Identification of chondritic krypton and xenon in Yellowstone gases and the timing of terrestrial volatile accretion

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Identifying the origin of noble gases in Earth's mantle can provide crucial constraints on the source and timing of volatile (C, N, H_2O, noble gases, etc.) delivery to Earth. It remains unclear whether the early Earth was able to directly capture and retain volatiles throughout accretion or whether it accreted anhydrously and subsequently acquired volatiles through later additions of chondritic material. Here, we report high-precision noble gas isotopic data from volcanic gases emanating from, in and around, the Yellowstone caldera (Wyoming, United States). We show that the He and Ne isotopic and elemental signatures of the Yellowstone gas requires an input from an undegassed mantle plume. Coupled with the distinct ratio of ^{129}Xe to primordial Xe isotopes in Yellowstone compared with mid-ocean ridge basalt (MORB) samples, this confirms that the deep plume and shallow MORB mantles have remained distinct from one another for the majority of Earth's history. Krypton and xenon isotopes in the Yellowstone mantle plume are found to be chondritic in origin, similar to the MORB source mantle. This is in contrast with the origin of neon in the mantle, which exhibits an isotopic dichotomy between solar plume and chondritic MORB mantle sources. The co-occurrence of solar and chondritic noble gases in the deep mantle is thought to reflect the heterogeneous nature of Earth's volatile accretion during the lifetime of the protosolar nebula. It notably implies that the Earth was able to retain its chondritic volatiles since its earliest stages of accretion, and not only through late additions.

origin of Earth's volatiles | accretion | mantle plume | noble gases | Yellowstone

Noble gas isotopes exhibit resolvable isotopic differences between chondritic (1), solar (2), and cometary reservoirs (3) and can be used to reveal important clues as to how the Earth acquired its early volatile budget (3–6). Differences in noble gas signatures between the deep plume and shallower mid-ocean ridge basalt (MORB) mantle sources (4, 5), as well as the atmosphere (3, 6), indicate that Earth experienced a heterogeneous history of volatile accretion. The highest $^{20}Ne/^{22}Ne$ ratio (13.03 ± 0.04) measured in plume-influenced samples is higher than that of solar wind-irradiated material (12.5 to 12.7) (7) and CI chondrites (8.2 ± 0.4) (8), therefore requiring the deep mantle to contain a nebular Ne component (13.36 ± 0.18) (4, 9). This nebular Ne component was most likely acquired by dissolution of a nebular atmosphere into the mantle during periods of global magma ocean (10, 11). The protosolar nebula is a transient feature in the solar system considered to have dispersed ~4 My after the formation of the solar system (taken as the formation age of Calcium–Aluminum Inclusions) (12). The nebular noble gas component present in the deep mantle must therefore have been added early to the growing proto-Earth, within the lifetime of the protosolar nebula (4, 13). Despite there being several plume-influenced samples with $^{20}Ne/^{22}Ne$ values greater than solar wind-implanted material and CI chondrites (4, 13, 14),

as of yet no plume-influenced sample has reached the nebular $^{20}Ne/^{22}Ne$ value. Therefore, the plume source mantle still requires the addition of a component with a $^{20}Ne/^{22}Ne$ lower than that of the solar nebula. It has been previously suggested that neon in the plume mantle source could represent a mixture between a nebular and solar wind-implanted component (14) or, alternatively, that the subduction of atmospheric neon in the mantle could have lowered the $^{20}Ne/^{22}Ne$ of the mantle over time (4).

While Ne in the deep mantle may have, at least in part, originated from the solar nebula, the $^{20}Ne/^{22}Ne$ of the upper mantle as measured in MORB (15) and continental well gases (5) is within the range of solar wind-irradiated material found in chondrites. This dichotomy in Ne isotopes between the depleted upper mantle and deep plume source mantle has been suggested to be the result of late additions of chondritic material to the upper mantle with an original solar-like composition (4). Preferential late additions of chondritic material to the Earth's surface and upper mantle may therefore have overprinted the original solar noble gas signature in the MORB reservoir, while the deep plume source mantle was able to better preserve its original solar noble gas signature (4).

Whether this apparent dichotomy in accretionary noble gas signatures can be extended to heavy noble gases (Kr and Xe)

Significance

Volatile elements play a critical role in the evolution of Earth. Nevertheless, the mechanism(s) by which Earth acquired, and was able to preserve its volatile budget throughout its violent accretionary history, remains uncertain. In this study, we analyzed noble gas isotopes in volcanic gases from the Yellowstone mantle plume, thought to sample the deep primordial mantle, to determine the origin of volatiles on Earth. We find that Kr and Xe isotopes within the deep mantle have a similar chondritic origin to those found previously in the upper mantle. This suggests that the Earth has retained chondritic volatiles throughout the accretion and, therefore, terrestrial volatiles cannot not solely be the result of late additions following the Moon-forming impact.

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

remains unknown. Krypton and xenon in the mantle are dominated by recycled atmosphere (16), rendering any evidence of accretionary signatures difficult to resolve. In order to circumvent this issue, large quantities of magmatic gas have been previously analyzed (6, 16, 17) to determine the primordial Kr and Xe signature of the mantle. Furthermore, a new protocol has been developed to accumulate mantle noble gases from highly vesicular basaltic MORB glass samples (18), which has enabled for the first time the primordial Kr and Xe signature from basaltic glass samples to be determined. The Kr and Xe isotopic data obtained from these studies supports a chondritic origin for heavy noble gases in the upper MORB source mantle (6, 18).

To date, no primordial heavy noble gas signatures have been identified in plume-influenced basaltic glass and olivine samples, with the light nonradiogenic ^{124,126,128}Xe isotopes being, for the most part, isotopically indistinguishable from atmosphere (19, 20). The lack of isotopic anomalies in these samples is most likely a function of the lower noble gas concentrations and therefore higher degree of atmospheric contamination compared with highly vesicular MORB glass (18). Recent attempts to determine the primordial heavy noble gas signature of the deep mantle have therefore been focused on the analysis of Xe in magmatic gases from the Eifel volcanic area in Germany (21). However, a recent reevaluation of Xe isotopes in Eifel has called into question whether it can be considered to originate from a deep, undegassed mantle source (17). Indeed, there is no supporting He isotope evidence, as ^{3}He/^{4}He values (<6 R_A, where $R_A = 1.39 \times 10^{-6}$, the ^{3}He/^{4}He ratio of air) in Eifel gas samples are lower than canonical MORB (8 ± 1 R_A) values and Ne isotopes follow the same trajectory as the air–MORB mixing line (17). The accretionary origin of heavy noble gases (Kr and Xe) in the deep mantle is therefore yet to be satisfactorily resolved.

Determining the origin of heavy noble gases in the deep mantle is key to understanding whether the deep mantle accreted volatiles from a fundamentally different reservoir from that found in the upper MORB mantle source. A change from solar toward chondritic-dominated accretion would have important implications regarding the timing of volatile delivery to Earth, potentially indicating that volatiles in the upper mantle and at Earth's surface were added late in the accretionary process (22). In order to address these questions, we present high-precision noble gas isotope measurements in CO_2-rich magmatic gases ($n = 13$) collected from three localities: Mud Volcano, Turbid Lake, and Brimstone Basin (Fig. 1), within Yellowstone National Park, where geochemical (e.g., ^{3}He/^{4}He up to 15R_A) (23) and geophysical (24) data indicate a relatively undegassed, deep-seated source of volcanism.

Results and Discussion

The ^{3}He/^{4}He of samples analyzed here range between 2.3 and 16.3 R_A ($R_A = ^3$He/^{4}He of atmosphere), which is within the range of previously reported values for Yellowstone magmatic gases (23, 25). The large range of ^{3}He/^{4}He is attributed to assimilation of crustal-derived ^{4}He from the surrounding Archean crust during magmatic gas migration (25). Assuming that magmatic gases originated from a mantle source with ^{3}He/^{4}He of 16.3 R_A (highest value measured in this study at Mud Volcano), then the crustal component would contribute up to 85% of the total He within the samples originating from Turbid Lake and Brimstone Basin (*SI Appendix*). Samples from Mud Volcano which exhibit high ^{3}He/^{4}He (>13 R_A), show a strong linear correlation for Ne isotopes, reflecting two-component mixing between the atmosphere and a high ^{20}Ne/^{22}Ne mantle component (Fig. 2). The steep slope of this mantle–air mixing line is characteristic of a mantle source enriched in primordial ^{22}Ne relative to nucleogenic ^{21}Ne. The trend defined by the samples is statistically distinct from the mass-dependent fractionation line, falling along a mixing line similar to that defined by samples
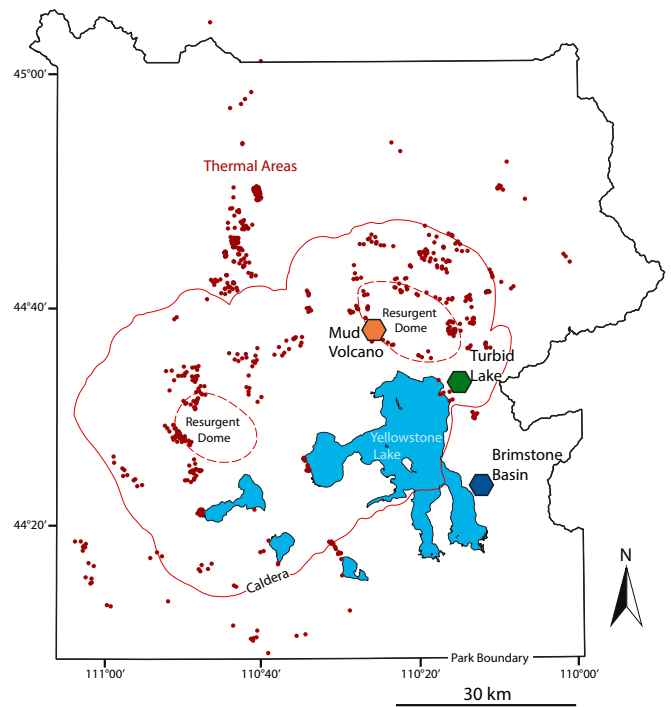

Fig. 1. Map of Yellowstone National Park. The locations of the three sampling sites that make up this study (Mud Volcano, Turbid Lake, and Brimstone Basin) are denoted as hexagons. Other thermal sites within the National Park are shown as red circles.

from the Loihi Seamount, Hawaii (26). The Mud Volcano sample with the highest measured ^{20}Ne/^{22}Ne ratio (Giggenbach sample 1B) is also offset from the mass-dependent fractionation line when ^{20}Ne/^{22}Ne is plotted against ^{38}Ar/^{36}Ar (*SI Appendix*, Fig. S5), indicating that measured Ne isotopic ratios are unlikely to be the result of mass fractionation and likely representative of the Yellowstone mantle source. This, taken together with high ^{3}He/^{4}He values, indicates the Yellowstone mantle source has preserved a high volatile to U+Th ratio and has therefore undergone less degassing of primordial noble gases compared with the MORB mantle source (30).

Samples from Brimstone Basin, which are characterized by the lowest ^{3}He/^{4}He, do not follow the same Ne isotopic trend as the other samples (Fig. 2). They exhibit higher ^{21}Ne/^{22}Ne and plot near the MORB–air mixing line, potentially indicating that the Brimstone Basin samples contain a secondary component in addition to that sampled at Mud Volcano. Brimstone Basin is situated outside the Yellowstone Caldera (Fig. 2), where low ^{3}He/^{4}He have previously been attributed to the incorporation of Archean-aged crustal material, rich in radiogenic ^{4}He, to an original high ^{3}He/^{4}He plume mantle source (25). This would also have the effect of increasing the ^{21}Ne/^{22}Ne through the addition of crustal-derived nucleogenic ^{21}Ne, likely accounting for why the Brimstone Basin samples are offset from the Ne isotopic trend defined by the Mud Volcano samples (Fig. 2).

The mantle noble gases from Brimstone Basin could also have originated from the MORB mantle reservoir, the subcontinental lithospheric mantle (SCLM), or a mixture between these reservoirs and the Yellowstone plume. However, the ^{3}He/^{4}He of Brimstone Basin (2.34 to 3.04 R_A) is lower than the average values for both MORB (8 ± 1 R_A) (30) and SCLM (6 ± 2 R_A) (31, 32) reservoirs, and, therefore, regardless of the original mantle source, the low ^{3}He/^{4}He measured in Brimstone Basin requires an additional crustal noble gas component enriched in radiogenic ^{4}He (25). As the addition of crustal ^{4}He should also
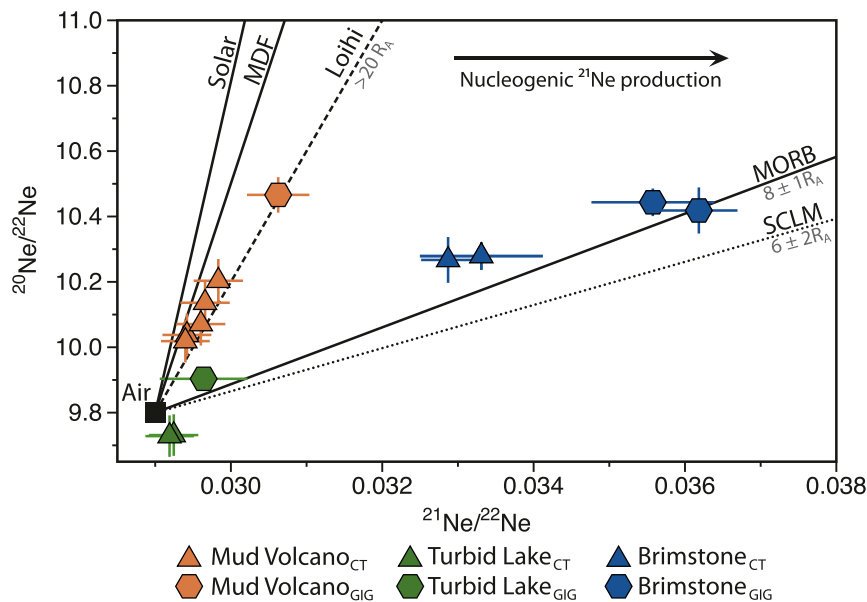
Broadley et al.

Fig. 2. Neon isotopic composition of Yellowstone volcanic gas. Data from samples collected ($n = 13$) at three localities are shown. Samples from Mud Volcano and Brimstone Basin show clear excesses from atmosphere. Gas collected in Giggenbach bottles (GIG) are less air-contaminated than samples collected in copper tubes (CT). Mud Volcano samples show a strong linear correlation with a slope approximate to that defined by the Loihi Seamount samples (26), confirming the Yellowstone plume samples a deep undegassed mantle reservoir. Brimstone Basin samples are offset toward the MORB–air mixing line (27) from the addition of crustal-derived nucleogenic ^{21}Ne, while samples from Turbid Lake are similar to atmosphere. The SCLM–air mixing line (28, 29) and mass-dependent fractionation line are shown for reference. Uncertainties are displayed at 1 σ.

be associated with the addition of nucleogenic ^{21}Ne, the slope of the air–mantle mixing line that passes through the Brimstone Basin samples should represent a minimum, as the addition of ^{21}Ne would serve to lower the steepness of the slope of the mixing line. Given that the Brimstone Basin samples plot along or slightly above the MORB–air mixing line in Fig. 2, this would rule out the SCLM as the primary mantle source for Brimstone Basin, despite the fact that volcanic products attributed to the Yellowstone plume are known to contain significant SCLM contributions (33). To reconcile the MORB-like Ne isotopes with the presumed high levels of crustal He present within Brimstone Basin requires the mantle source to contain a third, less-radiogenic component, which we surmise is the Yellowstone mantle plume component (as sampled at Mud Volcano).

To further determine whether the low $^3He/^4He$ Brimstone Basin and high $^3He/^4He$ Mud Volcano samples share a similar mantle component, we evaluate the relationship between primordial He and Ne isotopes in the samples. When $^{20}Ne/^{22}Ne$ is plotted against $^3He/^{22}Ne$ (Fig. 3), all of the samples in excess of atmosphere, with the exception of one outlier, form a clear linear correlation. Crucially, the isotopes that form this correlation are not produced in significant quantities by radiogenic and/or nucleogenic processes and therefore provide information on the mantle source, without being influenced by crustal assimilation, as can be the case for $^3He/^4He$ and $^{21}Ne/^{22}Ne$. However, $^3He/^{22}Ne$ can be affected by different physical processes such as degassing and dissolution, which can result in elemental fractionation altering the original mantle signature. If the $^3He/^{22}Ne$ of Yellowstone has been modified, then this should also be apparent in other noble gas elemental ratios such as $^4He/^{40}Ar^*$. The $^4He/^{40}Ar^*$ of the samples defining the He–Ne correlation in Fig. 3 (0.6 to 1.5) is similar to, if somewhat lower than, the mantle production ratio (1.6 to 4.2) (30), with the Turbid Lake and Brimstone Basin samples being corrected for crustal ^4He and ^{40}Ar contributions. The similarity between the measured $^4He/^{40}Ar^*$ in Yellowstone and the mantle production ratio

suggests that any elemental fractionation is likely to be minimal and the $^3He/^{22}Ne$ is likely representative of the Yellowstone mantle source (Fig. 3).

The linear correlation exhibited in Fig. 3 can therefore be considered to represent a mixing line between atmosphere and a common mantle component. Extrapolating the correlation line to the plume $^{20}Ne/^{22}Ne$ endmember value of ~13.4 (4) gives a $^3He/^{22}Ne$ ratio of 1.4 to 2.5 (Fig. 3). The $^3He/^{22}Ne$ of the Yellowstone mantle source therefore falls within the range previously published for plume-influenced samples (1.5 to 3) (14, 20) but is clearly distinct from MORB and SCLM values (>4.6) (34–36). Extrapolating to the MORB $^{20}Ne/^{22}Ne$ endmember (5) would result in an even lower $^3He/^{22}Ne$, therefore further distinguishing the Yellowstone mantle source from MORB. These observations suggest that the noble gases in Brimstone Basin and Mud Volcano originate from the same plume-derived mantle source and that the higher $^{21}Ne/^{22}Ne$ measured in Brimstone Basin is simply the consequence of higher crustal ^{21}Ne contributions (25).

The $^{40}Ar/^{36}Ar$ of the Brimstone Basin samples reach values greater than 1,400, which are the highest values yet measured in Yellowstone magmatic gas samples (37) and significantly higher than that measured in Mud Volcano and Turbid Lake (*SI Appendix*, Table S2). Importantly, crustal Ar contributions in the Brimstone Basin samples can be accounted for to derive the underlying mantle argon compositions (*SI Appendix*). Following correction for crustal $^{40}Ar^*$ contribution, the $^{40}Ar/^{36}Ar$ of Brimstone Basin sample 4B is 1,001 ± 42, which is still in excess of atmosphere. The corrected $^{40}Ar/^{36}Ar$ of Brimstone Basin remains higher than the other samples, suggesting that Brimstone Basin has the lowest degree of air contamination and greatest contribution of mantle-derived Ar. Unlike Mud Volcano and Turbid Lake, Brimstone Basin is not a thermal area but is still a significant degassing site (38). The low temperature of the Brimstone Basis system is considered to have limited boiling and therefore gas loss during transit toward the surface, potentially explaining why the diffusive magmatic CO_2 flux is so large for a
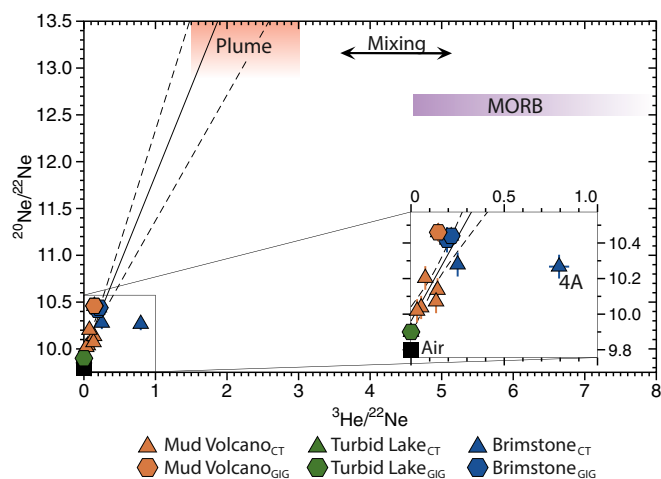
Fig. 3. $^{20}Ne/^{22}Ne$ versus $^{3}He/^{22}Ne$ of Yellowstone volcanic gas. The He and Ne isotopic signature of the Yellowstone samples, with the exception of one outlier, are correlated, yielding a linear mixing array between atmosphere and the Yellowstone mantle source. Extrapolating the correlation line to the primitive mantle $^{20}Ne/^{22}Ne$ value of 13.4 gives the $^{3}He/^{22}Ne$ ratio of the Yellowstone mantle source to be between 1.4 and 2.5. A similarly low $^{3}He/^{22}Ne$ for the Yellowstone mantle source ($\sim$3.6) is found following the method set out in ref. 34. The $^{3}He/^{22}Ne$ of the Yellowstone mantle source is within the range previously determined for other plume influenced samples (1.5 to 3.0) (14, 20) but clearly distinct from that of MORB (>4.6) (34, 35). The higher $^{3}He/^{22}Ne$ ratio in the copper tube (CT) sample 4A is the result of He and Ne not being adequately cryoseparated during sample preparation. The Giggenbach (GIG) sample of the same gas falls along the same mixing line as the other samples, and we therefore do not consider the higher $^{3}He/^{22}Ne$ measured in 4A to be representative of the mantle source. The dashed lines are the 1 σ confidence intervals fitted through all of the data minus the outlier sample 4A. Uncertainties on the measurements are displayed at 1 σ.

nonthermal site and why the noble gases are less contaminated by atmosphere. The greater mantle volatile contribution in Brimstone Basin has also been further substantiated by a recent innovative study that used the rare $^{15}N^{15}N$ isotopologue of N_2 to identify and correct for air contamination in volcanic gas emissions (39). This study revealed that not only did the Brimstone Basin samples contain the greatest contribution of mantle-derived N_2 of all of the Yellowstone samples measured but also that the $\delta^{15}N$ of the Yellowstone mantle source is distinct from MORB and in line with previous determinations of plume-derived samples (39).

The Brimstone Basin samples analyzed in this study were found to contain excesses in $^{129}Xe/^{130}Xe$ (Fig. 4) relative to atmosphere. Excesses in $^{129}Xe/^{130}Xe$ relative to atmosphere typically signify the addition of mantle-derived ^{129}Xe, produced from the decay of short-lived radiogenic ^{129}I, therefore further confirming the lower degree of atmospheric contamination in this sample. Assuming the Yellowstone magmatic source originated with a similar $^{129}Xe/^{130}Xe$ to the Icelandic plume source (6.98 ± 0.07) (20), we calculate that Brimstone Basin sample 4B, which has the highest measured $^{129}Xe/^{130}Xe$ (6.541 ± 0.002), contains between 7 and 12% mantle-derived Xe, with the remainder being from atmospheric contamination occurring at the near surface. These results reveal an unambiguous mantle-derived Xe anomaly within the Yellowstone mantle source.

Brimstone Basin sample 4B shows resolvable excesses in the heavy fissiogenic, and light nonradiogenic, Xe isotopes (Fig. 4). Heavy Xe isotopes ($^{131-136}Xe$) are produced in different proportions from the spontaneous fission of extinct ^{244}Pu ($T_{1/2}$ = 80 My) and extant ^{238}U ($T_{1/2}$ = 4.469 Gy) (40). Undegassed mantle reservoirs are typically enriched in Pu-derived Xe relative to U, with the ratio of Pu/U-derived Xe utilized to infer the degassing

state of different mantle reservoirs (20). However, measured excesses in fissiogenic Xe isotopes in Brimstone Basin sample 4B are higher than would be expected for a mantle-derived sample, containing up to 12% mantle-derived Xe (Fig. 4). The fissiogenic Xe signature in Brimstone Basin therefore contains an additional Xe component produced from the decay of ^{238}U in the surrounding Archean crust (*SI Appendix*, Fig. S9), which precludes using the fissiogenic Xe isotopes to gain further insights into the Yellowstone mantle source.

No significant production pathways exist for primordial ^{124}Xe, ^{126}Xe, ^{128}Xe, and ^{130}Xe within the mantle. These isotopes are considered to be a remnant of accretionary volatiles preserved since Earth's formation. The primordial Xe isotopes measured within the Brimstone Basin samples can therefore be used to make further inferences on the nature and composition of the Yellowstone mantle source. In Fig. 5, we show that the Yellowstone mantle source exhibits different $^{129}Xe/^{124,126,128}Xe$ ratios from that measured in MORB-derived samples (16–18). Although the difference is slight, the Brimstone Basin sample 4B has lower $^{129}Xe/^{124,126,128}Xe$ ratios than any previously measured MORB-derived sample. The lower $^{129}Xe/^{124,126,128}Xe$ measured in Yellowstone compared with MORB provides further evidence that the Yellowstone gas is unlikely to be sourced from a mantle reservoir with a MORB-like Xe isotopic signature.

Extrapolating the air–Yellowstone mixing line in Fig. 5 to the $^{129}Xe/^{130}Xe$ plume mantle endmember, as defined by the Iceland mantle source (6.98 ± 0.07) (20), enables the $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$, and $^{128}Xe/^{130}Xe$ of the Yellowstone mantle source to be estimated. The extrapolated $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$, and $^{128}Xe/^{130}Xe$ ratios of the Yellowstone mantle source are shown to be generally higher than the extrapolated values determined for the MORB mantle source. The extrapolated $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$, and $^{128}Xe/^{130}Xe$ ratios suggest that the Yellowstone
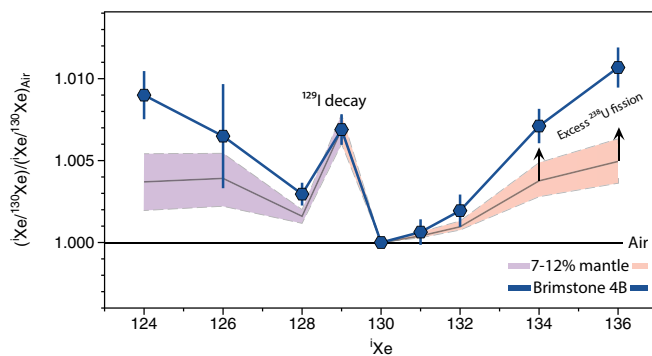

Fig. 4. Xenon isotopic spectrum of Yellowstone volcanic gas (sample 4B). Data are normalized to the isotopic composition of atmosphere and ^{130}Xe. Sample 4B is the least air-contaminated sample from Brimstone Basin. It shows resolvable $^{129}Xe/^{130}Xe$ excesses, confirming the contribution from mantle-derived xenon. Comparing the $^{129}Xe/^{130}Xe$ with that of the Icelandic plume source, we calculate the amount of mantle-derived Xe present within the sample to be between 7 and 12%. The Xe isotopic spectrum corresponding to this estimated mantle contribution is shown by the shaded area (*SI Appendix*). The estimated heavy isotope composition (orange shaded area) is estimated relative to the Icelandic plume mantle source (20), while the expected light xenon isotope signature (purple shaded area) is calculated based on the amount of primordial Xe present within the MORB source, as no previous estimates for the plume source mantle exist for light Xe isotopes. The excesses in heavy xenon isotopes in the sample are greater than expected for mantle-derived gases, indicating the sample contains an excess fissiogenic Xe component inherited from the surrounding Archean crust. The $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$, and $^{128}Xe/^{130}Xe$ ratios measured in Yellowstone are higher than would be expected from a MORB source given the excess in $^{129}Xe/^{130}Xe$, indicating that Yellowstone volcanism originates from mantle reservoir with a lower $^{129}Xe/^{Primordial}Xe$ than MORB. Uncertainties represent 1 SE.
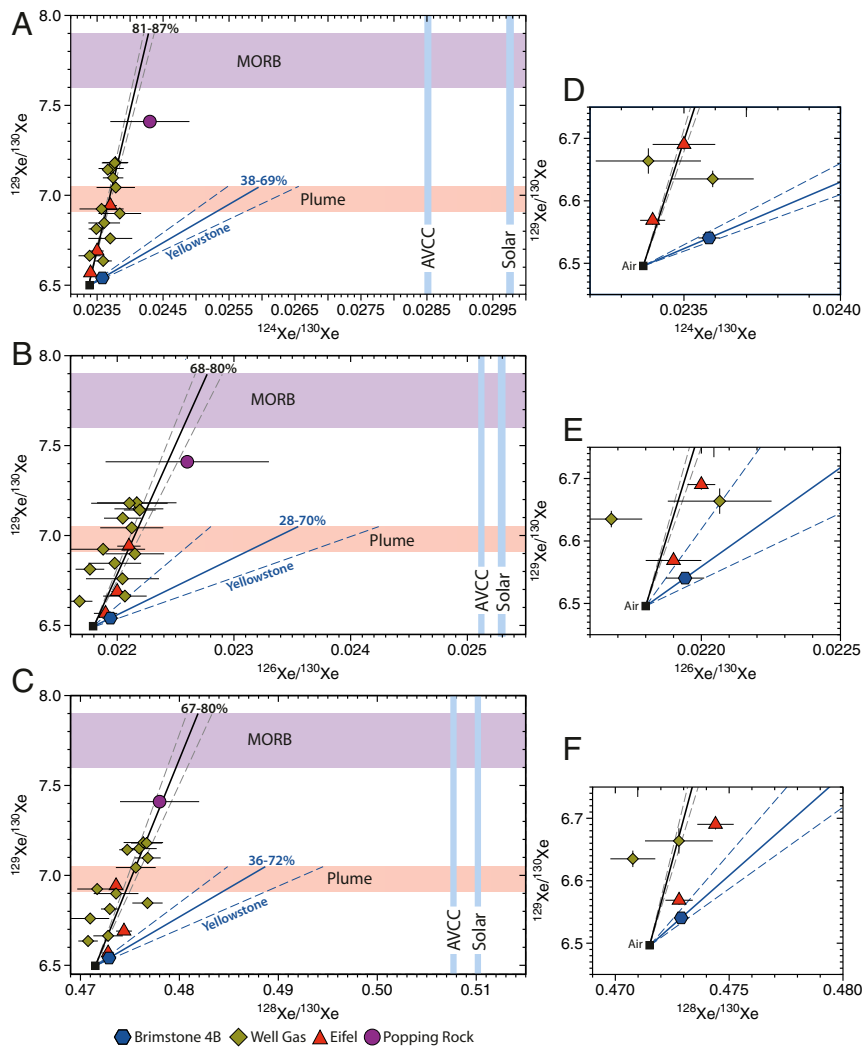
Fig. 5. Difference in Xe isotopic composition between the Yellowstone mantle source and MORB. (*A–C*) The $^{129}Xe/^{130}Xe$ versus $^{124}Xe/^{130}Xe$ (*A*), $^{126}Xe/^{130}Xe$ (*B*), and $^{128}Xe/^{130}Xe$ (*C*) of Brimstone Basin 4B is plotted together with MORB-derived samples (16–18). *D–F* represent zoomed in sections of figures *A–C*, respectively. The solid lines in these plots represent the mixing line between atmosphere and the mantle endmember composition. The Brimstone Basin sample has consistently lower $^{129}Xe/^{124,126,128}Xe$ ratios (defined from the slope of the mixing lines) when compared with MORB, suggesting that it originated from a mantle source with a lower I/Xe. The endmember $^{129}Xe/^{130}Xe$ composition for the MORB (16–18) and plume (20) mantle sources are shown for comparison. Extrapolated $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$, and $^{128}Xe/^{130}Xe$ values for Yellowstone are higher and closer to primordial AVCC (41) and solar values (2) than that calculated for the MORB source. The percentage of recycled atmosphere, relative to an AVCC starting composition, in the Yellowstone and MORB mantle sources are stated. The solid black line through the MORB data is an error-weighted fit forced through the atmospheric composition, with the dashed lines representing the 1 σ confidence interval. The Yellowstone correlation (solid blue line) is fitted through Brimstone Basin sample 4B, with the dashed lines representing the maximum extent of the uncertainty of the sample. Uncertainties for sample 4B represent 1 SE and are smaller than symbol size.

mantle source has a slightly higher ratio of primordial (Average Carbonaceous Chondrites [AVCC]) (41) to recycled atmospheric Xe than the MORB mantle source (Fig. 5). However, with the exception of $^{124}Xe/^{130}Xe$, the estimated amount of recycled atmospheric Xe isotopic in the Yellowstone plume and MORB mantle sources are within uncertainty of each other (Fig. 5), as has been previously suggested (42).

These estimates are dependent on the $^{129}Xe/^{130}Xe$ ratios chosen as the mantle endmember, so if, for instance, the $^{129}Xe/^{130}Xe$ endmember for Yellowstone was greater than that determined for the Iceland mantle source, and more similar to MORB, then the ratio of primordial to recycled Xe within the Yellowstone mantle source would be even higher (Fig. 5). Despite the large uncertainties, the Yellowstone mantle source appears to contain similar, if not slightly lower, proportions of recycled atmospheric Xe compared with the MORB mantle

source. Comparable estimates for the amount of recycled Xe in the plume and MORB mantle sources (42), despite the plume source being less degassed of its volatiles, suggest that volatiles may be more efficiently recycled to the deep plume source mantle.

Although it is difficult to reach definitive conclusions based on a single determination of light isotopes in plume-influenced samples, we suggest that to account for both the high proportion of recycled Xe and the lower $^{129}Xe/^{124,126,128}Xe$ of the Yellowstone samples requires that the Yellowstone mantle source have a lower $^{129}Xe/^{130}Xe$, similar to that measured in Iceland (Fig. 5 and ref. 20). These observations confirm that the plume and MORB mantle reservoirs evolved with different ratios of ^{129}Xe to primordial Xe isotopes (20). Since primordial Xe isotopes did not change during ^{129}Xe production from the decay of extinct ^{129}I over the first 100 My of Earth's history, the differences between the two mantle reservoirs are a function of
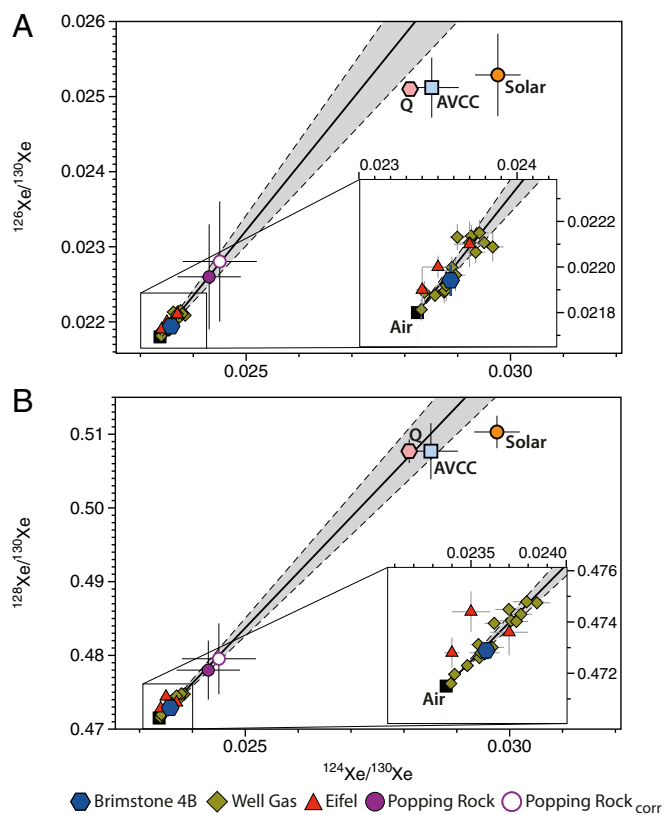
Fig. 6. Primordial light xenon isotopes in the Yellowstone mantle source. The $^{126}Xe/^{130}Xe$ (*A*) and $^{128}Xe/^{130}Xe$ (*B*) versus $^{124}Xe/^{130}Xe$ of Brimstone Basin gases plot along the same trend fitted through volcanic gas from Eifel (17), upper magmatic CO_2 well gases (16), the measured value and the end-member composition, corrected for atmospheric contamination, of MORB popping rock (18), therefore confirming the presence of primordial xenon in the Yellowstone mantle source. Phase Q (1), AVCC (41), and Solar Wind (2) compositions are shown for reference. Uncertainties for sample 4B represent 1 SE.

their different initial I/Xe ratios (20). The Yellowstone mantle source, as well as that feeding other mantle plumes (20, 43), must therefore have been separated from the MORB source mantle early in Earth's history (before 4.5 Ga), with limited mixing occurring between the two reservoirs since.

The plume origin of the noble gases from Brimstone Basin (Figs. 2, 3, and 5), coupled with their resolvable light Xe isotope excesses from atmosphere, presents an opportunity to determine the accretionary origin of the heavy noble gases in a plume-influenced mantle source. The $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$, and $^{128}Xe/^{130}Xe$ values plot along the same trend defined previously from the analysis of MORB-derived samples, which is considered to represent a mixing line between air and chondritic Xe: Phase Q, main carrier of chondritic noble gases (1), and AVCC (41). This is, in itself, not sufficient to conclude whether the Yellowstone mantle source is dominated by chondritic or solar noble gases, given the small measured isotope excess and the relatively minor difference between chondritic and solar Xe isotopic signatures (Fig. 6).

Unlike Xe, the Kr isotopic signatures of chondritic and solar endmembers are isotopically heavier and lighter than atmosphere, respectively, therefore constituting a powerful tool for distinguishing between chondritic and solar volatile sources in the mantle (6). However, resolving any mantle Kr contributions has proven difficult, given the relatively small isotopic difference, in comparison with Xe, between the atmosphere and potential accretionary sources (solar and chondritic). Despite this, recent

high-precision studies of CO_2 well gas and MORB popping rock have shown the upper mantle to contain a primordial chondritic Kr signature (6, 18).

After correcting for ^{84}Kr and ^{86}Kr produced by U fission in the crust (*SI Appendix*), we find that Brimstone Basin sample 4B maintains a $^{86}Kr/^{84}Kr$ excess relative to atmosphere, indicating a resolvable primordial mantle Kr component (Fig. 7). The non-atmospheric Kr signature measured within Yellowstone magmatic gas provides a unique insight into the origin of volatiles in the deep plume mantle source. Fig. 7 demonstrates that Kr and Xe isotopes from Brimstone Basin fall along the air–mantle mixing line defined by magmatic CO_2 well gases containing a chondritic inherited noble gas component (6). The identification of chondritic Kr is primarily based on the $^{86}Kr/^{84}Kr$ ratio, as the difference between the $^{82}Kr/^{84}Kr$ and $^{83}Kr/^{84}Kr$ composition of chondrites and the atmosphere is smaller and therefore more difficult to resolve from the atmosphere (*SI Appendix*, Fig. S4). Critically, the heavy noble gas composition of the Yellowstone and MORB mantle sources appears to be dominated by chondritic sources, with no evidence for the preservation of solar Kr and Xe isotopes in the mantle.
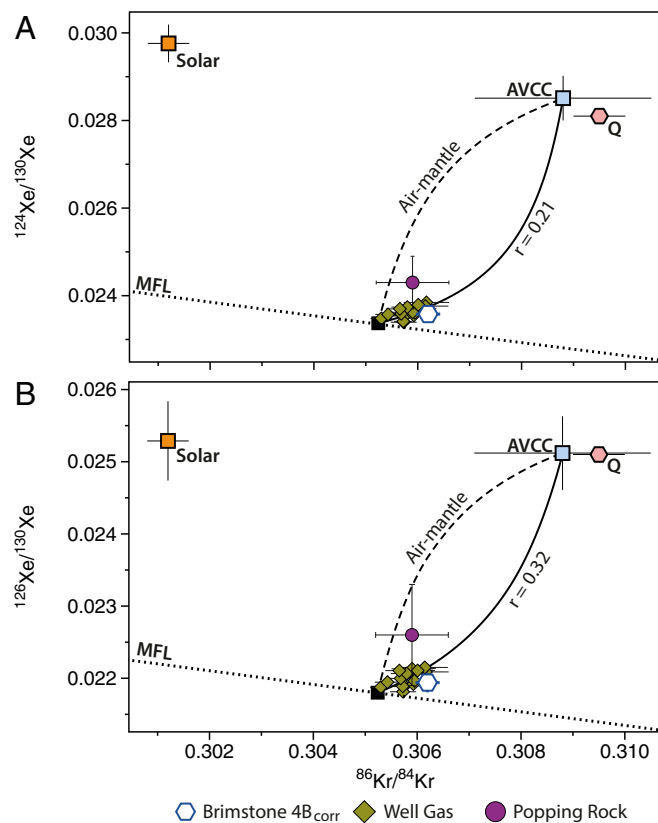

Fig. 7. Chondritic krypton and xenon isotopes in the deep mantle. Brimstone Basin falls along the same trend as magmatic CO_2 well gases (6) in $^{124}Xe/^{130}Xe$ (*A*) and $^{126}Xe/^{130}Xe$ (*B*) versus $^{86}Kr/^{84}Kr$ space. Magmatic CO_2 well gas and Yellowstone samples have been corrected for crustal U fission production of ^{86}Kr and ^{84}Kr. The curvature of the mixing hyperbola between air and the original mantle composition is defined by $[^{130}Xe/^{84}Kr]_{mantle}/[^{130}Xe/^{84}Kr]_{Air}$ and is calculated performing a total least-square hyperbolic fit (*SI Appendix*). The trajectory of the mantle–air mixing line for both the magmatic CO_2 well gas and Yellowstone samples indicates that both the plume and MORB mantle sources are dominated by chondritic—and not solar—Kr and Xe. The mass-dependent fractionation line and values for Phase Q (1), AVCC (41), Solar Wind (2), and MORB Popping Rock (18) are shown for reference. Uncertainties of Brimstone 4B represent 1 SE.

The identification of chondritic Kr and Xe in the deep plume mantle source is therefore in line with the chondritic origin of noble gases in the MORB mantle but in contrast with the convincing evidence for solar neon in plume-influenced samples (4). To account for the Ne isotopic dichotomy between the plume and MORB mantle reservoirs, it has been suggested that the MORB mantle originated from the plume mantle but was subsequently modified by additions of chondritic material following the dispersion of the solar nebula (4). This scenario is based on the fact that, in $^{20}Ne/^{22}Ne$ versus $^{36}Ar/^{22}Ne$ or $^{130}Xe/^{22}Ne$ space, plume-influenced basalts and MORBs lie along a mixing line between the solar nebula composition and a chondritic component similar to CI chondrites and/or ocean water values. Both mantle reservoirs would hence have originated with a solar noble gas composition, before being modified to variable extents by the latter addition of chondritic material (4).

To account for the chondritic Kr and Xe signature in the deep plume mantle, while preserving the solar Ne signature, therefore requires a mechanism that could overprint solar heavy noble gases without affecting solar light noble gases. Two main scenarios have been proposed to date to account for the origin of chondritic noble gases in Earth's mantle: 1) introduction of chondritic noble gases into the mantle through time via subduction of surface material and/or 2) direct injection of chondritic material to the growing Earth following the dissipation of the solar nebula, with impacting chondritic bodies preferentially populating the MORB mantle relative to the plume mantle (4).

The subduction of chondritic volatiles from Earth's surface could potentially introduce chondritic Kr and Xe to the plume source, considering the efficient recycling of Ar, Kr, and Xe (relative to Ne) to both the deep plume and MORB mantle sources (16, 42). However, subduction of atmospheric Xe to the mantle could not account for the chondritic Xe signature in the lower mantle. This is because the ancient atmospheric Xe component (U–Xe) was not solely chondritic but also contained up to 27% cometary Xe (3). The addition of cometary noble gases appears to be limited to the atmosphere (3), with no evidence of a U–Xe signature in the present-day mantle (18, 21). Furthermore, the efficient recycling of atmospheric Xe is not thought to commence until the atmosphere reached a modern isotopic composition, some 2.5 Ga (18, 44).

The second scenario, concerning the direct addition of chondritic material to the mantle, could be related to the purported late veneer, whereby the addition of ~0.5% of the Earth's mass was added following core formation and the moon-forming impact (45). A late veneer in the form of carbonaceous chondrite-like material could potentially have supplied the majority of Earth's volatiles (22). However, differences in $^{129}Xe/^{124,126,128,130}Xe$ between plume (Fig. 5) and MORB mantle reservoirs (20) require that the two reservoirs have experienced limited mixing over the last 4.45 Gy, including during the Moon-forming impact. Furthermore, Archean-aged komatiites that sample the ancient deep mantle are depleted in siderophile elements relative to the modern mantle (46), indicating that siderophile elements added to the Earth during the late veneer were not directly injected into the deep mantle but were progressively mixed in through time via mantle convection (47). The chondritic heavy noble gas component in the deep plume mantle source is therefore unlikely to have been introduced via top-to-bottom mixing of chondritic material arriving to Earth during the late veneer.

Further constraints on the timing of volatile accretion can be provided by examining differences in $^3He/^{22}Ne$ between the plume and MORB mantle reservoirs (Fig. 3). During ingassing of a gravitationally captured nebular atmosphere, He and Ne are expected to elementally fractionate in accordance with their different solubilities (34, 48). This results in the $^3He/^{22}Ne$ of the mantle rising from the nebular value of 1.5 to ~2 to 3 (similar to values observed for primitive plumes; Fig. 3 and ref. 34). It has

been suggested that, in order to increase the $^3He/^{22}Ne$ from the primitive plume reservoir value to that of the MORB mantle (6.6 ± 2.0) would require at least two further episodes of giant impact-driven atmospheric loss and magma ocean outgassing (34). The preservation of low $^3He/^{22}Ne$ within the deep mantle reservoir (as sampled here by the Yellowstone plume, with $^3He/^{22}Ne$ of 1.4 to 2.5) therefore indicates that it has remained at least partially isolated following the ingassing of the protosolar nebula and that subsequent giant impacts did not significantly affect its volatile element budget. This is consistent with the observed correlation between ^{182}W anomalies and $^3He/^4He$ in mantle plumes, which suggests that the plume mantle reservoir and its noble gas budget were generated no later than 60 My after the formation of the Solar System (49). We therefore conclude from the complementary constraints brought from $^3He/^{22}Ne$ and Xe isotope systematics that the chondritic heavy noble gases in the Yellowstone plume mantle, at the very least, predate the Moon-forming impact and are unrelated to the chondritic component in the MORB mantle.

The existence of solar Ne in the plume mantle requires that the Earth grew to be Mars-sized within the lifetime of the solar nebula (4). The Mars-sized proto-Earth was likely to have retained chondritic volatiles, as has been shown to be the case for other early accreting planetary embryos (50), prior to the ingassing of a nebular atmosphere. Ingassing of nebular volatiles to Earth's mantle would then preferentially alter the isotopic signature of Ne, relative to Kr and Xe (10, 11), due to the much higher $^{20}Ne/^{130}Xe$ ratio of the solar nebula compared with CI chondrites (8, 9) and greater solubility of Ne in basaltic melts in comparison with Xe (48). We calculate that to raise the $^{20}Ne/^{22}Ne$ of the mantle from CI chondrites-like values (9.03 ± 2.46) to its estimated primordial value of 13.23 ± 0.22 (4) would result in a negligible contribution of solar Kr (2%) and Xe (<1%) to the mantle inventory (*SI Appendix*, Fig. S10). These estimates would be even lower if the starting $^{20}Ne/^{22}Ne$ composition of the mantle was taken to be the chondritic Ne–B endmember (~12.7) (7).

The preservation of primordial chondritic Kr and Xe in the deep Yellowstone mantle source has broad implications regarding the origin and timing of volatile element delivery to Earth. It notably indicates that the Earth has been retentive to chondritic volatiles throughout accretion and that, contrary to the commonly held view, terrestrial volatiles were not solely inherited from Earth's latest stages of accretion (Moon-forming impact and late veneer). Our results imply that the dichotomy between the main sources of heavy (chondritic) and light (solar) noble gases in the deep mantle was already established within the proto-Earth's mantle during the lifetime of the protosolar nebula.

Materials and Methods

Samples were collected in August 2018 from three localities within Yellowstone National Park: Mud Volcano, Turbid Lake, and Brimstone Basin (Fig. 1 and *SI Appendix*, Table S1). The sites consisted of both hot (Mud Volcano [85 °C], Turbid Lake [80 °C]) and cold (Brimstone Basin [21 °C]) degassing features, which were specifically chosen as they previously showed $^{40}Ar/^{36}Ar$ values in excess of air (38), thus providing the highest probability of finding mantle-derived Kr and Xe signatures. Gas samples were collected in both refrigeration-grade copper tubes and Giggenbach bottles (i.e., preevacuated 200-cm^3 glass flasks filled with 50 to 80 cm^3 of 7N NaOH solution) (51). Prior to the samples being sealed, volcanic gas was flushed through the Tygon tubing and copper tubes for a minimum of 30 min to limit air contamination. Sample 4B from Brimstone Basin was flushed with gas overnight for a minimum of 12 h. Giggenbach samples were analyzed for He, Ne, Ar, and high-precision Kr and Xe (*SI Appendix*, Tables S3 and S4) isotopic analysis at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) noble gas analytical facility, using the ThermoFisher Scientific Helix SFT for helium and Helix MC+ for neon, argon, krypton, and xenon (13). Noble gas concentrations and He, Ne, and Ar isotopes were measured in the copper tube samples in the Noble Laboratory at

the University of Oxford, using a dual mass-spectrometer setup (52) (*SI Appendix*).

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Broadley et al.