

## The end of the isotopic evolution of atmospheric xenon

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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  $2425.6 \pm 2.6$  Ma ( $2\sigma$ ; 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  $2701 \pm 43$  Ma ( $1\sigma$ ) and a minimum age of  $2114 \pm 312$  ( $1\sigma$ ) Ma. The difference is likely due to the difficulties in estimating the initial amount of K in the fluid. The age of  $\approx 2701$  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  $2114 \pm 312$  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  $2501.5 \pm 1.7$  Ma and  $2441 \pm 1.6$  Ma (Amelin *et al.*, 1995), and  $2441 \pm 1.6$  Ma and  $2434 \pm 6.6$  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  $2441 \pm 1.6$  Ma for the quartz veins crossing Seidorechka Sedimentary Formation (FD1A ; Amelin *et al.*, 1995) and at  $2434 \pm 6.6$  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  $2\sigma$ .

## 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- $\mu\text{m}$  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  $\mu\text{m}$ . The interior of the grains contains bigger inclusions, up to 20  $\mu\text{m}$ , 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  $\text{CO}_2$  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  $\mu\text{m}$  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  $\mu\text{m}$  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 ( $T_{\text{fm}}$ ), 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 ( $T_{\text{h}}$ ). 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  $\text{CO}_2$  ( $-56.6\text{ }^{\circ}\text{C}$ ) and synthetic pure  $\text{H}_2\text{O}$  fluid inclusions with known transition temperatures. Precisions of the phase transition temperature measurements are about  $\pm 2\text{ }^{\circ}\text{C}$  for  $T_{\text{fm}}$ ,  $\pm 0.1\text{ }^{\circ}\text{C}$  for  $T_{\text{m car}}$ ,  $T_{\text{m ice}}$ ,  $T_{\text{fm}}$ , and  $T_{\text{m cla}}$ , and  $\pm 1\text{ }^{\circ}\text{C}$  for  $T_{\text{h}}$ .

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  $\text{Ar}^+$  laser operating at a wavelength of  $514.53\text{ nm}$  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  $\text{N}_2$  from air and  $\text{N}_2$  from the inclusion. Biphasic fluid inclusions often exhibited moving gas bubbles which prevented the acquisition of the Raman spectra. Spectra of  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2$  and  $\text{CO}_2$  in the gas phase were acquired separately in two different spectral windows. The absence of  $\text{H}_2$  was monitored in a third spectral window. Peak positions and areas were determined using the integration tool of LabSpec software (Horiba Jobin Yvon) at  $4156\text{ cm}^{-1}$  for  $\text{H}_2$ ;  $2917\text{ cm}^{-1}$  for  $\text{CH}_4$ ;  $2580\text{ cm}^{-1}$  for  $\text{H}_2\text{S}$  liquid;  $2331\text{ cm}^{-1}$  for  $\text{N}_2$  and the Fermi doublet at  $1285$  and  $1388\text{ cm}^{-1}$  for  $\text{CO}_2$  (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,  $L_{\text{aq}}$  and  $\text{CO}_2$  vap,



or (ii)  $Q_2$  program when clathrate dissociation occurred via a  $Q_2$  transition (coexistence of  $L_{aq}$ ,  $Cl_a$ ,  $CO_2$  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  $91.9 \pm 3.4$  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  $3.3 \pm 1.9$  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  $0.8 \pm 0.3$  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 CH<sub>4</sub>/CO<sub>2</sub> content, the monophasic liquid inclusions being enriched in the most volatiles species, are solids arguments for boiling and entrapment below the solvus within the H<sub>2</sub>O-CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>S-N<sub>2</sub> 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 <sup>238</sup>U (half-life of 4.47 Ga or <sup>244</sup>Pu (half-life of 82 Ma; Ozima and Podosek, 2002). We calculated the theoretical production of the isotopes: <sup>131</sup>Xe, <sup>132</sup>Xe, <sup>134</sup>Xe normalised to <sup>136</sup>Xe by fission of <sup>238</sup>U and <sup>244</sup>Pu (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 <sup>238</sup>U and <sup>244</sup>Pu fission spectrums in perspective with sample ratios, a <sup>238</sup>U origins of the heavy isotopes can be suggested for all our samples (Fig. 1; Fig. S-2)



### Mantle Contribution

The excess of  $^{129}\text{Xe}$  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  $\alpha$  as the fraction of the mantellic  $^{130}\text{Xe}$ . 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  $^{130}\text{Xe}$  contribution is thus an upper limit. From  $\alpha$  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  $^{129}\text{Xe}$  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  $^{238}\text{U}$  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  $^{129}\text{Xe}$  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  $\approx 7$  million years separating the formation of the 2 samples. Without  $^{129}\text{Xe}$  excesses (this study) or deficits (Avice *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  $^{130}\text{Xe}$  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).

|                               | $^{129}\text{Xe}/^{130}\text{Xe}$<br>( $2\sigma$ ) | $^{128}\text{Xe}/^{130}\text{Xe}$<br>( $2\sigma$ ) | Without atm regassing |   | With atm regassing    |   |
|-------------------------------|--|--|-----------------------|---|-----------------------|---|
|                               |  |  | % Mantle              | Expected<br>$^{128}\text{Xe}/^{130}\text{Xe}$ ( $2\sigma$ ) | % Mantle              | Expected<br>$^{128}\text{Xe}/^{130}\text{Xe}$ |
| 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 <sup>1,2</sup> | 14 (1)   | 0.507 (0.004)                                      |                       |   |                       |   |
| MORB <sup>3</sup>             | 6.92 (0.07)  |  |                       |   |                       |   |
| Modern air <sup>4</sup>       | 6.50   |  |                       |   |                       |   |

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

| N°<br>inclusion          | CO <sub>2</sub> | N <sub>2</sub> | % molar          |                 | Total   |
|--------------------------|-----------------|----------------|------------------|-----------------|---------|
|                          |                 |                | H <sub>2</sub> S | CH <sub>4</sub> |         |
| <b>FD1A - Biphasic</b>   |                 |                |                  |                 |         |
| 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 % |
| <b>FD3A - Biphasic</b>   |                 |                |                  |                 |         |
| 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 % |
| <b>FD3A - Monophasic</b> |                 |                |                  |                 |         |
| 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 % |

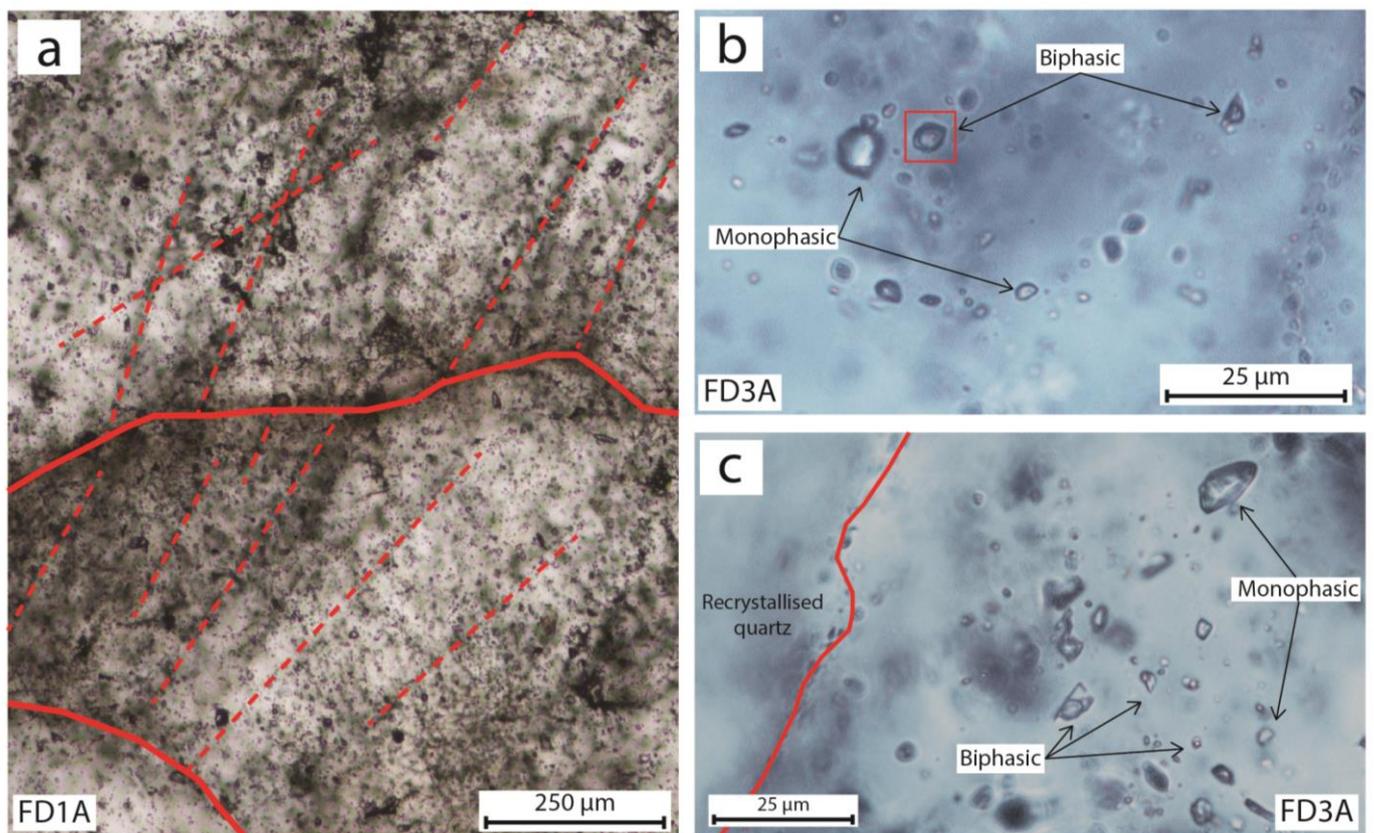


**Table S-3** Isotopic ratio of the noble gases of each replicate. Values in red are outliers according to the Chauvenet criterion (Anscombe, 1960) and were not taken into account in the calculation of the weighted average.

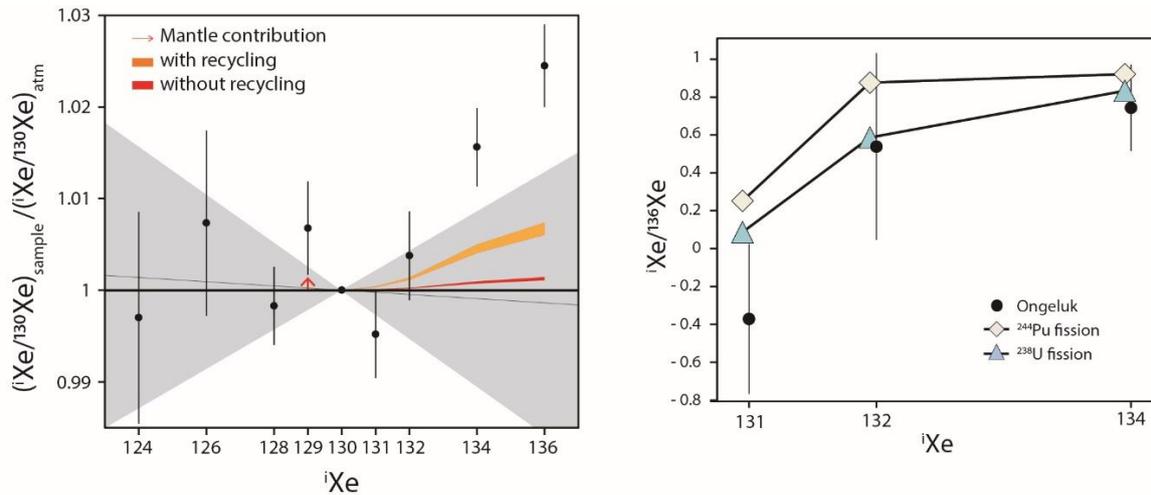
**Table S-4** Observed phase transitions for FD1A biphasic fluid inclusion; FD3A biphasic and monophasic fluid inclusion and calculated NaCl weight percent associated. Value n. o. corresponds to a non-observed phase change.

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>.

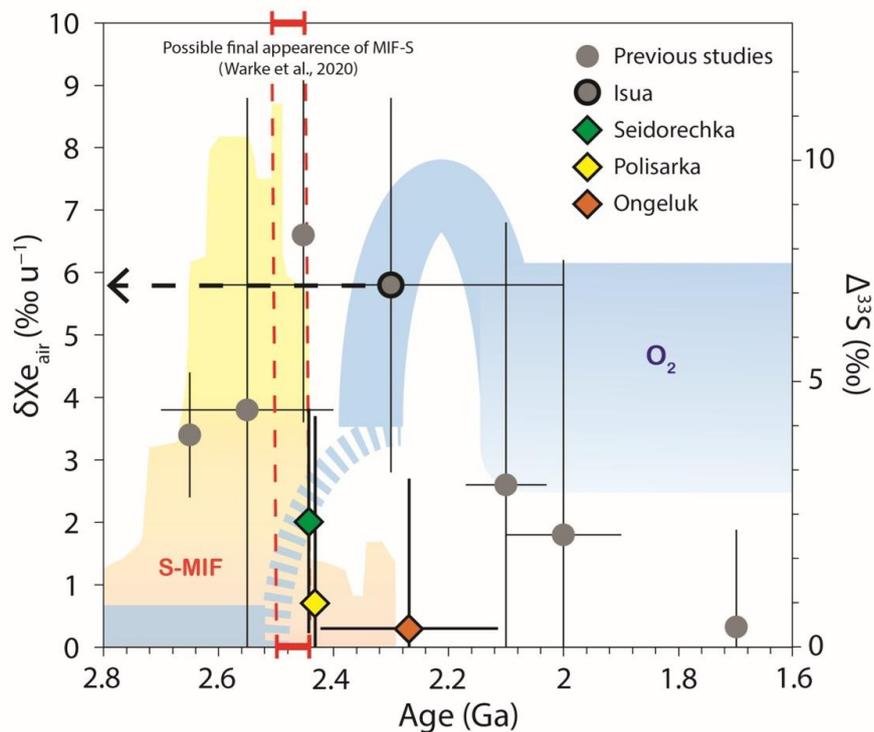
## Supplementary Figures



**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.

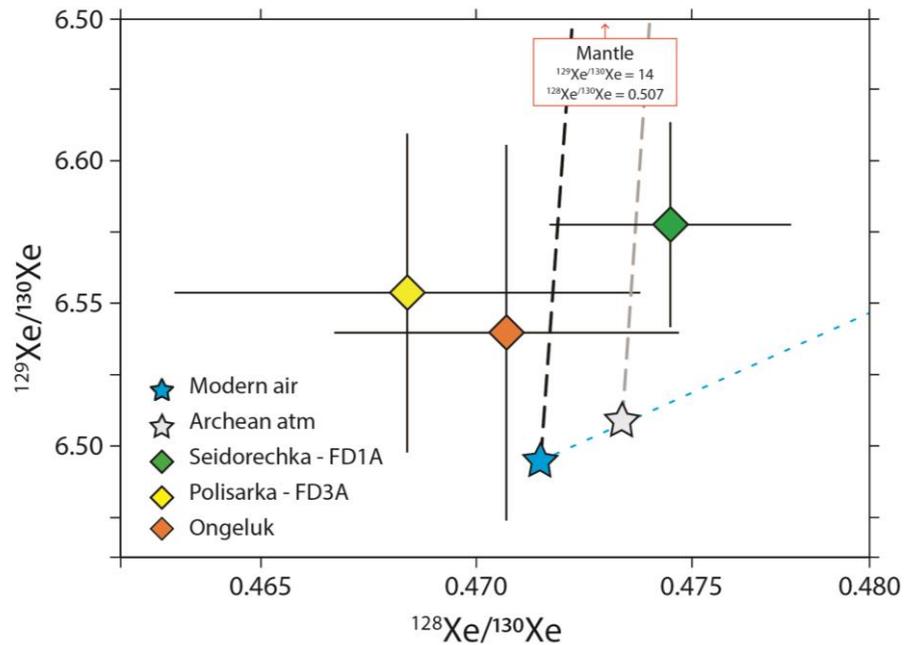


**Figure S-2** Isotopic spectra of Xe released from fluid inclusions in samples from the Ongeluk fm. Points represent the weighted average of 9 crushes of different quartz samples from the Ongeluk fm with error at  $1\sigma$ . The grey line corresponds to the isotopic trend of the  $^{124}, ^{126}, ^{128}, ^{130}\text{Xe}$  showing no mass-dependant fractionation. Error envelope is at  $2\sigma$ . 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  $^{238}\text{U}$  spontaneous fission with uncertainties at  $1\sigma$ .



**Figure S-3** Records of atmospheric oxygen ( $\text{O}_2$ , 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  $2\sigma$ .





**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  $2\sigma$ .

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