble (shorter acquisition time for moving bubble). Spectrum acquisition was systematically performed in the quartz matrix nearby the inclusion of interest at the same depth and same analytical conditions in order to distinguish between N_2 from air and N_2 from the inclusion. Biphasic fluid inclusions often exhibited moving gas bubbles which prevented the acquisition of the Raman spectra. Spectra of CH_4 , H_2S , N_2 and CO_2 in the gas phase were acquired separately in two different spectral windows. The absence of H_2 was monitored in a third spectral window. Peak positions and areas were determined using the integration tool of LabSpec software (Horiba Jobin Yvon) at 4156 cm^{-1} for H_2 ; 2917 cm^{-1} for CH_4 ; 2580 cm^{-1} for H_2S liquid; 2331 cm^{-1} for N_2 and the Fermi doublet at 1285 and 1388 cm^{-1} for CO_2 (Burke, 2001). The composition of biphasic inclusions in FD1A was acquired for 4 inclusions. For FD3A, 5 compositions were determined for biphasic inclusion and 8 compositions were determined for monophasic inclusions (Table S-2). The salinity of the fluid inclusions was calculated in single-salt $\text{NaCl-CO}_2\text{-CH}_4\text{-N}_2\text{-H}_2\text{O}$ system using *Clathrates* computer package (Bakker, 1997), by using either (i) the program *ICE* following the equations of Duan *et al.*, (1996) associated with $T_{\text{m ice}}$ and $T_{\text{m cla}}$ when clathrate dissociation occurred in presence of ice, L_{aq} and CO_2 vap,



or (ii) Q_2 program when clathrate dissociation occurred via a Q_2 transition (coexistence of L_{aq} , Cla, CO_2 liq and CO_2 vap), associated with T_m cla and T_h car and on the equations of Thiéry *et al.* (1994).

Results

For FD1A, the observed phase transitions were T_{fm} , T_m ice, T_m cla, and T_h for 17 inclusions (Table S-4). The T_{fm} were difficult to observe because of the small size of the fluid inclusions and the disappearance of the vapour bubble on cooling, leading to a metastable state of the inclusions until the sudden reappearance of the vapour bubble. Seven of the measured inclusions presented the typical double bubble of CO_2 permitting the observation of T_m car and T_h car. The average molar composition of the vapour phase in inclusions is 91.9 ± 3.4 mol % CO_2 , 3.2 to 10.7 mol % N_2 and < 1 mol % CH_4 . No significant variations were observed between biphasic and triphasic inclusion. The T_{fm} were observed from -21 to -41 °C and the T_h from 118 to over 200 °C. The inclusions with a $T_{fm} \approx -21$ °C presented the lowest T_h , between 118 and 187 °C, compared to the inclusions with a lower T_{fm} which generally presented a T_h over 200 °C. These observations point to the presence of two fluids: one where the salts present in the aqueous phase are made of pure NaCl and one where they are composed of a mixing between NaCl and another salt species. The total salinity was nonetheless calculated considering pure NaCl and varies uniformly between 0.8 and 25.4 weight % in the aqueous solution independently of the salt system. It is moreover important to note that there is no apparent correlation between salinity and volatiles species concentration.

The T_m ice, T_m cla and T_h were observed for 11 biphasic inclusions in FD3A (Table S-4). Vapour and sometimes solid phases in monophasic inclusions appeared at low temperatures (< -120 °C; $n = 14$). Biphasic fluid inclusion vapours in sample FD3A contained CH_4 from 9.8 up to 50.4 mole percent (Table S-2). H_2S was systematically present from 0.2 to 1.1 mole percent. N_2 could not be distinguished from atmospheric N_2 for half of the inclusions and reached a maximum of 2.4 mole percent. T_{fm} was difficult to observe in this sample and we assumed pure NaCl to calculate the salinity. It is on average 3.3 ± 1.9 weight percent. The T_h were higher than 174 and generally over 200 °C. Monophasic gaseous liquid inclusions are mostly composed of CH_4 (79.5 to 98.9 mole percent with one outlier at 26.2 mole percent), with minor amounts of H_2S of 0.8 ± 0.3 mole percent. N_2 is only present as a trace > 0.6 mol %. The CO_2 content varied between 4.8 and 19.5 mole percent with an outlier at 73.2 mole percent.

Discussion and interpretation

The dominant orientation of fluid inclusions along parallel pseudo-secondary trails in FD1A sample suggests a strong tectonic influence coherent with the long-term pulsed tectonomagmatic event that affected the Imandra-Varzuga rift zone (Chashchin *et al.*, 2008). However, the tectonically influenced-fluid inclusion planes rarely cross the grains boundaries. So, these fluid inclusions are representative of the fluid, including primary noble-gas composition, present



during quartz growth. Our observations attest the preservation of two fluids within the sample. The first one characterised by pure NaCl in the aqueous phase could be assimilated to a seawater-derived fluid. The second one, where the aqueous phase contains a mixture of NaCl and another salt species, could point to a magmatic signature (Heinrich, 2005) and the analysed fluid inclusions represent a mixture between high-salinity high-temperature magmatic fluids and the low-salinity low-temperature seawater. This is in accordance with the xenon isotopic composition, which indicate a mixing between an atmospheric endmember, derived from the seawater-fluid, and a minor mantle contribution, derived from the magmatic fluid.

Sample FD3A presents heterogeneous entrapment with the coexistence of monophasic and biphasic inclusions with a continuum of size of the vapour bubbles, from 20 to 90 % of the total volume. This observation linked with the co-variation of CH₄/CO₂ content, the monophasic liquid inclusions being enriched in the most volatiles species, are solids arguments for boiling and entrapment below the solvus within the H₂O-CH₄-CO₂-H₂S-N₂ system of a single fluid (Diamond, 2003). Contemporaneous recrystallisation induced the loss of some primary and pseudo-secondary fluid inclusions (Kerrick, 1976). No subsequent fluid circulation was noticed by secondary inclusions. The bulk noble gases composition issued from these fluid inclusions thus likely to reflect the composition of the late Palaeoproterozoic as this sample appears to have precipitated from one unique fluid.

Fissiogenic and mantle contribution

Fissiogenic contribution

Production of heavy Xe isotopes can be attributed to the spontaneous fission of ²³⁸U (half-life of 4.47 Ga or ²⁴⁴Pu (half-life of 82 Ma; Ozima and Podosek, 2002). We calculated the theoretical production of the isotopes: ¹³¹Xe, ¹³²Xe, ¹³⁴Xe normalised to ¹³⁶Xe by fission of ²³⁸U and ²⁴⁴Pu (rate of production from Alexander *et al.*, 1971; Ragetti *et al.*, 1994). The Xe isotope excess was calculated as Equation S-1:

$$\left(\frac{i\text{Xe}}{^{136}\text{Xe}}\right)_{\text{excess}} = \frac{\left(\frac{i\text{Xe}}{^{130}\text{Xe}}\right)_{\text{sample}} - \left(\frac{i\text{Xe}}{^{130}\text{Xe}}\right)_{\text{atm}}}{\left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_{\text{sample}} - \left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_{\text{atm}}} \quad (\text{Eq. S-1})$$

Associated uncertainties are as Equation S-2:

$$\sigma_{\left(\frac{i\text{Xe}}{^{136}\text{Xe}}\right)_{\text{sample}}} = \left(\frac{i\text{Xe}}{^{136}\text{Xe}}\right)_{\text{sample}} \times \left[\left(\frac{\sigma_{\left(\frac{i\text{Xe}}{^{130}\text{Xe}}\right)_{\text{sample}}}}{\left(\frac{i\text{Xe}}{^{130}\text{Xe}}\right)_{\text{sample}} - \left(\frac{i\text{Xe}}{^{130}\text{Xe}}\right)_{\text{atm}}} \right)^2 + \left(\frac{\sigma_{\left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_{\text{sample}}}}{\left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_{\text{sample}} - \left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_{\text{atm}}} \right)^2 \right]^{1/2} \quad (\text{Eq. S-2})$$

By plotting ²³⁸U and ²⁴⁴Pu fission spectrums in perspective with sample ratios, a ²³⁸U origins of the heavy isotopes can be suggested for all our samples (Fig. 1; Fig. S-2)



Mantle Contribution

The excess of ^{129}Xe is thought to show a binary mixing between Archean atmosphere and mantle-derived xenon in our samples such as Equation S-3:

$$\left(\frac{^{129}}{^{130}}\right)_{\text{Sample}} = \alpha \left(\frac{^{129}}{^{130}}\right)_{\text{Mantle}} + (1 - \alpha) \times \left(\frac{^{129}}{^{130}}\right)_{\text{Archean atmosphere}} \quad (\text{Eq. S-3})$$

with α as the fraction of the mantellic ^{130}Xe . The value used for $(^{129}/^{130})_{\text{Mantle}}$ is dependent on whether significant regassing of atmospheric Xe into the deep Earth is assumed to have occurred. Without regassing, we took the value $(^{129}/^{130})_{\text{Mantle}} = 14 \pm 1$ (Marty *et al.*, 2019). Considering regassing, we assume a MORB-type composition of $(^{129}/^{130})_{\text{Mantle}} = 6.92 \pm 0.07$ (Pető *et al.*, 2013), that is the lowest estimation in the literature (Holland and Ballentine, 2006; Mukhopadhyay, 2012; Parai and Mukhopadhyay, 2021). The calculated mantellic ^{130}Xe contribution is thus an upper limit. From α we calculated the associated $(^{128}/^{130})_{\text{Expected}}$ for FD1A assuming a $(^{128}/^{130})_{\text{Mantle}} = 0.51 \pm 0.01$ (primordial Xe, Ozima and Podosek, 2002). Results are available in Table S-1. Despite the heavy isotope discrepancies between the two bottles of FD1A, the excess of ^{129}Xe is identical for the two bottles (Table S-3) so we considered an equal mantellic contribution. The difference between the excess of $^{131}, ^{132}, ^{134}, ^{136}\text{Xe}$ is then due to a difference of crustal fissiogenic ^{238}U contribution.

There is potentially a weak positive correlation among individual data in Figure S-4 with all our measurements parallel to the Rayleigh fractionation trend. This imply a similar contribution from mantle gas to the hydrothermal fluids and it does not appear realistic for samples from different locations. Within the uncertainties, the youngest sample from the Ongeluk formation is atmospheric. The excesses of ^{129}Xe in the samples from the Kola Craton (Polisarka and Seidorechka formations) are consistent with the same mantle contribution to the hydrothermal fluids in this location. However, the oldest sample from Seidorechka formation presents higher $^{128}, ^{129}\text{Xe}$ compare to the modern-air and to the Polisarka sample. This stands for a slightly fractionated atmosphere at the time that disappeared within the ≈ 7 million years separating the formation of the 2 samples. Without ^{129}Xe excesses (this study) or deficits (Avicé *et al.*, 2017; Marty *et al.*, 2019), the measurements are expected to fall on the Rayleigh fractionation trend through modern air (Fig. S-4).



Supplementary Tables

Table S-1 Estimation of the ^{130}Xe mantellic contribution from two different endmembers composition. The Archean mantle $^{129}\text{Xe}/^{130}\text{Xe}$ ratio is used to calculate the % mantle without crustal regassing; The MORB $^{129}\text{Xe}/^{130}\text{Xe}$ ratio is used to calculate the % mantle with atmospheric regassing. 1 - Marty *et al.* (2019); Pepin (2003); 3 - Pető *et al.* (2013); 4 - Ozima and Podosek (2002).

	$^{129}\text{Xe}/^{130}\text{Xe}$ (2σ)	$^{128}\text{Xe}/^{130}\text{Xe}$ (2σ)	Without atm regassing		With atm regassing	
			% Mantle	Expected $^{128}\text{Xe}/^{130}\text{Xe}$ (2σ)	% Mantle	Expected $^{128}\text{Xe}/^{130}\text{Xe}$
FD1A	6.58 (0.04)	0.475 (0.003)	0.9 $^{+0.3}_{-0.4}$	0.474 (0.001)	16.8 $^{+7.1}_{-5.0}$	0.478 $^{+0.001}_{-0.003}$
Archean Mantle ^{1,2}	14 (1)	0.507 (0.004)				
MORB ³	6.92 (0.07)					
Modern air ⁴	6.50					

Table S-2 Molar percentage of volatiles species in some fluid inclusions determined by RAMAN spectrometry.

N° inclusion	CO ₂	N ₂	% molar		Total
			H ₂ S	CH ₄	
FD1A - Biphasic					
13	88.8 %	10.5 %	0.0 %	0.7 %	100.0 %
28	93.4 %	6.5 %	0.0 %	0.1 %	100.0 %
30	95.9 %	3.2 %	0.0 %	0.9 %	100.0 %
31	89.3 %	10.7 %	0.0 %	0.0 %	100.0 %
FD3A - Biphasic					
1	90.0 %	0.0 %	0.2 %	9.8 %	100.0 %
2	60.7 %	2.4 %	0.3 %	36.6 %	100.0 %
3	68.3 %	0.0 %	0.2 %	31.5 %	100.0 %
6	47.7 %	0.8 %	1.1 %	50.4 %	100.0 %
9	59.7 %	0.7 %	0.5 %	39.2 %	100.0 %
21	61.1 %	0.0 %	0.3 %	38.6 %	100.0 %
FD3A - Monophasic					
1	0.0 %	0.0 %	1.1 %	98.9 %	100.0 %
2	0.0 %	0.0 %	1.4 %	98.6 %	100.0 %
3	73.2 %	0.2 %	0.4 %	26.2 %	100.0 %
5	4.8 %	0.0 %	0.8 %	94.4 %	100.0 %
8	16.3 %	0.0 %	0.9 %	82.8 %	100.0 %
13	19.2 %	0.5 %	0.7 %	79.6 %	100.0 %
14	19.5 %	0.5 %	0.5 %	79.5 %	100.0 %
15	15.9 %	0.5 %	0.7 %	82.9 %	100.0 %



Table S-3 Isotopic ratio of the noble gases of each replicate. Values in red are outliers according to the Chauvenet criterion (Anscombe, 1960) and were not taken into account in the calculation of the weighted average.

Table S-4 Observed phase transitions for FD1A biphasic fluid inclusion; FD3A biphasic and monophasic fluid inclusion and calculated NaCl weight percent associated. Value n. o. corresponds to a non-observed phase change.

Tables S-3 and S-4 can be downloaded (Excel) from the online version of the article at <https://doi.org/10.7185/geochemlet.2207>.

Supplementary Figures

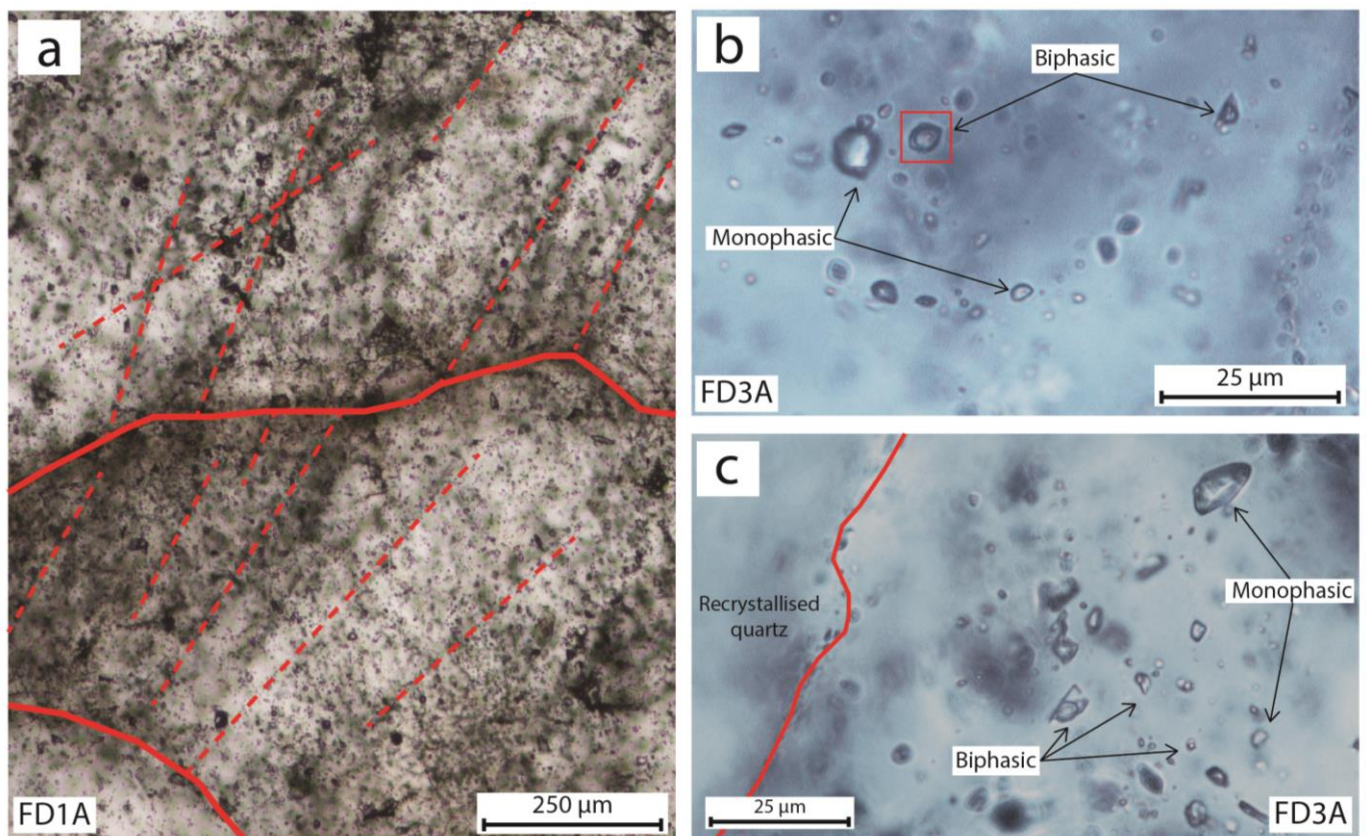


Figure S-1 (a) Thin section photographs highlighting quartz grain boundaries (solid lines) and trails of pseudosecondary fluid inclusions (dashed lines) in FD1A. (b) Coexisting monophasic and biphasic fluid inclusions in FD3A. The red square shows a biphasic inclusion with a small rim of liquid. (c) Heterogeneous entrapment in a fluid inclusion assemblage showing the coexistence of monophasic and biphasic inclusions with variable % of vapour in FD3A characteristic of boiling process. The grain on the left is devoid of fluid inclusions as a result of recrystallisation.

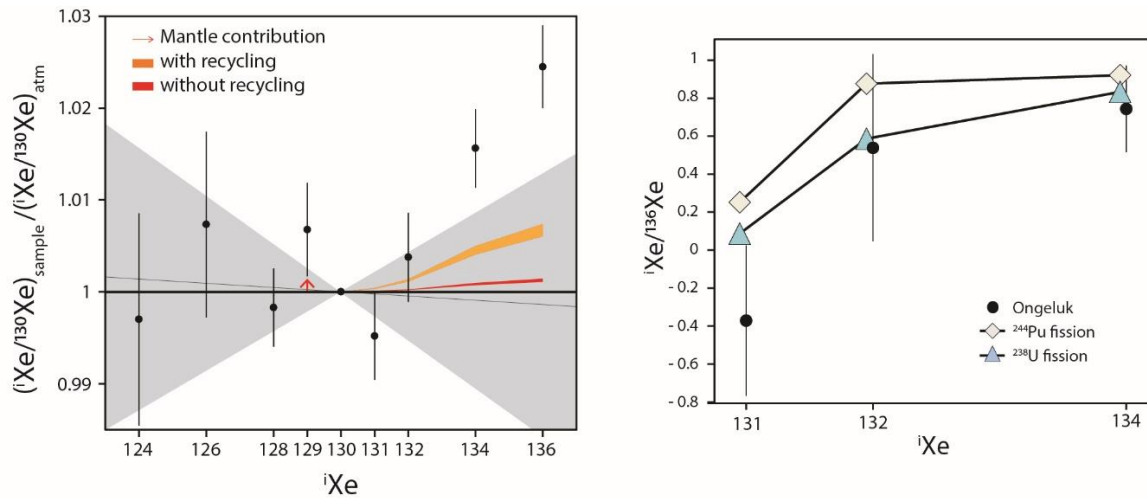


Figure S-2 Isotopic spectra of Xe released from fluid inclusions in samples from the Ongeluk fm. Points represent the weighted average of 9 crushes of different quartz samples from the Ongeluk fm with error at 1σ . The grey line corresponds to the isotopic trend of the $^{124}, ^{126}, ^{128}, ^{130}\text{Xe}$ showing no mass-dependant fractionation. Error envelope is at 2σ . The mantellic contribution is calculated considering a starting atmospheric composition as no isotopic fractionation is observed. The associated fission spectrum shows the major influence of ^{238}U spontaneous fission with uncertainties at 1σ .

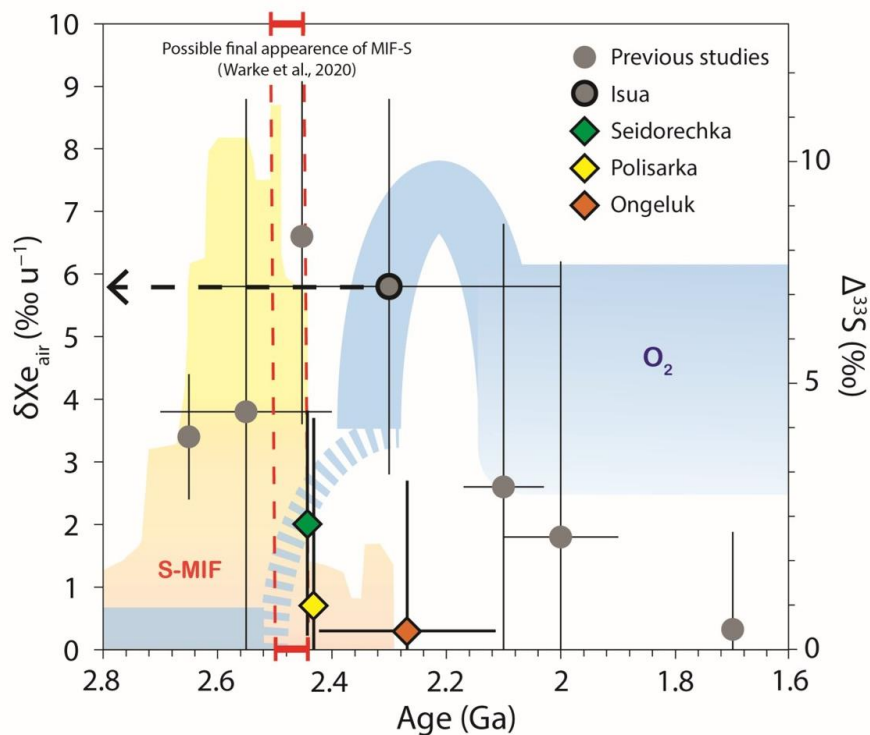


Figure S-3 Records of atmospheric oxygen (O_2 , blue; Lyons *et al.*, 2014), mass-independent fractionation of sulfur isotopes (MIF-S, orange; data from Killingsworth *et al.*, 2019) and mass dependent fractionation of xenon isotopes over the GOE period (previous data from Avice *et al.*, 2018; Almayrac *et al.*, 2021), errors are at 2σ .



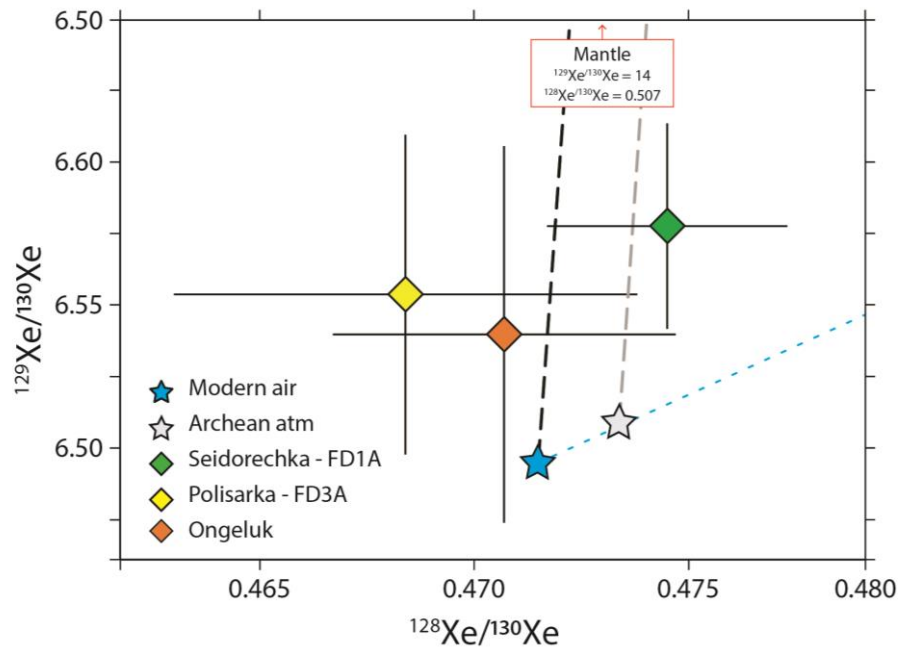


Figure S-4 Isotopic ratios $^{129}\text{Xe}/^{130}\text{Xe}$ vs. $^{128}\text{Xe}/^{130}\text{Xe}$ in this study. The black (a) and grey (b) dashed lines show a mixing between a non-regassed mantle and: (a) the modern air (Ozima and Podosek, 2002); (b) the Archean atmospheric ratio calculated from FD1A. Mantle $^{129}\text{Xe}/^{130}\text{Xe}$ composition comes from Marty *et al.* (2019) and AVCC-like $^{128}\text{Xe}/^{130}\text{Xe}$ (Pepin, 2003). The blue dashed line shows a Rayleigh fractionation trend through modern air. Uncertainties at 2σ .

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