Geochemical Perspectives Letters

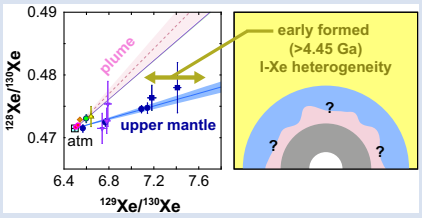
Primordial noble gas isotopes from immoderate crushing of an Icelandic basalt glass

R. Parai[1,2*]

OPEN ACCESS

https://doi.org/10.7185/geochemlet.2331

Abstract



Noble gas isotopes carry important information about volatile accretion, mantle differentiation and the preservation of early formed radiogenic isotope heterogeneities. However, extremely low abundances and pervasive atmospheric contamination make precise determinations of mantle source heavy noble gas isotopic compositions challenging. Furthermore, the precision achieved in ratios of the rarest noble gas isotopes (the primordial isotopes) is typically poor. Here an approach that combines heavy crushing of a large quantity of sample along with more traditional temperate crushing is adopted to analyse noble gases in a basalt glass from Iceland. The method yields high precision Xe primordial isotope data resolved from the atmospheric composition. $^{128}Xe/^{130}Xe$–$^{129}Xe/^{130}Xe$ systematics indicate a distinct, low $^{129}Xe/^{130}Xe$ in the plume mantle source compared with that in the upper mantle, demonstrating the survival of an early formed (>4.45 Ga) radiogenic isotope heterogeneity in the modern mantle. Future sampling efforts may plan to dedicate large quantities (>20 g) of material for high precision noble gas analysis to leverage the advantages of a mixed analytical approach.

Received 27 March 2023 | Accepted 11 August 2023 | Published 5 October 2023

Introduction

Precise determinations of mantle heavy noble gas (Ne, Ar, Kr and Xe) isotopic compositions have the power to shed light on the delivery of volatiles to Earth during accretion, and transport of volatiles among terrestrial reservoirs (*e.g.*, Parai and Mukhopadhyay, 2015; Péron and Moreira, 2018; Bekaert *et al.*, 2019; Broadley *et al.*, 2020; Péron *et al.*, 2021). Two characteristics make the noble gases sensitive tracers of volatile transport: (1) due to their extremely low abundances in the solid Earth, production of specific isotopes by radioactive decay generates large radiogenic isotope signatures, even when the parent nuclide is itself rare, and (2) the noble gases tend to partition into gas phases when possible – that is, they broadly follow the major volatiles (such as water and carbon dioxide) and escape from the mantle to melts, and from lavas to the atmosphere, over time. These characteristics also make noble gases difficult to measure in volcanic rocks, especially in light of pervasive atmospheric contamination of volcanic rock samples (*e.g.*, Burnard *et al.*, 1997; Ballentine and Barfod, 2000; Roubinet and Moreira, 2018). Analytical challenges have limited the number and type of samples for which magmatic heavy noble gas isotopic ratios have been resolved from the atmospheric composition.

Various approaches have been adopted to battle atmospheric contamination and constrain mantle source noble gas isotopic compositions. Step release of gas from samples by crushing or heating has long been used to generate data arrays trending from the atmospheric isotopic signature towards a mantle composition (*e.g.*, Sarda *et al.*, 1988; Marty, 1989); linear or hyperbolic mixing arrays can be used to determine a model mantle composition by assuming a solar-like mantle $^{20}Ne/^{22}Ne$ ratio (see Parai *et al.*, 2019). Step release approaches have been used to determine mantle source $^{21}Ne/^{22}Ne$, $^{40}Ar/^{36}Ar$, and Xe isotopic compositions in mid-ocean ridge basalt and plume basalt samples. However, wide coverage of upper mantle and ocean island heterogeneity is yet to be achieved. Furthermore, mantle compositions for Kr and the rarest Xe isotopes (^{124}Xe, ^{126}Xe, and ^{128}Xe) are limited to unusually gas-rich basalt samples (Moreira *et al.*, 1998), continental well gases (Caffee *et al.*, 1999; Holland and Ballentine, 2006; Caracausi *et al.*, 2016; Bekaert *et al.*, 2019) and volcanic gases (Broadley *et al.*, 2020; Bekaert *et al.*, 2023), where large quantities of gas are available for analysis.

Recent studies have demonstrated the utility of a screening and accumulation method (Péron and Moreira, 2018) to achieve high precision measurements of rare noble gas isotopes (Péron *et al.*, 2021). In this approach, gas from crush steps with $^{20}Ne/^{22}Ne$ above a certain threshold is progressively collected on a cold trap, and a large quantity of gas with a composition close to the mantle source is accumulated for Ar, Kr and Xe isotopic measurements (Péron and Moreira, 2018; Péron *et al.*, 2021). This approach enables precise analysis of rare isotope ratios in accumulated gas with a reduced contribution from atmospheric contaminants. However, atmospheric contaminants may affect Ar, Kr and Xe isotopes in a given release step more strongly than Ne isotopes due to high Ar/Ne, Kr/Ne and Xe/Ne ratios in the atmospheric contaminant compared to mantle gas. Thus, an accumulation approach using screening based on Ne isotopes may reduce but not eliminate atmospheric contamination in

1. Department of Earth and Planetary Sciences Washington University in St. Louis, St. Louis, MO 63130
2. McDonnell Center for the Space Sciences Washington University in St. Louis, St. Louis, MO 63130
* Corresponding author (Email: parai@wustl.edu)

Ar, Kr and Xe. The trade off between the loss of information (*e.g.*, no mixing array from multiple gas release steps) and the gain in approaching the mantle composition using screened accumulation techniques must be weighed, and a hybrid approach may be best.

Another intuitive strategy to pursue precise measurements of rare noble gas isotopes in typical basalt samples is to crush heavily to release a very large amount of gas from a very large amount of sample in a single extraction step. However, the net benefit of this approach is unknown: in practice, the largest gas release steps tend to be close to atmospheric in composition, particularly in gas-poor basalts (Parai *et al.*, 2012; Parai and Mukhopadhyay, 2015). By repeatedly crushing a sample in very small steps, one may generate (with less precise data) a well defined mixing array between atmosphere and the mantle composition, with some steps nearing a pure mantle composition (Mukhopadhyay, 2012; Parai and Mukhopadhyay, 2021). Very heavy crushing runs the risk of overwhelming small amounts of mantle gas with larger amounts of atmospheric gas in a single large gas release step, such that one obtains a very precise measurement of a nearly pure atmospheric contaminant rather than a good constraint on the mantle composition. However, this approach has not been tested in detail, potentially due to the risk it poses in making poor use of precious sample material.

Noble gas geochemistry is currently discussed in terms less specific ("plume mantle" *vs.* upper mantle) than the detailed discussions of mantle components in the broader mantle isotope geochemistry field. Radiogenic Sr, Nd, Pb and Hf isotopic co-variations among ocean island basalts shed light on multiple distinct compositional components within the plume mantle (*e.g.*, HIMU, EM-I and EM-II; see Weis *et al.*, 2023 for a recent review); the heavy noble gas isotopic signatures of these components remain to be determined. In order to bring valuable insights from heavy noble gases to bear on a wider array of mantle samples, it is critical to develop strategies that enable precise determinations of mantle source noble gas compositions in typical gas-poor volcanic samples. Here I report results from an experiment in which a hybrid crushing strategy was applied to a large quantity of Icelandic basalt glass. A few moderate crush steps were used to roughly calibrate subsequent gas release through several very large crush steps, with ~10–100× as much gas released *per* step than in prior studies that used a small step crush technique (Mukhopadhyay, 2012; Parai *et al.*, 2012; Pető *et al.*, 2013; Parai and Mukhopadhyay, 2015). While one cannot control the gas content of a given volcanic rock sample, very large amounts of sample can be collected for analysis using this heavy crushing method, unlocking new insights into heterogeneous volatile accretion and differentiation of the Earth's interior.

Sample and Methods

Subglacial basalt glass was collected in the summer of 2009 from near Miðfell, Iceland (Supplementary Information). A large quantity of basalt glass rich in olivine crystals was collected from an outcrop of glassy pillow basalts by the eastern shore of Þingvallavatn off Route 36, near the location reported for the DICE sample (Harrison *et al.*, 1999; Mukhopadhyay, 2012) and DG2017 (Péron *et al.*, 2021).

He, Ne, Ar and Xe abundances and isotopic compositions were measured in the WUSTL Noble Gas Laboratory. Details of gas processing, mass spectrometry, and preparation of the gas standards are given in the Supplementary Information (Fig. S-2).

A mixed-size step crushing strategy was followed. Two small crush steps were used to roughly calibrate the expected ^{129}Xe signal as a function of the manometer reading. Steps 3–7 were "mega-crushes" targeting a ^{129}Xe signal ~50× higher than normally targeted in the laboratory (10,000 counts *per* second ^{129}Xe instead of 200 counts *per* second; see Supplementary Information for typical sensitivities) to enable precise measurement of the rarest Xe isotopes. None of the mega-crush steps required more than a single actuation of the hydraulic cylinder, which was slowly extruded while monitoring manometer pressure (in contrast to vigorous solenoid driven crushing). Once an audible change in the type of sound generated by crushing was noted (from cracks and pops to fainter crunches), the smaller crush method was resumed (Steps 8–13) to exhaust the gas supply in the sample. Xe blanks in the mass spectrometer were monitored after the large crushes to check for memory effects; no increase in the line blank was observed.

Results and Discussion

He, Ne, Ar and Xe abundances and isotopic compositions from thirteen step crushes are reported in Supplementary Table S-1. Estimated $CO_2/^3$He, ^{4}He/^{21}Ne*, ^{4}He/^{40}Ar* and other elemental

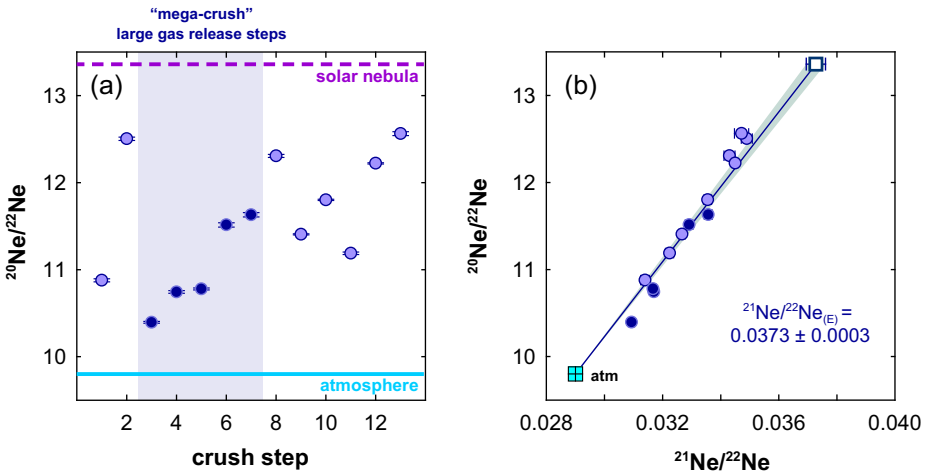


Figure 1 Ne isotopes in MiðfellRP09 step crushes. ^{20}Ne/^{22}Ne is shown **(a)** as a function of crush step and **(b)** against ^{21}Ne/^{22}Ne (error bars 1σ). Dark circles represent the heavy crush steps, referred to as "mega-crush" steps. Ne in mega-crush steps starts off close to atmospheric, and progressively shifts towards mantle compositions. All crush steps taken together define a mixing line between atmosphere and an extrapolated mantle source ^{21}Ne/^{22}Ne of 0.0373 ± 0.0003 (1σ) assuming a solar-like mantle ^{20}Ne/^{22}Ne of 13.36.

abundance ratios are also given and are discussed in the Supplementary Information (Figs. S-3, S-4). The weighted average $^{4}He/^{3}He$ for the MiðfellRP09 sample is 41,200 ± 100 (1σ), in good agreement with prior studies of the DICE and DG2017 samples (Harrison *et al.*, 1999; Mukhopadhyay, 2012; Péron *et al.*, 2021). Ne, Ar and Xe isotopic compositions are shown in Figures 1–4.

Mantle-atmosphere mixing systematics. Ne isotope ratio variations among the 13 individual crush steps are shown (Fig. 1) with the "mega-crush" gas release steps highlighted. The mantle source $^{21}Ne/^{22}Ne_{(E)}$ calculated for mantle $^{20}Ne/^{22}Ne$ of 13.36 (solar nebular gas; Heber *et al.*, 2012) is 0.0373 ± 0.0003 (1σ; Fig. 1b), in good agreement with prior studies of Ne in DICE and DG2017 (Harrison *et al.*, 1999; Mukhopadhyay, 2012; Péron *et al.*, 2021). The first mega-crush step had the lowest measured $^{20}Ne/^{22}Ne$, corresponding to a large proportion of atmospheric contaminant in the measured gas, and over the course of five mega-crushes, the $^{20}Ne/^{22}Ne$ steadily increased (Fig. 1a).

Mixing between mantle and atmospheric compositions generates hyperbolic arrays in $^{20}Ne/^{22}Ne$ *vs.* $^{40}Ar/^{36}Ar$ space, reflecting distinct $^{36}Ar/^{22}Ne$ ratios in the mixing end members (Fig. 2). Ar/Ne and Xe/Ne ratios in the atmosphere and in air-saturated seawater are higher than those in mantle sources (Williams and Mukhopadhyay, 2019), and hyperbolic mixing arrays generated by step crushing thus have pronounced curvatures: addition of a small amount of atmospheric contaminant greatly affects Ar and Xe, without strongly affecting Ne (see Ne-Ar in Southwest Indian Ridge mid-ocean ridge basalt; Parai *et al.*, 2012). The pronounced increase in $^{20}Ne/^{22}Ne$ in progressive mega-crush steps of the MiðfellRP09 sample is thus muted in $^{40}Ar/^{36}Ar$, $^{129}Xe/^{130}Xe$ and $^{129}Xe/^{132}Xe$, though the measured gas is still not totally overwhelmed by atmosphere.

Best fit mixing hyperbolae (Fig. 2) were determined by error weighted orthogonal least squares (Parai *et al.*, 2012). The mantle source $^{40}Ar/^{36}Ar$ was not well resolved given the scatter in the data in Ne-Ar space (Fig. 2a) – good fits could be achieved with many pairings of mantle $^{40}Ar/^{36}Ar$ and curvature parameters (Fig. S-5). Applying a curvature parameter ($k = 0.25$) consistent with the contrast between $^{36}Ar/^{22}Ne$ in the atmosphere and Iceland mantle source (Williams and Mukhopadhyay, 2019) yields a best mantle source $^{40}Ar/^{36}Ar$ of 9,000 (Fig. S-5). This mantle source $^{40}Ar/^{36}Ar$ was used to find best fit mantle source $^{129}Xe/^{130}Xe$ and $^{129}Xe/^{132}Xe$ (Fig. 2b,c). Given the concave down curvature of the mixing arrays in Ar-Xe space, the extrapolated mantle source Xe isotopic compositions are only weakly sensitive to the exact mantle source $^{40}Ar/^{36}Ar$. Despite having only 13 crush steps, the estimated mantle source Xe isotope compositions (Table S-2) are in excellent agreement with those determined using the 51 small crush steps in Mukhopadhyay (2012). However, the inclusion of a mix of small and mega-crush steps seems critical: the small crush steps provide a spread in compositions ranging towards mantle-like values, while the mega-crush steps provide precise measurements that are tightly clustered and define a mixing hyperbola (Fig. 2c).

The promising $^{129}Xe/^{130}Xe$ excesses compared to atmosphere in the mega-crush steps raise the question of whether $^{124}Xe/^{130}Xe$, $^{126}Xe/^{130}Xe$ and $^{128}Xe/^{130}Xe$ are also well resolved from atmosphere. In the small crush steps, the primordial Xe isotope ratios are highly uncertain and scattered around the atmospheric composition (Fig. 3). In the mega-crush steps, primordial Xe isotope ratios are determined with much greater precision. $^{129}Xe/^{130}Xe$ is well resolved from atmosphere, while primordial isotope ratios either are not resolved (Fig. 3d) or show slight excesses (Fig. 3c,e) compared to atmosphere. The $^{129}Xe/^{130}Xe$ ratios are well resolved from atmosphere in part due to greater precision (Fig. S-2), but also due to the ~10× greater proportional difference between mantle source and atmospheric end member compositions in $^{129}Xe/^{130}Xe$ (~6.9 and 6.496, respectively) compared to the primordial isotope ratios (*e.g.*, $^{128}Xe/^{130}Xe$ of ~0.475 and 0.4715 in the mantle source and atmosphere, respectively).

Early formed mantle heterogeneity in $^{129}Xe/^{130}Xe$. The improved precision and clear excess compared to atmosphere enable investigation of the nature of $^{129}Xe/^{130}Xe$ variations in the mantle. High $^{129}Xe/^{130}Xe$ in the mantle was generated by decay of short lived ^{129}I in the first ~100 Myr of Earth history, while high mantle $^{136}Xe/^{130}Xe$ was generated by a spontaneous fission of both short lived ^{244}Pu and extant ^{238}U. By plotting $^{129}Xe/^{130}Xe$ against a ratio of two primordial isotopes, $^{3}He/^{130}Xe$, in the DICE sample (Iceland) and a North Atlantic mid-ocean ridge basalt, Mukhopadhyay (2012) argued for low $^{129}Xe/^{130}Xe$ in the mantle sources (corrected for atmospheric contamination) of plumes compared to the upper mantle, supported by additional data from mantle-derived samples with unfractionated elemental ratios (Pető *et al.*, 2013; Parai and Mukhopadhyay, 2021). A similar comparison can be made using a ratio of two primordial Xe isotopes (*e.g.*, $^{128}Xe/^{130}Xe$) if precise,

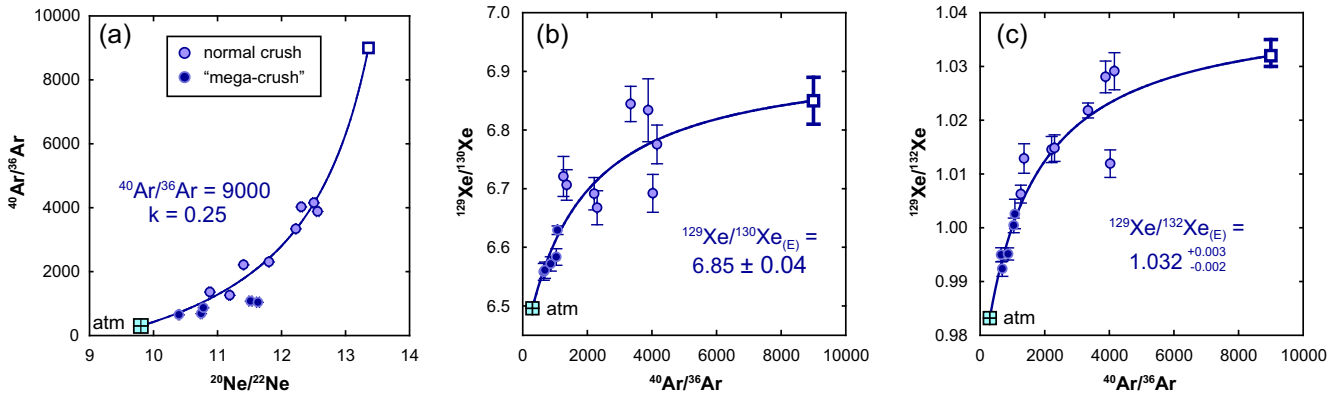


Figure 2 Ne-Ar and Ar-Xe mixing systematics in MiðfellRP09 step crushes. Data are shown along with best fit two component mixing hyperbola determined by total least squares (error bars 1σ). **(a)** In $^{40}Ar/^{36}Ar$ *vs.* $^{20}Ne/^{22}Ne$, comparable fits can be achieved for a range of mantle end member $^{40}Ar/^{36}Ar$ ratios with compensating variation in the curvature parameter. Data and best fit mixing hyperbolae for $^{40}Ar/^{36}Ar$ *vs.* **(b)** $^{129}Xe/^{130}Xe$ and **(c)** $^{129}Xe/^{132}Xe$ are shown. In Ar-Xe, the mega-crush step data are tightly clustered and constrain the mixing hyperbolae, though they are more affected by atmospheric contamination than the relatively scattered normal-sized crush step data.

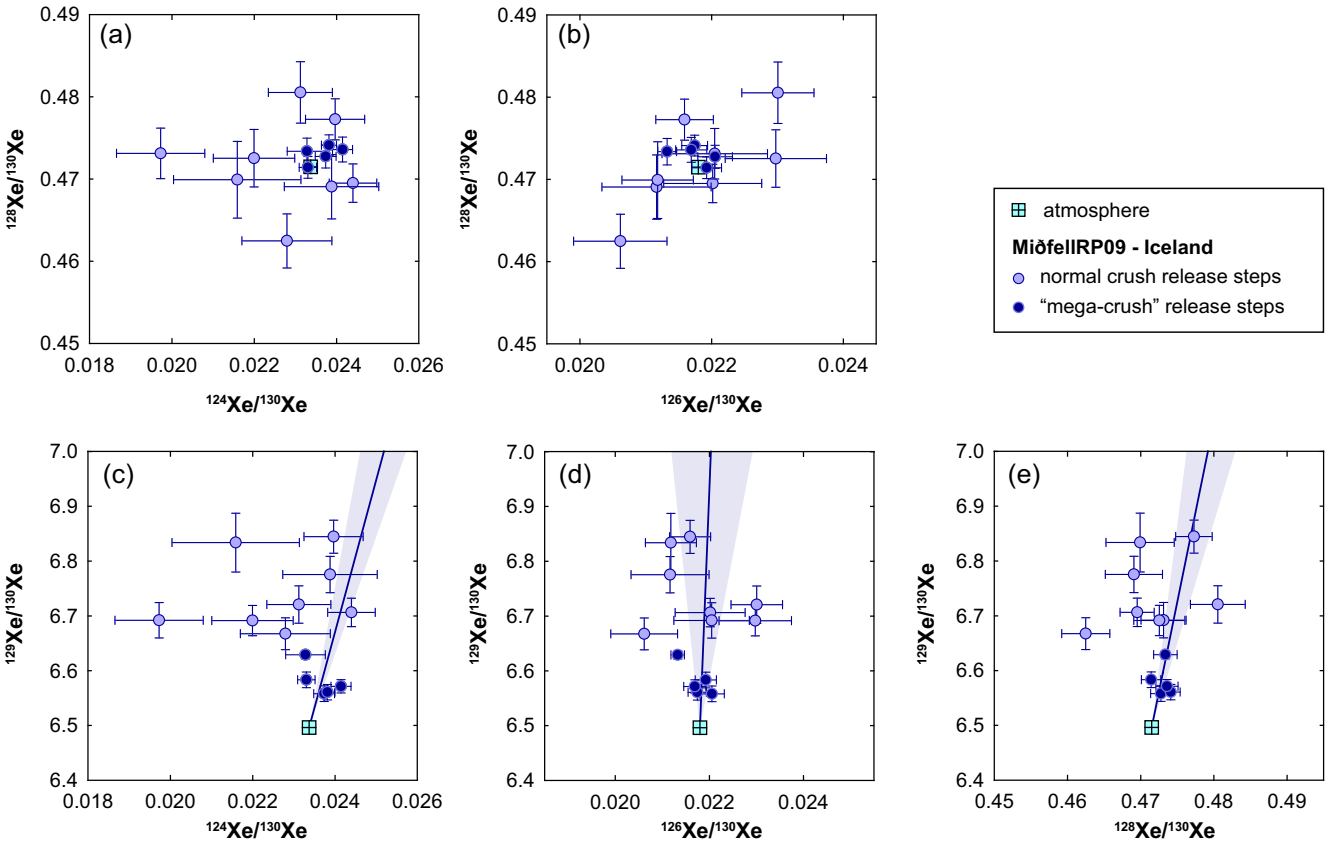


Figure 3 Xe primordial isotopes and $^{129}Xe/^{130}Xe$. Data are shown with 1σ error bars. Among the normal crush steps, data are scattered with large error bars around the atmospheric composition. The mega-crush step data include steps that are resolved from the atmospheric composition in **(a)** $^{124}Xe/^{130}Xe$ and $^{128}Xe/^{130}Xe$, though the relationship is not evident in **(b)** $^{128}Xe/^{130}Xe$ *vs.* $^{126}Xe/^{130}Xe$. $^{129}Xe/^{130}Xe$ is plotted against the primordial isotope ratios in panels **(c–e)** along with fits through atmosphere and the error weighted averages of mega-crush data.

non-atmospheric data are available. Such a Xe three isotope plot has the advantage of being insensitive to whether elemental abundance ratios were fractionated by magmatic degassing (which does not generate resolvable Xe isotopic fractionation), meaning that Xe data from degassed samples may be included.

The error weighted average of MiðfellRP09 mega-crush steps gives a high precision determination of a trapped magmatic gas composition with clear excesses relative to atmosphere in $^{128}Xe/^{130}Xe$–$^{129}Xe/^{130}Xe$ space, and shows a distinct, steeper slope for Iceland compared to the upper mantle (Fig. 4b; see Fig. S-6 for discussion of individual data sources). This translates to low $^{129}Xe/^{130}Xe$ in the plume mantle after accounting for atmospheric contributions (shallow contamination or regassing). The precise primordial isotope ratio ($^{128}Xe/^{130}Xe$) determined by mega-crushing thus confirms that the plume mantle had a low I/Xe ratio in the first 100 Myr of Earth history, and that early formed ^{129}Xe heterogeneity from ^{129}I decay has been preserved through ~4.45 Gyr of mantle convection.

Conclusions

This study leveraged a new analytical method of heavy crushing of basalt glass to determine mantle source noble gas isotopic compositions. Precise determination of $^{128}Xe/^{130}Xe$–$^{129}Xe/^{130}Xe$ in MiðfellRP09 indicates that early formed $^{129}Xe/^{130}Xe$ heterogeneity persists in the mantle today. A hybrid analytical approach that leverages the advantages of different techniques may be the optimal strategy for future work, but requires large quantities of material: likely >20 g of basalt glass *per* sample, perhaps more material for olivines. Future sampling efforts should incorporate this need in order to shed light on whether noble gas isotopic signatures of volatile origins, early differentiation and long term mantle outgassing vary among the full range of diverse mantle components sampled by oceanic basalts.

Acknowledgments

I am very grateful to David Graham and an anonymous reviewer for comments that improved the manuscript, and thank Anat Shahar for editorial handling. I thank Julian Rodriguez, Xinmu Zhang and Nathan Vaska for their vital assistance in the assembly, calibration and tuning of the gas extraction and purification line and mass spectrometer at Washington University. This work was supported by NSF EAR Petrology and Geochemistry grant 2145663 to RP.

Editor: Anat Shahar

Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2331.

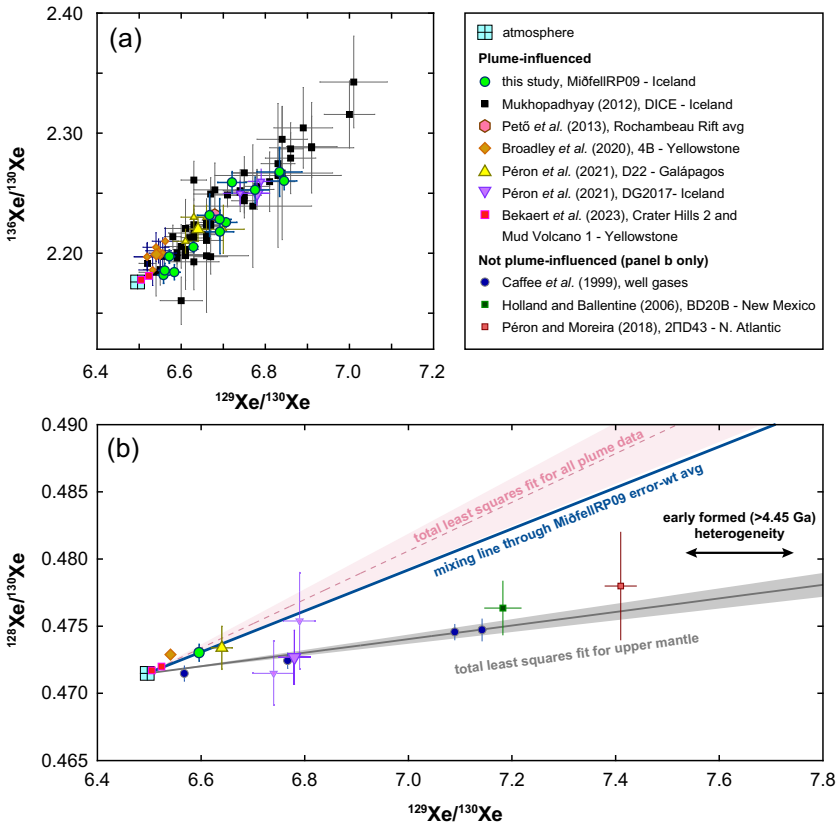


Figure 4 MiðfellRP09 and literature Xe isotopic data. Small symbols are individual data, while larger symbols are averages. **(a)** Mega-crush and regular crush step $^{136}Xe/^{130}Xe$ *vs.* $^{129}Xe/^{130}Xe$ data (1σ error bars) are consistent with prior Xe measurements in Iceland samples (Mukhopadhyay, 2012; Péron *et al.*, 2021) and plume-influenced samples from Rochambeau Rift (Samoan plume), Galápagos, and Yellowstone (Pető *et al.*, 2013; Broadley *et al.*, 2020; Bekaert *et al.*, 2023). **(b)** The error weighted average of mega-crush step $^{128}Xe/^{130}Xe$ *vs.* $^{129}Xe/^{130}Xe$ data (1σ error bars), along with average or most mantle-like compositions from plume and upper mantle samples (Péron and Moreira, 2018; Caffee *et al.*, 1999; Holland and Ballentine, 2006; Bekaert *et al.*, 2023; see Fig. S-6 for details). Fits forced through atmosphere and a mixing line between the MiðfellRP09 average and atmosphere are shown. The slope of the plume fit is strongly affected by the precisely determined Yellowstone 4B average, which may reflect some mass dependent fractionation in the hydrothermal system (Bekaert *et al.*, 2023). While individual measurements for DG2017 (Péron *et al.*, 2021) are shown, only the average was used to compute the best plume slope and its uncertainty. Despite a larger uncertainty in the plume fit, the plume and upper mantle fits have distinct slopes. The MiðfellRP09 mega-crush average is precisely determined, shows a prominent excess relative to atmosphere, and is consistent with data from other plume localities. The MiðfellRP09 average lies on a steeper slope than the upper mantle fit, indicating a plume mantle source with a lower $^{129}Xe/^{130}Xe$ at a given $^{128}Xe/^{130}Xe$ than the upper mantle.

Cite this letter as: Parai, R. (2023) Primordial noble gas isotopes from immoderate crushing of an Icelandic basalt glass. *Geochem. Persp. Let.* 27, 32–37. https://doi.org/10.7185/geochemlet.2331

References

Ballentine, C.J., Barfod, D.N. (2000) The origin of air-like noble gases in MORB and OIB. *Earth and Planetary Science Letters* 180, 39–48. https://doi.org/10.1016/S0012-821X(00)00161-8

Bekaert, D.V., Broadley, M.W., Caracausi, A., Marty, B. (2019) Novel insights into the degassing history of Earth's mantle from high precision noble gas analysis of magmatic gas. *Earth and Planetary Science Letters* 525, 115766. https://doi.org/10.1016/j.epsl.2019.115766

Bekaert, D.V., Barry, P.H., Broadley, M.W., Byrne, D.J., Marty, B., *et al.* (2023) Ultrahigh-precision noble gas isotope analyses reveal pervasive subsurface fractionation in hydrothermal systems. *Science Advances* 9, eadg2566. https://doi.org/10.1126/sciadv.adg2566

Broadley, M.W., Barry, P.H., Bekaert, D.V., Byrne, D.J., Caracausi, A., Ballentine, C.J., Marty, B. (2020) Identification of chondritic krypton and xenon in Yellowstone gases and the timing of terrestrial volatile accretion. *Proceedings of the National Academy of Sciences* 117, 13997–14004. https://doi.org/10.1073/pnas.2003907117

Burnard, P., Graham, D., Turner, G. (1997) Vesicle-Specific Noble Gas Analyses of "Popping Rock": Implications for Primordial Noble Gases in Earth. *Science* 276, 568–571. https://doi.org/10.1126/science.276.5312.568

Caffee, M.W., Hudson, G.B., Velsko, C., Huss, G.R., Alexander Jr., E.C., Chivas, A.R. (1999) Primordial Noble Gases from Earth's Mantle: Identification of a Primitive Volatile Component. *Science* 285, 2115–2118. https://doi.org/10.1126/science.285.5436.2115

Caracausi, A., Avice, G., Burnard, P.G., Füri, E., Marty, B. (2016) Chondritic xenon in the Earth's mantle. *Nature* 533, 82–85. https://doi.org/10.1038/nature17434

Harrison, D., Burnard, P., Turner, G. (1999) Noble gas behaviour and composition in the mantle: constraints from the Iceland Plume. *Earth and Planetary Science Letters* 171, 199–207. https://doi.org/10.1016/S0012-821X(99)00143-0

Heber, V.S., Baur, H., Bochsler, P., McKeegan, K.D., Neugebauer, M., Reisenfeld, D.B., Wieler, R., Wiens, R.C. (2012) Isotopic mass fractionation of solar wind: Evidence from fast and slow solar wind collected by the *Genesis* mission. *The Astrophysical Journal* 759, 121. https://doi.org/10.1088/0004-637X/759/2/121

Holland, G., Ballentine, C.J. (2006) Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* 441, 186–191. https://doi.org/10.1038/nature04761

Marty, B. (1989) Neon and xenon isotopes in MORB: implications for the earth-atmosphere evolution. *Earth and Planetary Science Letters* 94, 45–56. https://doi.org/10.1016/0012-821X(89)90082-4

Moreira, M., Kunz, J., Allègre, C. (1998) Rare Gas Systematics in Popping Rock: Isotopic and Elemental Compositions in the Upper Mantle. *Science* 279, 1178–1181. https://doi.org/10.1126/science.279.5354.1178

Mukhopadhyay, S. (2012) Early differentiation and volatile accretion recorded in deep-mantle neon and xenon. *Nature* 486, 101–104. https://doi.org/10.1038/nature11141

Parai, R., Mukhopadhyay, S. (2015) The evolution of MORB and plume mantle volatile budgets: Constraints from fission Xe isotopes in Southwest Indian Ridge basalts. *Geochemistry, Geophysics, Geosystems* 16, 719–735. https://doi.org/10.1002/2014GC005566

Parai, R., Mukhopadhyay, S. (2021) Heavy noble gas signatures of the North Atlantic Popping Rock 2ΠD43: Implications for mantle noble gas heterogeneity. *Geochimica et Cosmochimica Acta* 294, 89–105. https://doi.org/10.1016/j.gca.2020.11.011

Parai, R., Mukhopadhyay, S., Standish, J.J. (2012) Heterogeneous upper mantle Ne, Ar and Xe isotopic compositions and a possible Dupal noble gas signature recorded in basalts from the Southwest Indian Ridge. *Earth and Planetary Science Letters* 359–360, 227–239. https://doi.org/10.1016/j.epsl.2012.10.017

Parai, R., Mukhopadhyay, S., Tucker, J.M., Pető, M.K. (2019) The emerging portrait of an ancient, heterogeneous and continuously evolving mantle plume source. *Lithos* 346–347, 105153. https://doi.org/10.1016/j.lithos.2019.105153

Péron, S., Moreira, M. (2018) Onset of volatile recycling into the mantle determined by xenon anomalies. *Geochemical Perspectives Letters* 9, 21–25. https://doi.org/10.7185/geochemlet.1833

Péron, S., Mukhopadhyay, S., Kurz, M.D., Graham, D.W. (2021) Deep-mantle krypton reveals Earth's early accretion of carbonaceous matter. *Nature* 600, 462–467. https://doi.org/10.1038/s41586-021-04092-z

Pető, M.K., Mukhopadhyay, S., Kelley, K.A. (2013) Heterogeneities from the first 100 million years recorded in deep mantle noble gases from the Northern Lau Back-arc Basin. *Earth and Planetary Science Letters* 369–370, 13–23. https://doi.org/10.1016/j.epsl.2013.02.012

Roubinet, C., Moreira, M.A. (2018) Atmospheric noble gases in Mid-Ocean Ridge Basalts: Identification of atmospheric contamination processes. *Geochimica et Cosmochimica Acta* 222, 253–268. https://doi.org/10.1016/j.gca.2017.10.027

Sarda, P., Staudacher, T., Allègre, C.J. (1988) Neon isotopes in submarine basalts. *Earth and Planetary Science Letters* 91, 73–88. https://doi.org/10.1016/0012-821X(88)90152-5

Weis, D., Harpp, K.S., Harrison, L.N., Boyet, M., Chauvel, C., Farnetani, C.G., Finlayson, V.A., Lee, K.K.M., Parai, R., Shahar, A., Williamson, N.M.B. (2023) Earth's mantle composition revealed by mantle plumes. *Nature Reviews Earth & Environment* 4, 604–625. https://doi.org/10.1038/s43017-023-00467-0.

Williams, C.D., Mukhopadhyay, S. (2019) Capture of nebular gases during Earth's accretion is preserved in deep-mantle neon. *Nature* 565, 78–81. https://doi.org/10.1038/s41586-018-0771-1