End-Permian extinction amplified by plume-induced release of recycled lithospheric volatiles

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1 **End-Permian extinction amplified by plume-induced release of recycled**
2 **lithospheric volatiles**

3

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14

15 **Magmatic volatile release to the atmosphere can lead to climatic changes and**
16 **significant environmental degradation including the production of acid rain,**
17 **ocean acidification and ozone depletion, potentially resulting in collapse of the**
18 **biosphere. The largest recorded mass extinction in Earth's history occurred at**
19 **the end-Permian, coinciding with the emplacement of the Siberian large**
20 **igneous province, suggesting that large-scale magmatism is a key driver of**
21 **global environmental change. However, the source and nature of volatiles in**
22 **the Siberian large igneous province remain contentious. Here we present**
23 **halogen compositions of sub-continental lithospheric mantle xenoliths**
24 **emplaced prior to, and after the eruption of the Siberian flood basalts. We**
25 **show that the Siberian lithosphere is massively enriched in halogens from the**
26 **infiltration of subducted seawater-derived volatiles and that a significant**
27 **amount (up to 70%) of lithospheric halogens are assimilated into the plume**
28 **and released to the atmosphere during emplacement. Plume-lithosphere**
29 **interaction is therefore a key process controlling the volatile content of large**
30 **igneous provinces and as such the extent of environmental crises, leading to**
31 **mass extinctions during their emplacement.**

32

33 Large igneous provinces (LIP) are the product of rapid eruptions of large volumes of
34 magma over short geological time scales. The Permo-Triassic Siberian flood basalts
35 (SFB) erupted $\sim 4 \times 10^6$ km³ of basalt in less than 1 Ma¹. The eruption of the SFB is
36 contemporaneous with the main stage of the end-Permian crisis and is hypothesized
37 to have contributed to environmental changes that resulted in loss of >90% of all
38 marine, and >70% of all terrestrial species^{2,3}. The end-Permian mass extinction has
39 been attributed to sharp fluctuations in global temperatures and/or increased levels

40 of ultraviolet radiation resulting from extensive ozone depletion both of which are
41 associated with the magmatic release of volatiles to the atmosphere^{2,4-7}. Yet the
42 amount of volatiles expected to be released from the SFB assuming conventional
43 plume source magmatism is insufficient to account for the environmental degradation
44 and climatic fluctuations that occurred during the end-Permian crisis, requiring an
45 additional source of volatiles to be released during SFB emplacement^{8,9}. To reconcile
46 the missing SFB volatiles, it has been variously argued for significant quantities of
47 volatiles released via contact metamorphism of a sedimentary sequence^{1,5}; melting
48 of recycled eclogite within the mantle plume¹⁰; or melting of the cratonic lithosphere⁷.
49 However, the source of volatile species responsible for climatic fluctuations and
50 ozone depletion during the end-Permian crisis remains unknown.

51

52 Here we report the first detailed halogen (Cl, Br and I) data for peridotite xenoliths
53 from two Siberian kimberlites: one (Udachnaya, 360 Ma) emplaced before, and the
54 other (Obnazhennaya, 160 Ma) after the SFB eruption ~250 Ma^{11,12} (Supplementary
55 Fig. 1). The Udachnaya peridotite xenoliths (n=9) represent melt extraction from the
56 depleted cratonic mantle; whereas Obnazhennaya xenoliths (n=6) contain both
57 Archean cratonic lithosphere and melt residues generated from the SFB plume
58 (Supplementary Information)¹³. Determining the halogen composition of the cratonic
59 sub-continental lithospheric mantle (SCLM; Udachnaya) and the SFB plume
60 residues (Obnazhennaya) provides a means to estimate the composition of the SFB
61 prior to eruption, and quantify the contribution of the lithospheric mantle to the
62 halogen budget of the SFB.

63

64 **Lithospheric mantle as a reservoir for halogens**

65 Due to its isolation and non-convective nature, the SCLM retains geochemical
66 heterogeneities introduced through interactions with mantle, crustal and subduction-
67 related sources^{14,15}. Metasomatic components infiltrating the SCLM are sampled by
68 mantle xenoliths. Rapidly transported to the surface during kimberlite volcanism,
69 these xenoliths provide a window into the composition and origin of SCLM volatiles¹⁶⁻
70 ¹⁸.

71

72 The halogen and noble gas composition of the Udachnaya and Obnazhennaya
73 xenoliths was determined using neutron-irradiated noble gas mass spectrometry
74 (Methods). The results are summarised in Supplementary Tables 2 and 3 and
75 displayed in Fig. 1. The range of Cl, Br and I concentrations within the Udachnaya
76 and Obnazhennaya xenoliths are significantly different, with the average
77 concentrations from crushing and step heating being consistently higher in
78 Udachnaya samples indicating they originate from distinct domains within the SCLM
79 (Supplementary Information). Halogen-bearing fluids present in the samples, as
80 indicated by release during crushing experiments, have a similar range of Br/Cl and
81 I/Cl in both Udachnaya and Obnazhennaya xenoliths (Fig. 2a). During stepped-
82 heating of crushed residues the xenoliths show evidence for distinct endmember
83 halogen compositions (Fig. 2b). Udachnaya retains similar Br/Cl and I/Cl as
84 measured during crushing, whilst Obnazhennaya samples have more mantle-like
85 Br/Cl and I/Cl values (Table S3).

86

Previously published helium isotopic data also varies between the xenoliths suites, with the average $^3\text{He}/^4\text{He}$ of Udachnaya ($0.4 \pm 0.3 R_A$) consistently lower than Obnazhennaya ($4.2 \pm 0.9 R_A$), which has a maximum $^3\text{He}/^4\text{He}$ ($8.4 \pm 0.3 R_A$) similar to mid ocean ridge basalts (MORB)¹⁸. $^3\text{He}/^4\text{He}$, Br/Cl and I/Cl values appear to be coupled (Fig. 3), showing that fluids within the Obnazhennaya xenoliths represent a mixture between a component rich in radiogenic ^4He , Br and I, and a component with mantle-like $^3\text{He}/^4\text{He}$ and halogen compositions. The lower $^3\text{He}/^4\text{He}$ and elevated Br/Cl and I/Cl as characterised by Udachnaya xenoliths, is considered representative of the ancient metasomatised section of the SCLM (metasomes) that was present before significant influence of the SFB mantle plume. In contrast, Obnazhennaya also contains variable amounts of a mantle-like halogen and He component. Given the similarity in rare earth elements (REE) patterns and extraction age for the Obnazhennaya xenoliths with regards to the SFB¹³, it is considered that mantle-like volatiles were added by the Siberian plume which interacted with the lithosphere having a volatile composition characterised by fluids trapped in the Udachnaya xenoliths (Fig. 3).

The initial inventory of halogens within the metasomatised section of Siberian SCLM prior to plume impingement can be estimated using the composition of Udachnaya xenoliths. The Siberian SCLM transitions from depleted harzburgite and lherzolites to predominantly metasomatised peridotites at 180-190 km¹⁹. Assuming that the Udachnaya peridotite xenoliths are representative of metasomatised peridotites in the lower 30 km of the SCLM, and taking the surficial area of the Siberian Craton ($4 \times 10^6 \text{ km}^2$), then the metasomatised portion of the Siberian SCLM contains approximately $0.6\text{--}1.5 \times 10^{19}$, $1.6\text{--}2.7 \times 10^{17}$ and $0.5\text{--}1.1 \times 10^{14}$ kg of Cl, Br and I

respectively (Supplementary Table 1 and Supplementary Information). The metasomatised Siberian SCLM is therefore enriched in Cl, Br and I by factors of up to 125, 675 and 100 times, respectively, relative to the depleted MORB mantle (DMM)²⁰. Thus, the SCLM is a significantly larger and more heterogeneous halogen reservoir than previously considered and may impart a significant influence on global volatile cycles²¹.

Release of lithospheric halogens during LIP emplacement

The comparatively large quantity of halogens residing in the base of the Siberian SCLM means that even small proportions released to the surface will have significant consequences for the global halogen cycle. The eruption of halogens into the stratosphere catalyses ozone-destroying reactions, raising surface levels of biologically damaging UV radiation^{22,23}. Transit of the SFB plume through the SCLM could potentially have liberated significant amounts of halogens and other volatiles to the atmosphere, contributing to species decline and extinction during the end-Permian crisis.

Udachnaya xenoliths formed at significantly deeper depths (>50km difference)¹⁷ in the lithosphere compared to Obnazhennaya. The identification of Udachnaya-like metasomatic signatures in Obnazhennaya indicates that volatiles residing in the metasomatised basal SCLM were mobilised and ascended to shallower parts of the SCLM. Obnazhennaya xenoliths have trace element signatures within the range of previously reported values of the SFB¹⁷, strong P-PGE depletions uncharacteristic of

cratonic lithosphere and Os isotopic compositions consistent with a formation age similar to the time of plume impingement¹³. These characteristics indicate that the part of the lithosphere sampled by the Obnazhennaya kimberlite represents the melt residue of the SFB-plume (Fig. 4d)¹³. The identification of metasomatised SCLM signatures within the Obnazhennaya xenoliths therefore suggests that as the SFB plume impacted the base of the lithosphere, the resulting melts incorporated volatiles mobilised from the deeper metasomatised SCLM, before being erupted at the surface or stalling in the lithosphere. The contribution of SCLM-derived volatiles to the SFB plume can therefore be estimated using differences in halogen and noble gas signatures between the Udachnaya (metasomatised SCLM) and Obnazhennaya (SFB + metasomatised SCLM) xenoliths.

Assuming that the melt residues in the Obnazhennaya lithosphere had a starting composition similar to the SFB plume (12.7R_A and mantle-like Br/Cl and I/Cl)^{24,25} then the amount of assimilation from the SCLM (Udachnaya) can be estimated from the extent of mixing between the two sources (Fig. 2, 3, Supplementary Information). Comparing He, Br and I systematics between the SFB plume and the SCLM component represented by Udachnaya, requires that up to 70% of volatiles in Obnazhennaya be derived from the SCLM (Fig. 3a,b, Supplementary Fig. 2). Furthermore, any potential overprinting related to crustal assimilation affecting the halogen composition of the melt can be excluded as the rapid transport of xenoliths to the surface via kimberlite volcanism limits any potential interaction with the surrounding crust^{26,27}.

Taking the volume of Cl degassed as calculated from the SFB melt inclusions (8.7×10^{15} kg), then the total fluxes of Br and I to the atmosphere are estimated to be 2.3×10^{13} kg and 9.6×10^{10} kg respectively. This calculation assumes the melt had Br/Cl and I/Cl values similar to Obnazhennaya and considers that halogens are not fractionated during degassing²⁸. Explosive eruptions inject reactive HCl and HBr gases into the lower stratosphere (~12-25 km) and deplete ozone levels, whereas effusive eruptions lead to soluble HCl being washed-out prior to reaching the stratosphere²⁴. Considering only explosive events (20-30% of the SFB)²⁹, a ~75% rate of stratospheric injection³⁰, and the amount of Cl measured within the SFB³¹, then the mass of Cl released to the stratosphere over the main eruptive phase of the SFB (two thirds of the total eruptive volume over 300ky)³² is the equivalent to 0.5-1.0 Pinatubo (1991-1992) eruptions, which caused a 15-20% reduction in global ozone³³, every year for 300ky. Models of ozone depletion during the SFB eruption, using estimated stratospheric HCl fluxes predict a 30-55% reduction in ozone over the same eruptive timeframe⁴. These stratospheric HCl flux estimates are 5 times lower than the predicted from the SFB melt inclusions (8.7×10^{15} kg)³¹. Furthermore, these estimates do not take into account the consequences of Br degassing on ozone depletion. The large release of Br to the stratosphere during the SFB, as indicated by the high Br/Cl of the Siberian SCLM, likely further exacerbated ozone depletion. Bromine has a much greater capacity for depleting ozone (~45× more effective²⁴) and could have reduced ozone levels by a further 20% during SFB eruption. Although there are several uncertainties in the rate and magnitude of volatile degassing during SFB magmatism, the scale of halogen degassing fluxes presented here are sufficient to incur a near to total loss of global ozone during the end-Permian crisis.

Melt inclusions within the SFB contain between 0.01-0.33 wt.% Cl^{10,31}, which is an order of magnitude higher than the maximum measured Cl concentrations in other LIPs^{8,31}. Inclusions with high Cl concentrations are found to be equally enriched in other volatiles species such as fluorine (1.95 wt. %) and sulphur (0.51 wt. %)³¹. To create such high volatile contents within these melts, starting from a DMM-like composition, would require very low degree partial melting, or the assimilation of volatiles from another unknown reservoir. Low degrees partial melting can concentrate volatiles in the melt fraction, however the high Mg contents measured within the melt inclusions preclude low degree partial melting, suggesting that the assimilation of volatile-rich material is most likely cause of the high volatile contents in the SFB.

The composition of the Obnazhennaya xenoliths, assumed to represent plume melt residues, can be used to estimate the pre-eruptive SFB melt composition and establish if the SCLM is the potential source of the SFB volatile enrichment. Obnazhennaya xenoliths require ~30% melt extraction to account for the elevated Fo_{>92} of the olivines¹³ and therefore the Cl composition of this melt can be estimated using a batch melting model³⁴. Experimentally determined partition coefficients for Cl between olivine ($D_{Cl}^{Ol/Melt} = 1.9 \times 10^{-2}$) and pyroxene ($D_{Cl}^{Pyx/Melt} = 1.5 \times 10^{-2}$) were used to calculate the Cl concentration of the melt at 1500°C, prior to eruption³⁵. Using the range of Cl concentrations in the olivine and pyroxene minerals from Obnazhennaya xenoliths yield Cl concentrations of 0.1-0.2 wt.% in the melt. These estimates are considered upper limits given the potential for an unknown proportion of intact fluid inclusions to remain following crushing, thus Cl data based on stepped heating is likely to overestimate the Cl abundance within the minerals. However, it is notable

that the melt Cl estimates are consistent with previous values for the eruptive melt composition (0.01-0.33 wt.% Cl)^{10,32} providing confidence in the assumptions we have made and confirming that the SFB melt was already enriched in Cl prior to eruption. These arguments therefore provide further (albeit indirect) support for a SCLM origin for the majority of halogens in SFB melts.

Implications for the end-Permian extinction

Ozone depletion during the end-Permian crisis is considered to have led to the decline in the dominant terrestrial plant species at the time, followed by the rapid expansion of opportunistic lycopsids³⁶. The global distribution of preserved microspores from these emerging lycopsides exhibit features indicative of a failure in the normal development process of the spores. The global dispersion of these mutagenic spores suggest that this was a reaction to global stress factors, unlikely to be related to changes in global temperature from the release of gases such as SO₂ and CO₂ during SFB emplacement⁴. Experiments on the effects of end-Permian UV-B regimes on modern conifers led to a fivefold increases in the occurrence of mutagenic malformations, and complete sterilisation³⁷. This would have caused widespread deforestation and the collapse of the terrestrial biosphere, indicating ozone depletion was a major contributing factor in the end-Permian mass extinction event^{4,37}.

The peak occurrence of mutagenic spores occurs prior to the rapid negative shift in $\delta^{13}\text{C}$ in end-Permian carbonates attributed to the extinction of calcified marine life³⁶.

The $\delta^{13}\text{C}$ excursions coincide with a change from predominantly extrusive to intrusive eruptions of the Siberian LIP¹. The emplacement of sills into volatile rich sediments was considered to have released vast quantities of volatiles including CO_2 and halocarbons gases to the atmosphere leading to rapid climate change and ozone depletion^{1,5}. However, from the palynological evidence³⁶ it is clear that a reduction in terrestrial biodiversity was occurring prior to the onset of marine extinction. Furthermore, evidence for reduced sedimentation rates prior to and up to the PTB, indicates that there was global eustatic sea-level regression potentially caused by falling global temperatures and the onset of glaciation³⁸. The rapid fall in temperatures has been linked to the emission of SO_2 to the atmosphere during the eruptive phase of the SFB⁷.

The concurrent timing of the eruptive phase of the SFB and the palynological evidence for ozone depletion is not consistent with the idea of sedimentary brines degassing during later intrusive phases of igneous activity being the primary source of halogens causing ozone destruction. As we have shown in this study the majority of halogens in the SFB were added during plume-lithosphere interaction followed by their subsequent release to the atmosphere during explosive eruptions. Sulphur enrichments, co-existing with halogens in SFB³¹, may also have been derived from the SCLM (Fig. 4c). Evidence for terrestrial species decline prior to PTB therefore suggests that the release of halogens and gaseous sulphur species, and the subsequent decline in ozone and global temperatures respectively were the predominant factors in initiating the end-Permian mass extinction. The change in eruptive phase from explosive to intrusive may have played a role in extending the extinction from a mainly terrestrial phenomenon to a global extinction event.

257

258 **Subducted origin of volatiles in the Siberian lithosphere**

259 The high concentrations of halogens in the Udachnaya xenoliths indicate the
260 Siberian SCLM has been enriched in volatiles by metasomatic processes.
261 Udachnaya xenoliths have Br/Cl and I/Cl similar to fluids trapped within minerals in
262 the altered oceanic crust (AOC), suggesting that the metasomatism of the Siberian
263 SCLM was potentially driven by subduction derived fluids (Fig. 2)³⁹. Combined with
264 the noble gases (Fig. 3; Supplementary Fig. 3 and 4) the Udachnaya xenoliths show
265 an evolution from seawater-like $^3\text{He}/^4\text{He}$, Br/Cl and I/Cl values, to values with
266 increasingly radiogenic $^3\text{He}/^4\text{He}$ and enriched Br/Cl and I/Cl (Fig. 3), further
267 suggesting that the metasomatic fluid originated as seawater but subsequently
268 evolved, during subduction or within the SCLM, due to halogen fractionation and the
269 production of ^4He from U-Th decay¹⁸. Eclogite xenoliths from the Udachnaya
270 kimberlite exhibit $\delta^{18}\text{O}$ up to +7.7‰⁴⁰, outwith the normal mantle range (+5.4 ±
271 0.2‰)⁴¹ indicating that they originated as oceanic crust that underwent low
272 temperature alteration⁴⁰. Eclogites formed from the subduction of oceanic crust have
273 been shown to retain the halogen and oxygen isotopic signature of the oceanic crust
274 protolith during metamorphism, providing a mechanism for the delivery of
275 subduction-derived halogens to the Siberian SCLM^{42,43}.

276

277 As we have shown in this study, up to 70% of the volatile content of the Siberian
278 plume originated from assimilation of metasomatised lithospheric material. The
279 composition of the SCLM therefore plays an integral role in controlling the volatile
280 content of LIPs, and as such the overall effect they have on the global environment.

Based on the evolution of the Br/Cl, I/Cl and $^3\text{He}/^4\text{He}$ of the xenoliths from seawater to AOC-like values, coupled with the AOC-like $\delta^{18}\text{O}$ within eclogite xenoliths from Udachnaya, it appears that the origin of the Siberian SCLM volatiles is from the subduction of a seawater derived component within the AOC. Enrichment of seawater-derived volatiles in the Siberian SCLM provided the plume with an abundant supply of halogens, which were released to the atmosphere during eruption and resulted in globally extensive reductions in ozone levels and the decline of the biosphere. The SCLM is also a major repository for other subducted volatile species including sulphur and carbon^{44,45}, which can also contribute to environmental degradation during plume-lithosphere interaction and LIP emplacement⁷. The SCLM can therefore act as a repository of subducted volatile that can periodically be mobilised and released to the Earth's surface and atmosphere during deep-seated melting and volcanism leading to devastating impacts on the global environment.

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474

475 **Author contributions**

M. W. B, P. H. B and R. B conceived the project and prepared the initial manuscript. L.A.T provided the samples and M. W. B and R. B performed the analysis. All authors contributed to data analysis and preparation of the final manuscript.

Competing financial interests

The authors declare no competing financial interests.

Figure Captions

Figure 1. Halogen and K abundances in Udachnaya and Obnazhennaya xenoliths. Abundances of (a) Br, (b) I and (c) K plotted against Cl showing the enrichment of Br and I within the Siberian SCLM relative to the MORB/OIB mantle source and seawater²⁴. Crushing (“crush”) data are shown by open symbols and stepped-heating (“melt”) by closed symbols. Errors bars are consistently covered by symbol. Uncertainties are presented at 1σ .

Figure 2. Halogen composition of the Siberian SCLM. Br/Cl versus I/Cl (a) crushing and (b) step heating of the Udachnaya and Obnazhennaya xenoliths. Xenoliths show a range of halogen compositions which overlap the range of Br/Cl and I/Cl observed in altered oceanic crust (AOC fluids) and eclogites. Seawater evaporation trend (SET) is shown, indicating that sedimentary brines cannot be responsible for the halogen signature of the xenoliths. Br/Cl and I/Cl results from halogen fractionation (black arrows) of AOC fluids (green star). Seawater, marine

498 pore fluids and MORB/OIB compositions are shown for reference^{24,46}. Figure
499 symbols are the same as in Figure 1. Uncertainties are 1σ .

500

501 **Figure 3. Helium isotopes and halogen systematics.** $^3\text{He}/^4\text{He}$ versus **(a)** I/Cl and
502 **(b)** Br/Cl from crushed release of Udachnaya and Obnazhennaya xenoliths.

503 Udachnaya has $^3\text{He}/^4\text{He}$, Br/Cl and I/Cl, which range from values similar to seawater
504 (blue star) towards higher Br/Cl and I/Cl and lower $^3\text{He}/^4\text{He}$ characteristic subduction
505 modified seawater. Obnazhennaya has higher $^3\text{He}/^4\text{He}$ ranging from Udachnaya-like
506 towards OIB-like values, from the influx of plumes melts. Mixing lines [$r =$
507 $(^4\text{He}/\text{Cl})_{\text{plume}} / (^4\text{He}/\text{Cl})_{\text{SCLM}}$] shown between a hypothetical SCLM component (black
508 diamond, intercept through the data) and plume melts with the relative percentage of
509 SCLM assimilation shown. Figure symbols are same as used in Figure 1.
510 Uncertainties are 1σ .

511

512 **Figure 4. Schematic of plume-lithosphere interaction within the Siberian**
513 **craton.** a) SCLM is composed partly of metasomatised peridotite from addition of
514 subducted volatiles, which potentially seeds diamond formation. b) Intermittent
515 influence of the Siberian plume drives kimberlite volcanism c) Plume melt impinges
516 on the lithosphere, incorporating volatile rich SCLM material. Halogens released to
517 the atmosphere during explosive SFB eruptions leading to the extensive ozone
518 depletion. d) Plume retreats leaving a much-reduced SCLM with veins of melt
519 residue, followed by a second period of kimberlitic volcanism, transporting melt
520 residues and SCLM material to the surface.

521

522 **Methods**

523 **Neutron irradiation noble gas mass spectrometry (NI-NGMS)**

524 Olivine and clinopyroxene mineral separates from Udachnaya and Obnazhennaya
525 peridotite xenoliths were selected for heavy halogen (Cl, Br and I) and K analysis
526 using neutron-irradiated noble gas mass spectrometry (NI-NGMS)⁴⁷⁻⁵². Samples
527 weighing between 0.015 and 0.062 g were first cleaned with deionised water in an
528 ultrasonic bath for 20 minutes, followed by a further 5 minutes in acetone. Samples
529 were then dried under a heat lamp at 100°C, wrapped in Al foil and sealed in
530 evacuated fused-silica tubes together with Hb3gr, scapolite and Shallowater
531 meteorite standards to monitor noble gas proxy production from K and halogens⁵¹.

532

533 Samples were irradiated in the GRICIT (MN2014b) facilities of the TRIGA Reactor,
534 Oregon State University for a few hours each day between 22/04/2014 and
535 01/07/2014 giving a total irradiation time of 205 hours. Irradiation details and monitor
536 values for this irradiation have been reported previously⁵¹.

537

538 Noble gas proxy isotopes (³⁸Ar_{Cl}, ⁸⁰Kr_{Br}, ¹²⁸Xe_I and ³⁹Ar_K) formed during irradiation as
539 well as natural Ar, Kr and Xe isotopes were measured on the MS1 mass
540 spectrometer⁵². A subset of samples and repeat analyses were also performed on a
541 Thermo Fisher Scientific ARGUS VI mass spectrometer⁵¹. Noble gases were firstly
542 extracted from trapped fluid inclusions by loading samples into hand-operated

modified Nupro[®] valve crushers⁵³ (MS1 mass spectrometer). For bulk sample analysis, powders from crushing analyses were loaded into in a tantalum resistance furnace (MS1) and step heated using four temperature steps of 600°C, 1000°C, 1400°C and 1600°C to release halogens contained within the mineral matrix. Halogens from four samples (UV33, UV88, UV357 and O129-74) were extracted using a 10.6 µm wavelength CO₂ laser (Teledyne CETAC Fusions CO₂ – ARGUS VI). In order to test that both extraction methods gave the similar results, sample O97-12 was analysed using both the furnace and laser, Br/Cl and I/Cl varied by less than 20% and 35% respectively between laser and furnace extraction suggesting halogens were released in similar proportions using both extraction methods. Halogens abundances were then calculated using the well-defined conversion standards with known halogen concentrations (Hb3gr, scapolite and Shallowater meteorite)^{50,51}, which monitor the efficiency of noble gas production through thermal and epithermal neutron reactions.

Air calibrations and blanks were analysed daily to check the sensitivity and background of the spectrometers, with maximum furnace blank values at 1600°C on the MS1 being $1.65 \times 10^{-10} \text{ cm}^3 \text{ STP } ^{40}\text{Ar}$, $2.92 \times 10^{-13} \text{ cm}^3 \text{ STP } ^{84}\text{Kr}$ and $3.54 \times 10^{-14} \text{ cm}^3 \text{ STP } ^{132}\text{Xe}$ and ARGUS VI blanks being $5.76 \times 10^{-12} \text{ cm}^3 \text{ STP } ^{40}\text{Ar}$ and $1.41 \times 10^{-15} \text{ cm}^3 \text{ STP } ^{132}\text{Xe}$, with Kr blanks below detection limit. Noble gas purification analytical procedures for the MS1 and ARGUS VI mass spectrometers as well as the data reduction procedures have been documented previously^{52,56}. External precision is reported at 3% (1σ) for Cl and 7% (1σ) for Br and I determinations.

567 **Data availability**

568 All data pertaining to this study is presented in the paper and the supplementary
569 information. Correspondence and requests for materials should be addressed to the
570 corresponding author.

571

572 **Method References**

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598

> 360 Ma Metasomatic episodes

~ 360 Ma Eruption of Udachnaya

~ 250 Ma Eruption of Siberian Flood Basalts

~ 160 Ma Eruption of Obnazhennaya