Editor summary:

The formation of continental crust may have trapped – and thus not degassed - substantial magmatic nitrogen over Earth's history, according to geochemical analyses of igneous rocks from the Hekla volcanic system in Iceland.

Peer Review Information:

Primary handling editors: Tamara Goldin and Rebecca Neely, in collaboration with the Nature Geoscience team.

Nature Geoscience thanks Tobias Fischer, Ralf Halama, Olgeir Sigmarsson and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

1. Supplementary Information:

A. PDF Files

Item	Present?	Filename Whole original file name including extension. i.e.: Smith_SI.pdf. The extension must be .pdf	A brief, numerical description of file contents. i.e.: *Supplementary Figures 1-4, Supplementary Discussion, and Supplementary Tables 1-4.*
Supplementary Information	Yes	Boocock et al_Hekla Supplement.pdf	Supplementary Figures 1-6 and Supplementary Discussion

B. Additional Supplementary Files

Type	Number Each type of file (Table, Video, etc.) should be numbered from 1 onwards. Multiple files of the same type should be listed in sequence, i.e.: Supplementary Video 1, Supplementary Video 2, etc.	Filename Whole original file name including extension. i.e.: *Smith_ Supplementary_Video_1.mov*	Legend or Descriptive Caption Describe the contents of the file
Supplementary Data	1	Data_Hekla All Data.xlsx	Spreadsheet
Supplementary Data	2	Data_Felsic N Compilation.xlsx	Spreadsheet

3. Source Data

Parent Figure or Table	Filename Whole original file name including extension. i.e.: *Smith_SourceData_Fig1.xls,* or *Smith_ Unmodified_Gels_Fig1.pdf*	Data description i.e.: Unprocessed western Blots and/or gels, Statistical Source Data, etc.
Source Data Fig. 1	Data_Hekla All Data.xlsx	Geochemical Data
Source Data Fig. 2	Data_Hekla All Data.xlsx	Geochemical Data
Source Data Fig. 3	Data_Hekla All Data.xlsx	Geochemical Data
Source Data Extended Data Fig./Table 1	Data_Hekla All Data.xlsx	Geochemical Data
Source Data Extended Data Fig./Table 2	Data_Hekla All Data.xlsx	Geochemical Data

Source Data Extended Data Fig./Table 3	Data_Hekla All Data.xlsx	Geochemical Data
Source Data Extended Data Fig./Table 4	Data_Hekla All Data.xlsx	Geochemical Data
Source Data Extended Data Fig./Table 5	Data_Hekla All Data.xlsx	Geochemical Data

19

20

A primary magmatic source of nitrogen to the Earth's crust

Toby J. Boocock[1,*], Sami Mikhail[1], Adrian J. Boyce[2], Julie Prytulak[3], Paul S. Savage[1], Eva E. Stüeken[1]

[1]*School of Earth & Environmental Sciences, University of St Andrews, KY16 9AL, UK*

[2]*Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride, G75 0QF, UK*

[3]*School of Earth Sciences, University of Durham, Durham, DH1 3LE, England, UK*

---

*Corresponding Author: tjb7@st-andrews.ac.uk

ORCID IDs

Toby J. Boocock - 0000-0003-0452-4824

Sami Mikhail - 0000-0001-5276-0229

Adrian J. Boyce - 0000-0002-9680-0787

Julie Prytulak - 0000-0001-5269-1059

Paul S. Savage - 0000-0001-8464-0264

Eva E. Stüeken - 0000-0001-6861-2490

The igneous portion of Earth's continental crust represents a long-term sink of terrestrial nitrogen, but the origin of the nitrogen in this reservoir remains ambiguous. Possible sources include magmatic differentiation of mantle-derived melts (i.e., magmatic nitrogen) and/or the burial of biomass (i.e., fixed atmospheric nitrogen). Identifying the source of crustal nitrogen is required to accurately reconstruct the evolution of Earth's atmospheric pressure, and therefore habitability, over geologic timescales. Here we present analyses of the nitrogen geochemistry of extrusive igneous rocks from Hekla volcano, Iceland, that has been previously used as a natural laboratory to study the effects of magmatic differentiation on stable isotope systems. We find that bulk rock nitrogen abundance increases as rocks become more evolved, with up to 23 µg/g of nitrogen in felsic igneous samples, with non-systematic and negligible nitrogen isotopic fractionation across the suite. Our findings support nitrogen that is magmatic in origin and that behaves as an incompatible trace element during magmatic differentiation. Assuming Hekla is representative of differentiating systems more broadly, the observed nitrogen enrichment would satisfy 31-52% of Earth's felsic crust-hosted nitrogen. We suggest that continental crust formation can act as nitrogen trap between the mantle and the atmosphere. Therefore, nitrogen degassing from Earth's interior to the atmosphere over geological time may have been previously overestimated.

The mass and composition of Earth's atmosphere are crucial variables for maintaining habitability over billion-year timescales, and yet one critical parameter remains poorly constrained: the long-term evolution of atmospheric pressure[1,2]. Conservation of mass requires that changes in one reservoir (i.e., the atmosphere, where nitrogen is the major contributor of total pressure) must be balanced by reciprocal changes in other reservoirs (i.e., the crust or mantle). As such, the processes that cycle nitrogen between these reservoirs need to be constrained in order to understand the processes that enrich this bio-essential element on planetary surfaces[2]. The atmosphere and mantle are the largest nitrogen reservoirs, and they dynamically exchange nitrogen via subduction zone plate tectonics and volcanism[3,4] (Fig. 1a). Between them is a third reservoir, Earth's continental crust. The crust is important as it stores roughly half as much nitrogen as the present-day atmosphere[1]. Although lithologically heterogeneous, around 50% of the Earth's upper crust is of felsic igneous composition, making magmatic differentiation an important process during crust formation. These felsic igneous rocks can contain up to ca. 250 µg/g nitrogen[1] (Fig 1b), and with residence times of over 1000 Myr they offer potential as long term stores of nitrogen and as a key substrate for the development and evolution of life.

The upper crustal igneous reservoir can have two primary nitrogen sources: anatexis of nitrogen-enriched sediments (i.e., burial, diagenesis, partial melting), and magmatic differentiation of effectively mantle-derived nitrogen. The former would mean that the felsic igneous nitrogen reservoir was derived predominantly from the atmosphere via biomass burial, implying that this amount of nitrogen was once part of the atmospheric N_2 budget. In contrast, magmatic enrichment would imply the exact opposite, meaning that crustal differentiation can act as a trap for mantle nitrogen and thereby limit volcanically degassed atmospheric N_2 accumulation.

To address the origin of Earth's felsic igneous nitrogen reservoir, we have determined the nitrogen geochemistry for a suite of well-characterised[8-17] volcanic igneous samples from Hekla volcano, Iceland. Hekla is an active volcanic system situated in the South Iceland Volcanic Zone that produces a range of extrusive igneous rocks spanning the tholeiitic magmatic series (Fig. 2a), manifesting as aphyric lavas and tephra. Eruptions span historical timescales with 18 eruptions since 1104 A.D and the most recent activity in 2000 A.D.[8]. Eruptions typically began explosively (Si-rich), followed by later effusive (Si-poor) behaviour with the degree of Si enrichment being related to the repose time of magma storage[8]. Our samples are phenocryst-poor (containing << 5% of plagioclase, pyroxene, titanomagnetite, olivine and apatite[9]). The source of primary magmas at Hekla are estimated to come from 17-28 km depths[11] and represent melts derived by ca. 10% partial melting of the Icelandic mantle[17]. There remains debate surrounding the petrogenesis of differentiated Hekla rocks. One view is that Hekla samples are a cogenetic magmatic suite produced by variable degrees of fractional crystallisation of mantle-derived basaltic melt; broadly, this model is based on the fact that, for all Hekla samples, many major and trace element tracers of fractional crystallisation plot on a single liquid line of descent with limited evidence for crustal assimilation[8]. However, this simple model does not seem to agree with evidence from U-series isotopes and associated trace-element (e.g. Th) systematics; broadly, these models imply that it is only Hekla basaltic andesites that are derived from the fractionation crystallisation of mantle melts, and that partial melting of basaltic rocks (i.e. older Icelandic crust) is required to generate the dacites and rhyolites (the andesites are formed from mixing between these two melt sources)[10,12,20]. Therefore, it is conceivable that Hekla erupts material that has experienced fractional crystallisation, partial melting and/or magma mixing of two distinct sources (mantle and hydrated mafic crust)[17].

Hekla has been successfully used as a natural laboratory to study of the effect of magmatic differentiation *sensu lato* on many stable isotope systems (O, Tl, Li, Fe, Si, K, Zr, Mo, V, Zn)[9-10,13-20]. Importantly, for most of these isotope systems, their variations (or lack thereof) at Hekla can be explained well with either model of petrogenesis. Furthermore, the systematics of stable isotope fractionation in Hekla rocks are comparable to that measured in other geologically distinct systems (e.g. Kīlauea, Hawaii[15-16,18] and Anatahan, Mariana Islands[15-16]), suggesting that Hekla is not a special case, but provides samples representative of a differentiating system. For the case of nitrogen, its chemical behaviour best matches that of the large ion lithophile elements (LILE) at Hekla (see later). These elements can be modelled using a simple fractional crystallisation model and so initially we follow this approach for nitrogen. However, we acknowledge, and discuss, the effect that the more complicated petrogenesis model has on nitrogen and its isotopes and conclude that application of either model does not significantly affect our conclusions.

We selected and measured 17 replicate (n = 2 to 4) Hekla samples (Supplementary table S1) for their bulk rock nitrogen abundance and stable isotope compositions ($\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{air} - 1] \times 1000$), using a custom-built sealed tube combustion line[21]. These data represent total nitrogen hosted in the silicate. This is inclusive of – not limited to – nitrogen bound in silicate lattices and nitrogen dissolved in the structure of a glass (formerly, melt) and should not be confused with N_2 measurements liberated from *in-vacuo* crushing of

fluid or gas inclusions, where the measured $N_{2\ (gas\ phase)}$ is less than N^{total}. As is well established, nitrogen is incorporated into silicates systems (crystals, melt, fluids) as multiple molecular species (e.g., N_2, NH_3, NH_4^+, N^{3-})[22–24] both lattice-bound and as impurities. As such, our bulk combustion methodology *sensu stricto* measures total silicate nitrogen. Bulk rock stable oxygen isotope values ($\delta^{18}O = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{VSMOW} - 1] \times 1000$) were also measured by laser fluorination as a tracer for crustal assimilation and alteration (see Methods and supplementary material, Fig.S1-2). Major and trace element abundances and published isotope values were compiled from previous studies[8–10,13,20]. Our data show an eight-fold increase in nitrogen abundance as the rocks become more evolved (Fig 2b) from ca. 3 µg/g in the basalt samples to ca. 23 µg/g in the rhyolite samples with no systematic fractionation of nitrogen isotopes across the suite (averaging $\delta^{15}N = +1.3 \pm 1.8‰$; fig 2c) and, for most samples, no deviation in geochemical behaviour between nitrogen and the large ion lithophile elements (LILEs, such as rubidium; fig 2b,d).

The Origin of Nitrogen Enrichment at Hekla

We posit that the nitrogen systematics at Hekla are best explained by nitrogen behaving as an incompatible trace element during magmatic differentiation. The enrichment in nitrogen abundance between the basaltic and rhyolitic samples (Fig.2b) cannot be explained by degassing or late-stage fluid alteration. Our data show no systematic fractionation of nitrogen isotope values from basalt to rhyolite (Fig 2c), and we note that the variability for observed $\delta^{15}N$ values are within the range documented for the Icelandic mantle plume[25] ($\delta^{15}N = -2.29$ to $+5.71‰$). The constancy of the $\delta^{15}N$ value (averaging $\delta^{15}N = +1.3 \pm 1.8‰$) relative to silica (Fig.2c) is consistent with small magnitude equilibrium stable isotope fractionation at high temperature[31] and generally inconsistent with the loss or gain of nitrogen from interaction with fluids[29]. This lack of alteration is in agreement with previously published radiogenic[8,10,20] and stable[9,13,14,16–19] isotope datasets for Hekla volcanics (more information is provided in the supplementary material, sections S1.3 and S1.4). Our $\delta^{18}O$ values show a slight increase between +4.0 to +5.0‰ as a function of melt evolution (Fig.S1), and this general increase in $\delta^{18}O$ of ca. +1‰ as the system evolves is fully consistent with equilibrium fractional crystallisation of basalt to rhyolite in tholeiitic systems[30]. We can therefore rule out secondary sources of nitrogen as the control on the relative enrichment of nitrogen in the evolved units relative to the mafic lavas.

In a system where degassing was the dominant driver for nitrogen geochemistry one would predict the evolved lithologies (dacites and rhyolites) to be depleted in nitrogen abundance relative to the more mafic samples (basaltic and andesitic) due to progressive loss of a volatile component, but we observe the opposite (Fig. 2b). The lack of significant nitrogen degassing is further supported by the constancy of the N/Rb ratio across the sample suite (Fig. 2d). Moreover, the N/Rb of our samples are well below the range expected for hydrothermally sourced nitrogen (Fig. 2d) and suggests a behavioural coupling of nitrogen and rubidium as the magmatic system evolves. Since rubidium concentrations exhibit typical non-volatile incompatible trace element behaviour in Hekla eruption products (Fig 2b – r^2 = 0.99, rubidium vs barium), the invariance of the N/Rb ratio between the basalts and rhyolites suggests that, in the Hekla volcanic system, nitrogen is behaving in the same manner to a LILE.

We have modelled the effect of degassing on N/Rb if nitrogen were lost to a gas phases (volatile behaviour where $D_{N\ fluid\text{-}melt}$ = 60-10000, ref [29]) whilst rubidium was not (lithophile behaviour where $D_{Rb\ mineral\text{-}melt}$ = 0.001). The estimate for the N-partition coefficient is valid for highly reduced (fO_2 <IW) to highly oxidised (fO_2 >NNO) systems of both basaltic ($D_{N\ fluid\text{-}melt}$ = 10,000) and felsic ($D_{N\ fluid\text{-}melt}$ = 60) compositions. Taking even the most conservative values ($D_{N\ fluid\text{-}melt}$ = 60), and assuming 100% degassing, we find that the molar N/Rb ratio would rapidly decrease, which is inconsistent with these data. The maximum amount of volatile nitrogen that the model permits is 1-5% ($D_{N\ fluid\text{-}melt}$ = 0.6-3), and this may explain the slight dip in N/Rb observed between the basalts and basaltic andesites (Fig. 2d), but fails to satisfy the plateau in nitrogen abundance between the same samples in nitrogen versus barium space (Fig.2b) when rubidium and barium are positively correlated throughout the suite (Fig.S3). Collectively, these data require that > 95% of nitrogen behaved as an incompatible lithophile element. Importantly, these calculations were performed with a conservative fluid-melt partition coefficient for felsic melts as a baseline value to represent 100% degassing ($D_{N\ fluid\text{-}melt}$ = 60). If instead we use the partition coefficients for basaltic melts ($D_{N\ fluid\text{-}melt}$ = 10,000), then only 0.006-0.03% of the total nitrogen could have behaved as a volatile element to fit these data.

The isotope data also support a model where nitrogen is retained and not degassed. If degassing was the key control on the nitrogen geochemistry of this system then one might predict modification of the primary $^{15}N/^{14}N$ of the melt resulting in progressive ^{15}N enrichment[26] following Rayleigh degassing trend(s)[32]. It is worth noting, however, that some previous studies have found limited fractionation (< 1 to 2‰) of nitrogen isotopes between olivine fluid inclusion hosted nitrogen liberated by *in-vacuo* crushing and geothermal gasses from the same volcanic systems[33], whereas others have noted significant resolvable isotopic fractionation associated with degassing[26]. Therefore, although lack of isotopic fractionation alone is not definitive, we argue that the combined 8-fold enrichment in nitrogen abundance alongside the lack of resolvable fractionation for N/Rb and $^{15}N/^{14}N$ are inconsistent with degassing being the major control over nitrogen geochemistry on Hekla. Hence any nitrogen degassing that did occur was very minor (<5%) relative to the amount of nitrogen that was retained by the melt (>95%).

Up to now we have considered that fractional crystallisation is the major igneous process causing magmatic differentiation on Hekla. If we instead follow the model wherein the dacites and rhyolites are generated via partial melting of basaltic Icelandic crust and subsequent fractional crystallisation[12], we find that this generates nitrogen compositions that plot on arrays that are co-linear with rubidium and caesium (Fig 2b); that is, they plot on the same liquid line of descent that would be predicted if fractional crystallisation of the basalt generated the magmatic suite on Hekla. Therefore, in terms of igneous processes, partial melting of older hydrated Icelandic basalts generates melts with nitrogen concentrations that would be predicted if nitrogen was behaving as an incompatible LILE, and not a volatile element. One argument is that the remelting of (hydrated) basaltic crust could be sampling source rocks that have had secondary nitrogen enrichment; however, the consistency of our nitrogen isotope data, as well as the lack of evidence for assimilation of non-igneous sources on Hekla[8] (e.g. a linear relationship between Li vs SiO_2; Fig S2; consistency of Li and Tl isotope

compositions across the Hekla suite[13,16]) implies that all the nitrogen sampled at Hekla is igneous in origin. To explain the nitrogen concentrations in the basaltic andesites and andesites in terms of this more complicated petrological model, small amounts of nitrogen degassing could have occurred when the mantle-derived basalt differentiated to form the basaltic andesites. The array of nitrogen concentrations in the andesites could then be generated via mixing between relatively N-rich dacitic and rhyolitic melts, and the partially degassed basaltic andesite melt, leading to andesites which have the widest range of nitrogen concentrations. This is consistent with the data (Fig 2b) and resulting in what appears to be an unbroken cogenetic relationship between basaltic andesites and rhyolites at Hekla[12].

To summarise, the behaviour of nitrogen and its isotopes in Hekla samples is consistent with whichever petrological model is accepted (e.g., Ref 8 vs Ref 12). Furthermore, we infer that all nitrogen in Hekla rocks is ultimately magmatic in origin, and we posit that in an undersaturated magma, nitrogen exhibits similar behaviour to the incompatible element rubidium, a large ion lithophile, and is progressively enriched during magmatic differentiation.

A Mantle Source for Crustal Nitrogen

The lack of evidence for volatile behaviour during magmatic differentiation at Hekla has important implications for Earth's geological nitrogen cycle. Our data show that nitrogen can behave like an incompatible element comparable to the LILEs (Rb, Cs) during magmatic differentiation, possibly spanning the whole tholeiitic magma series, but certainly applicable to when a lower crustal hydrated basalt partially melts to form a dacite or rhyolite, with a bulk partition coefficient ($D_{N\ mineral\text{-}melt}$) << 1. Importantly, the process of lower crustal anatexis via dehydration melting of meta-mafic rocks is how I-type granites (granites with dominantly igneous source rocks) are formed. Our data suggest that when the system is nitrogen undersaturated, nitrogen should not be considered a strictly volatile element during magmatic differentiation. To extrapolate our results to global average crust, we can therefore treat nitrogen as a highly incompatible trace element (Fig. 3). We chose the trace element barium as a differentiation proxy since it is highly incompatible (r^2=0.99, Ba vs SiO_2) in the Hekla system (Fig. 2b). Due to a paucity of relevant partitioning data for systems similar to Hekla, we assume $D_{N\ mineral\text{-}melt}$ value of 0.001 for nitrogen in our model (see Supplementary material, S1.5). The best fit model for our data requires a maximum $D_{N\ mineral\text{-}melt}$ of 0.01, below which variation in $D_{N\ mineral\text{-}melt}$ has negligible impact on the calculated slope.

Taking average values and uncertainties for the bulk rubidium concentration in the middle continental crust (MCC) and upper continental crust (UCC)[34] and propagating those to a fractional crystallisation model for nitrogen versus rubidium allows us to estimate the amount of nitrogen enrichment that is possible during magmatic differentiation in the formation of typical mantle-derived rocks in the continental crust. Here we choose rubidium as it is an incompatible trace element that is expected to partition similarly to nitrogen in igneous materials due to the similar ionic charge and radius of Rb^+ and NH_4^+ ions. This estimate does assume that in both cases nitrogen and rubidium are fully behaving as lithophile elements, and that the average rubidium content of the MCC and UCC are

representative of the concentration obtained by magmatic differentiation. Varying proportions of sediments may impact the rubidium concentration estimates, particularly in the UCC estimates, whereas previous studies suggest that the average rubidium content of the felsic crust (ca. 90-150 µg/g)[35] is similar to that of the sedimentary crust (100-200 µg/g)[36]. As such these are suitable first order estimates of the amount of nitrogen derived by differentiation. The fractional crystallisation model assumes a basaltic starting composition with 3.3 µg/g nitrogen (i.e. the abundance measured in the least evolved basaltic sample Hek 06-09), which is consistent with a estimates for mantle plume nitrogen abundances[37], and typical of the Icelandic mantle plume[25]. The results of our model suggest that the magmatic contribution to the felsic igneous crust could amount to 16-19 µg/g (MCC estimate) or 18-27 µg/g (UCC estimate) nitrogen. Taking a total continental crust mass of 1.9×10^{22} kg (ref. 1) and assuming that 53% of this mass is the UCC[1] and that the UCC is made up of ca. 50% felsic magmatic rocks[1] we can estimate the mass of nitrogen stored in the continental crust that may have been derived by magmatic differentiation using the concentration of 16-27 µg/g. These calculations suggest that between 8.06×10^{16} kg to 1.36×10^{17} kg of nitrogen in the UCC could be derived from magmatic differentiation of a mantle melts alone. By comparison with the total mass of nitrogen in the felsic (filtered to >60% SiO_2 – Fig 1b) UCC (2.62×10^{17}kg N)[1], this represents between 31-52% of felsic-stored nitrogen. For greater context, this mass of nitrogen is equivalent to the biosphere[1,7,38] and accounts for 5-8% of the estimated total mass of nitrogen in the total continental crust (if including sediments)[1]. It is worth noting that we only consider the felsic compositions of the upper continental crust and therefore do not consider nitrogen contributions from the more mafic lower crust, nitrogen retained in igneous minerals that are reworked in sediments, or the primary magmatic fraction in metamorphic rocks not lost during metamorphism. Nevertheless, our results highlight that magmatic processes alone can enrich nitrogen in the igneous crust. While the (meta-)sedimentary component of the crust has certainly archived past atmospheric N_2, a large proportion of the felsic igneous nitrogen reservoir is mantle-derived and may never contributed to atmospheric pressure. In summary, the formation of felsic crusts can act as a nitrogen trap between the mantle and the atmosphere on Earth and other telluric planets. Therefore, the flux of nitrogen from Earth's interior to the atmosphere over geological time may have been overestimated[1-5] because nitrogen is not always lost to degassing during igneous differentiation.

Acknowledgements:

Funding was provided by a Natural Environment Research Council studentship (grant NE/R012253/1) to TJB and a National Environmental Isotope Facility access in-kind grant (NEIF – 2313.0920) to EES, SM and TJB. SM acknowledges support from NERC standard grant NE/PO12167/1. EES is financially supported by a NERC Frontiers grant (NE/V010824/1). We thank Alison MacDonald at SUERC for measuring the bulk oxygen isotope data.

Contributions:

TB, SM, JP and EES designed the study. PSS collected the samples and undertook initial sample preparation and major/trace element characterisation. TB collected the nitrogen data and wrote the original manuscript draft. AB collected the oxygen isotope data. All authors

contributed to the interpretation of the results and the review and editing of the manuscript and supplemental information.

Competing interests:

The authors declare no competing interests.

References

1. Johnson, B. W. & Goldblatt, C. The nitrogen budget of Earth. *Earth-Science Rev.* **148**, 150–173 (2015).

2. Zerkle, A. L. & Mikhail, S. The geobiological nitrogen cycle: From microbes to the mantle. *Geobiology* **15**, 343–352 (2017).

3. Sano, Y. *et al.* Volcanic flux of nitrogen from the Earth. *Chem. Geol.* **171**, 263–271 (2001).

4. Halama, R., Bebout, G. E., John, T. & Schenk, V. Nitrogen recycling in subducted oceanic lithosphere: The record in high- and ultrahigh-pressure metabasaltic rocks. *Geochim. Cosmochim. Acta* **74**, 1636–1652 (2010).

5. Goldblatt, C. *et al.* Nitrogen-enhanced greenhouse warming on early Earth. *Nat. Geosci. 2009 212* **2**, 891–896 (2009).

6. Kerrich, R., Jia, Y., Manikyamba, C. & Naqvi, S. M. Secular variations of N-isotopes in terrestrial reservoirs and ore deposits. in *Evolution of Early Earth's Atmosphere, Hydrosphere, and Biosphere: Constraints from Ore Deposits* 81 (2006).

7. Galloway, J. N. The Global Nitrogen Cycle. *Treatise on Geochemistry* **8**, 682 (2003).

8. Geist, D. *et al.* Hekla Revisited: Fractionation of a Magma Body at Historical Timescales. *J. Petrol.* (2021). doi:10.1093/PETROLOGY/EGAB001

9. Savage, P. S., Georg, R. B., Williams, H. M., Burton, K. W. & Halliday, A. N. Silicon isotope fractionation during magmatic differentiation. *Geochim. Cosmochim. Acta* **75**, 6124–6139 (2011).

10. Sigmarsson, O., Condomines, M. & Fourcade, S. A detailed Th, Sr and O isotope study of Hekla: differentiation processes in an Icelandic Volcano. *Contrib. Mineral. Petrol. 1992 1121* **112**, 20–34 (1992).

11. Geirsson, H. *et al.* Volcano deformation at active plate boundaries: Deep magma accumulation at Hekla volcano and plate boundary deformation in south Iceland. *J. Geophys. Res. Solid Earth* **117**, 11409 (2012).

12. Sigmarsson, O., Bergþórsdóttir, I. A., Devidal, J. L., Larsen, G. & Gannoun, A. Long or short silicic magma residence time beneath Hekla volcano, Iceland? *Contrib. Mineral. Petrol.* **177**, (2022).

13. Schuessler, J. A., Schoenberg, R. & Sigmarsson, O. Iron and lithium isotope systematics of the Hekla volcano, Iceland — Evidence for Fe isotope fractionation during magma differentiation. *Chem. Geol.* **258**, 78–91 (2009).

14. Yang, J. *et al.* Absence of molybdenum isotope fractionation during magmatic differentiation at Hekla volcano, Iceland. *Geochim. Cosmochim. Acta* **162**, 126–136 (2015).

15. Prytulak, J. *et al.* Stable vanadium isotopes as a redox proxy in magmatic systems? *Geochemical Perspect. Lett.* **3**, 75–84 (2017).

16. Prytulak, J. *et al.* Thallium elemental behavior and stable isotope fractionation during magmatic processes. *Chem. Geol.* **448**, 71–83 (2017).

17. Tuller-Ross, B., Savage, P. S., Chen, H. & Wang, K. Potassium isotope fractionation during magmatic differentiation of basalt to rhyolite. *Chem. Geol.* **525**, 37–45 (2019).

18. Chen, H., Savage, P. S., Teng, F. Z., Helz, R. T. & Moynier, F. Zinc isotope fractionation during magmatic differentiation and the isotopic composition of the bulk Earth. *Earth Planet. Sci. Lett.* **369**–**370**, 34–42 (2013).

19. Inglis, E. C. *et al.* Isotopic fractionation of zirconium during magmatic differentiation and the stable isotope composition of the silicate Earth. *Geochim. Cosmochim. Acta* **250**, 311–323 (2019).

20. Chekol, T. A., Kobayashi, K., Yokoyama, T., Sakaguchi, C. & Nakamura, E. Timescales of magma differentiation from basalt to andesite beneath Hekla Volcano, Iceland: Constraints from U-series disequilibria in lavas from the last quarter-millennium flows. *Geochim. Cosmochim. Acta* **75**, 256–283 (2011).

21. Boocock, T. J. *et al.* Nitrogen Mass Fraction and Stable Isotope Ratios for Fourteen Geological Reference Materials: Evaluating the Applicability of Elemental Analyser Versus Sealed Tube Combustion Methods. *Geostand. Geoanalytical Res.* **44**, 537–551 (2020).

22. Mikhail, S. & Sverjensky, D. A. Nitrogen speciation in upper mantle fluids and the origin of Earth's nitrogen-rich atmosphere. *Nat. Geosci.* **7**, 816–819 (2014).

23. Jackson, C. R. M., Cottrell, E. & Andrews, B. Warm and oxidizing slabs limit ingassing efficiency of nitrogen to the mantle. *Earth Planet. Sci. Lett.* **553**, 116615 (2021).

24. Mysen, B. Nitrogen in the Earth: abundance and transport. *Prog. Earth Planet. Sci. 2019 61* **6**, 1–15 (2019).

25. Halldórsson, S. A., Hilton, D. R., Barry, P. H., Füri, E. & Grönvold, K. Recycling of crustal material by the Iceland mantle plume: New evidence from nitrogen elemental and isotope systematics of subglacial basalts. *Geochim. Cosmochim. Acta* **176**, 206–226 (2016).

26. Cartigny, P., Jendrzejewski, N., Pineau, F., Petit, E. & Javoy, M. Volatile (C, N, Ar) variability in MORB and the respective roles of mantle source heterogeneity and degassing: the case of the Southwest Indian Ridge. *Earth Planet. Sci. Lett.* **194**, 241–257 (2001).

27. Busigny, V., Cartigny, P., Philippot, P., Ader, M. & Javoy, M. Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe

(western Alps, Europe). *Earth Planet. Sci. Lett.* **215**, 27–42 (2003).

28. Yokochi, R., Marty, B., Chazot, G. & Burnard, P. Nitrogen in peridotite xenoliths: Lithophile behavior and magmatic isotope fractionation. *Geochim. Cosmochim. Acta* **73**, 4843–4861 (2009).

29. Li, Y., Huang, R., Wiedenbeck, M. & Keppler, H. Nitrogen distribution between aqueous fluids and silicate melts. *Earth Planet. Sci. Lett.* **411**, 218–228 (2015).

30. Bucholz, C. E., Jagoutz, O., VanTongeren, J. A., Setera, J. & Wang, Z. Oxygen isotope trajectories of crystallizing melts: Insights from modeling and the plutonic record. *Geochim. Cosmochim. Acta* **207**, 154–184 (2017).

31. Li, Y., Li, L. & Wu, Z. First-principles calculations of equilibrium nitrogen isotope fractionations among aqueous ammonium, silicate minerals and salts. *Geochim. Cosmochim. Acta* **297**, 220–232 (2021).

32. Haendel, D., Muehle, K., Nitzsche, H.-M., Stiehl, G. & Wand, U. Isotopic variations of the fixed nitrogen in metamorphic rocks. *Geochim. Cosmochim. Acta* **50**, 749–758 (1986).

33. Fischer, T. P., Takahata, N., Sano, Y., Sumino, H. & Hilton, D. R. Nitrogen isotopes of the mantle: Insights from mineral separates. *Geophys. Res. Lett.* **32**, 1–5 (2005).

34. Rudnick, R., and Gao, S., (2003) The Composition of the continental crust. In: Holland, H. D. & Turekian, K. K., Eds, Treatise on Geochemistry, Vol. 3, *The Crust*, Elsevier-Pergamon, Oxford, 1–64.

35. Taylor, S. R. Abundance of chemical elements in the continental crust: a new table. *Geochim. Cosmociem. Acta* **28**, 1273–1285 (1964).

36. McDonough, W. F., Sun, S., Ringwood, A. E., Jagoutz, E. & Hofmann, A. W. Potassium, rubidium, and cesium in the Earth and Moon and the evolution of the mantle of the Earth. *Geochim. Cosmochim. Acta* **56**, 1001–1012 (1992).

37. Marty, B. Nitrogen content of the mantle inferred from N2–Ar correlation in oceanic basalts. *Nat. 1995 3776547* **377**, 326–329 (1995).

38. Gruber, N. & Galloway, J. N. An Earth-system perspective of the global nitrogen cycle. *Nature* **451**, 293–296 (2008).

Methods

All samples were collected, cut, cleaned and powdered during previous investigations[9]. In this study, the powders were cleaned once again to ensure removal of any modern surficial contaminants that may have accumulated during transport and storage. This was done by sequential washing and agitation with 18 $M\Omega \cdot cm^{-1}$ DI-water and methanol (reagent grade) for 1 minute each step. A centrifuge was used to remove the liquids with no observed loss of fine powdered material. Samples were subsequently dried for 48 hrs in an oven at 70 °C and stored in pre-cleaned glass scintillation vials ready for analysis.

Nitrogen abundances and isotope values were obtained via a custom-built combustion and tube cracker system[21], optimised for accurate isotopic analyses of silicate

materials with low nitrogen abundances (< 10 μg/g). This stainless-steel gas line is coupled to a Thermo MAT-253 isotope ratio mass spectrometer via a ConFlo IV and operates under continuous helium flow (50 ml/min). All reagents are pre cleaned via combustion at 800-1000 °C for at least 6 hrs to ensure that any adsorbed N_2 impurities are liberated. Exact procedural steps can be found in ref [21]. Approximately 300-500 mg of sample powder were weighed into the base of quartz glass tubing, using a glass thistle funnel. Around 1.0-1.1g CuO wire were also added. Sample tubes were attached to a custom-built vacuum manifold and left to evacuate to < 10^{-6} mbar overnight. The base of the sample tubes was heated to ca.150°C at this stage to remove any remaining moisture and volatile contaminants from the powders. Tubes were then sealed and removed using an oxy-propane blow-torch. The sealed evacuated sample tubes, containing the sample powder, were then placed into a muffle furnace. Samples were combusted at 1050°C for 4 hrs followed by a controlled cooling step to 600°C for 2 hrs and subsequent cooling to room temperature. This liberates all silicate bound nitrogen into gaseous form. The CuO reagent acts as both the oxygen source and acceptor preventing the formation of NO_x gases and enabling total liberation as N_2 gas from the sample. These gas samples were purified and analysed using an on-line tube cracker gas line operating under continuous helium flow through a ConFlo IV into the MAT-253 IRMS. All analyses were calibrated with USGS-61 and USGS-62 Caffeine international reference materials. Procedural blanks were measured throughout the analytical campaign and had an average composition of 22.3 ± 3.8 nmol total nitrogen with a $\delta^{15}N$ value of -1.3 ± 1.6 ‰. This average analytical blank was subtracted from all standard and sample data and generally represented <20% of the sample peak area. To assess analytical accuracy, we analysed four aliquots of BHVO-2 Basalt and obtained an isotopic value of 1.9 ± 0.2 ‰ and a total nitrogen abundance of 20.2 ± 1.4 μg/g, which agrees well with previous studies [21,39]. We also measured analysed four aliquots of FKN Feldspar (CRPG) and obtained an isotopic value of 4.2 ± 0.5 ‰ and a total nitrogen abundance of 10.6 ± 2.2 μg/g, which similarly agrees very well with previous work[21]. These standard data are reported in the supplementary material (Table S1).

Oxygen isotopes on bulk rock samples were obtained via conventional laser fluorination at the Scottish Universities Environmental Research Centre (SUERC)[40]. Around 2mg of powder were weighed into the sample holder. Samples were heated using a CO_2 laser in the presence of ClF_3 gas. Oxygen is converted to CO_2 using a heated graphite rod. Replicate analyses of standards UWG2 Garnet, GP147 Garnet and YP2 Quartz were within 0.35‰ (2 s.d.) of accepted values. Data are reported using the conventional delta notation ($\delta^{18}O$ [‰] = $[(^{18}O/^{16}O_{sample}/^{18}O/^{16}O_{standard}) - 1] \times 1000$) relative to the Vienna Standard Mean Ocean Water (V-SMOW). Quantitative yields to confirm the total liberation of oxygen were determined via a calibrated gas manometer. No samples were discarded for low gas yields.

Carbon abundances were obtained to determine if the unexplained enrichment of sample 21-09 was organic in nature. These abundances were obtained via an Elemental Analyser isolink system coupled to the same ConFlo IV and MAT253 isotope ratio mass spectrometer as the nitrogen measurements. Approximately 20mg of powdered rock samples were weighed into tin capsules for flash combustion following routine protocols[41]. International reference materials USGS-40 and USGS-41 were used for calibration. Measured sample peak areas were on the order of 6.0-13.4Vs with an average analytical blank of 2.6Vs.

Method-only references

39. Feng, L., Li, H. & Liu, W. Nitrogen Mass Fraction and Isotope Determinations in Geological Reference Materials Using Sealed-Tube Combustion Coupled with Continuous-Flow Isotope-Ratio Mass Spectrometry. *Geostand. Geoanalytical Res.* **42**, 539–548 (2018).

40. Sharp, Z. A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochim. Cosmochim. Acta* **54**, 1353–1357 (1990).

41. Stüeken, E. E., Boocock, T. J., Robinson, A., Mikhail, S. & Johnson, B. W. Hydrothermal recycling of sedimentary ammonium into oceanic crust and the Archean ocean at 3.24 Ga. *Geology* **49**, 822–826 (2021).

Data Availability Statement:

All supporting data for this study is included in the extended data files associated with this manuscript and is deposited in a figshare repository which can be accessed through the followingI:

https://doi.org/10.6084/m9.figshare.22242517

Figure Captions

Figure 1 a) Compilation of Earth reservoir size estimates for nitrogen[1,5–7]. BSE = Bulk Silicate Earth. Typical nitrogen concentrations for each reservoir are shown in black above the estimates. The crust represents the third largest nitrogen reservoir and contains multiple orders of magnitude more nitrogen than the dynamic short term biological nitrogen cycle. This estimate represents total crust, including continental and oceanic crust. **b)** Compilation of felsic igneous nitrogen abundance data filtered to SiO_2 >60% to represent typical upper continental crust. Underlying data and associated references can be found in extended data files.

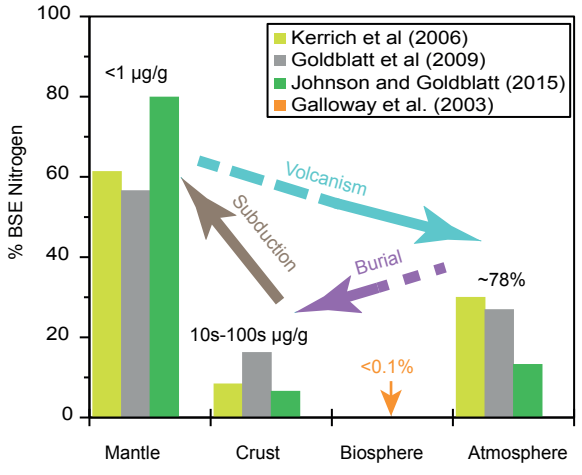
Figure 2 Nitrogen abundance and isotope systematics for the Hekla volcanic suite a) Total Alkali Silica diagram for Hekla samples measured in this study compared with literature data[9 8,10,13,20]. **b)** Measured nitrogen abundances compared with Rb and Cs concentrations[9] plotted against barium as a highly incompatible trace element which systematically increases as the system differentiates. Nitrogen data represent average of 2-4 replicate analyses with error bars representing one standard deviation around the mean. Similar partitioning behaviour is observed for nitrogen when compared with the large ion lithophile elements (Rb and Cs). Fractional crystallisation models for Rb, Cs and N, assuming a partition coefficient << 1 ($D_{mineral\text{-}melt}$ = 0.001, see supplemental material, Fig.S3-4). Note that sample 21-09 likely reflects some localised enrichment perhaps involving organic matter (also see supplementary material, Fig.S5). **c)** Nitrogen isotope ($\delta^{15}N$) values compared with the Icelandic mantle plume[25], atmospheric air (defined as $\delta^{15}N = 0.0$) and average convecting upper mantle (i.e., MORB)[26]. **d)** Molar N/Rb ratio versus silica showing a general constancy across the differentiation suite. N/Rb values for subducting slab sediments/altered oceanic crust[27] and the lithospheric mantle[28] are highlighted. The constancy of N/Rb ratio indicates a similar behaviour between nitrogen and rubidium during magmatic differentiation. Were nitrogen degassing (fluid-melt D_N = 60-10000)[29] and Rb behaving incompatibly (D_{Rb} = 0.001) the N/Rb ratio would decrease rapidly, which is not observed by our data. Modelled lines show predicted N/Rb variations if a fraction of the total silicate nitrogen was degassing (0%, 1%, 5% and 100%) calculated using the most conservative fluid-melt D_N = 60 (measured on felsic compositions). This is a maximum estimate as it is likely

494 more appropriate to use the fluid-melt D_N = 10,000 (measured on basaltic compositions) which suggest only
495 0.006-0.03% of nitrogen can have degassed.

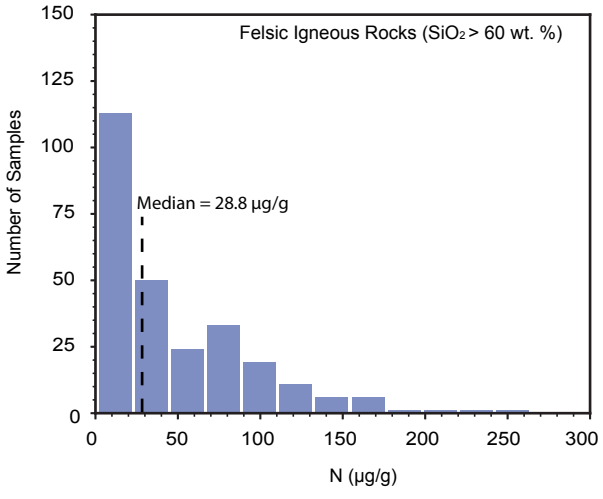
496 **Figure 3 Nitrogen versus rubidium for the Hekla suite and fractional crystallisation model.** Rubidium contents
497 of the Middle Continental Crust (MCC) of 65 ± 4 μg/g and Upper Continental Crust (UCC) of 84 ± 17 μg/g taken
498 from ref [34] and propagated up to the modelled fractional crystallisation lines. White dotted line represents the
499 mean value, with shaded grey/pink bars the one standard deviation on the mean for this estimate. Nitrogen
500 error bars represent the standard deviation of the mean value of between 2-4 replicate analyses of each sample.

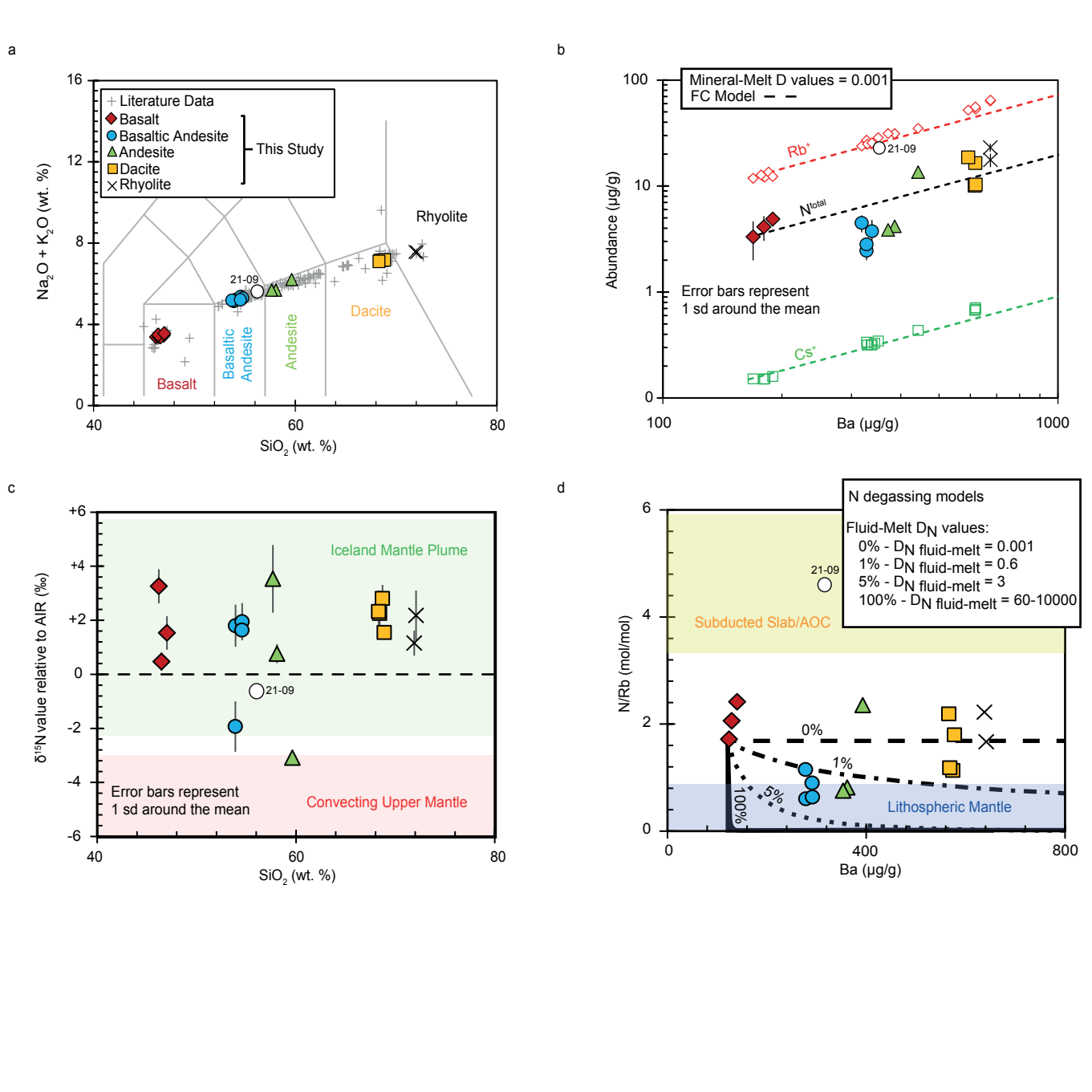
501

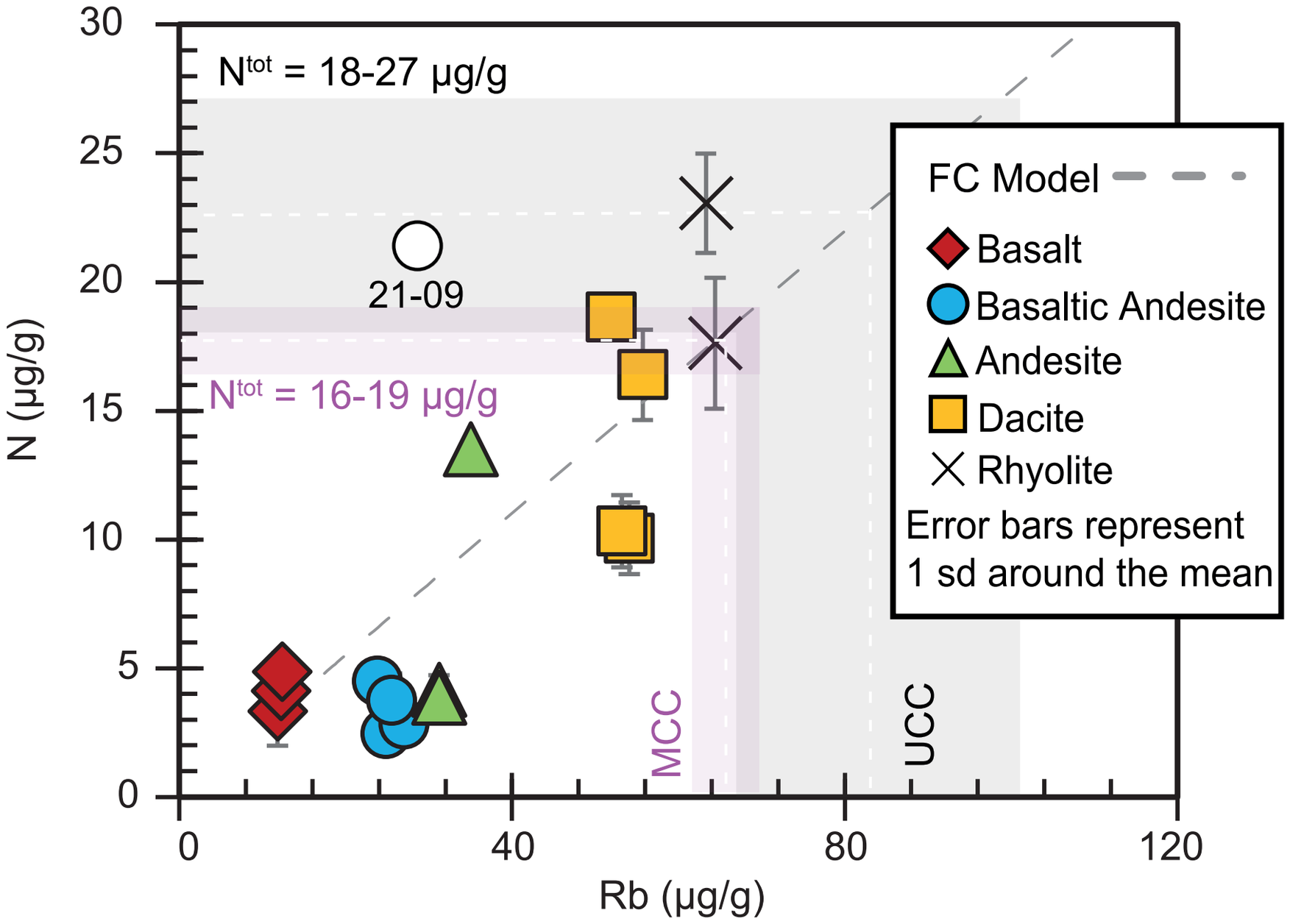
a


% BSE Nitrogen
100
80
60
40
20
0
Kerrich et al (2006)
Goldblatt et al (2009)
Johnson and Goldblatt (2015)
Galloway et al. (2003)
<1 µg/g
Volcanism
Subduction
Burial
~78%
10s-100s µg/g
<0.1%
Mantle
Crust
Biosphere
Atmosphere

b


Felsic Igneous Rocks (SiO2 > 60 wt. %)
Number of Samples
150
125
100
75
50
25
0
Median = 28.8 µg/g
0
50
100
150
200
250
300
N (µg/g)


a
Literature Data
Basalt
Basaltic Andesite
Andesite
Dacite
Rhyolite
This Study
Rhyolite
21-09
Dacite
Basaltic Andesite
Andesite
Basalt
Na2O + K2O (wt. %)
SiO2 (wt. %)
b
Mineral-Melt D values = 0.001
FC Model
Rb+
21-09
Ntotal
Error bars represent
1 sd around the mean
Cs+
Abundance (µg/g)
Ba (µg/g)
c
Iceland Mantle Plume
21-09
Error bars represent
1 sd around the mean
Convecting Upper Mantle
δ15N value relative to AIR (‰)
SiO2 (wt. %)
d
N degassing models
Fluid-Melt DN values:
0% - DN fluid-melt = 0.001
1% - DN fluid-melt = 0.6
5% - DN fluid-melt = 3
100% - DN fluid-melt = 60-10000
21-09
Subducted Slab/AOC
0%
1%
5%
100%
Lithospheric Mantle
N/Rb (mol/mol)
Ba (µg/g)


N^{tot} = 18-27 µg/g
N^{tot} = 16-19 µg/g
21-09
MCC
UCC
FC Model
Basalt
Basaltic Andesite
Andesite
Dacite
Rhyolite
Error bars represent
1 sd around the mean
N (µg/g)
Rb (µg/g)
0
5
10
15
20
25
30
0
40
80
120