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The origin of nitrogen in Earth's mantle: constraints from basalts $^{15}N/^{14}N$ and $N_2/^{3}He$ ratios

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6 Abstract

7 Plate tectonics is thought to be a major driver of volatile redistribution on Earth. The 8 budget of nitrogen in Earth's mantle has been suggested to be almost entirely surfacederived. Recycling would contribute nitrogen with relatively heavy ¹⁵N/¹⁴N isotope ratios to 9 10 Earth's mantle. This could explain why the Earth's mantle ¹⁵N/¹⁴N isotope ratio is 11 substantially higher than both solar gases and chondritic parent bodies akin to enstatite chondrites. Here, published nitrogen isotope data of mid-ocean ridge and ocean island 12 13 basalts are compiled and used to evaluate the nitrogen subduction hypothesis. Nitrogen isotope ratios are used in conjunction with published $N_2/^{3}$ He and K_2O/TiO_2 ratios on the 14 same basalts. Assuming that ³He is not recycled, $N_2/^3$ He ratios are argued to trace nitrogen 15 addition to mantle sources via subduction. Various mantle source enrichments for basalts 16 17 are tracked with K_2O/TiO_2 ratios: elevated K_2O/TiO_2 ratios are assumed to primarily reflect 18 the contributions of recycled components in the basalts mantle sources. The main result of our data compilation is that for most basalts, $\delta^{15}N$ and $N_2/^{3}He$ remain constant across a vast 19 range of K_2O/TiO_2 ratios. Mid-ocean ridge basalts have $\delta^{15}N$ signatures that are lower than 20 air by ~ 4‰ and an average N₂/³He ratio of 3.7 (±1.2) x10⁶ (95% confidence, n= 30). 21 Published δ^{15} N and N₂/³He are invariant across K₂O/TiO₂ ratios that vary over a factor of ~ 22 20. Using estimates of slab K₂O/TiO₂ and [TiO₂], the observed invariant δ^{15} N and N₂/³He may 23

be fit with slabs containing ~ 0.1 ppm N. A mass balance shows that adding $\sim 10\%$ recycled 24 slabs to the convective mantle only raises the $N_2/^{3}$ He by < 5%. Lavas from Iceland, Galapagos 25 and Hawaii have high ³He/⁴He and ¹⁵N/¹⁴N ratios relative to the convective mantle. Only 26 seven samples show nitrogen isotopic signatures that are unaffected by air contamination, 27 although those samples are poorly characterized for $N_2/^{3}$ He. The seven basalts show $\delta^{15}N$ 28 29 between -2 and 0% that do not vary systematically with K_2O/TiO_2 ratios that vary over a factor of ~ 5. The N₂/³He ratios of these seven basalts is unknown, but the high 3 He/⁴He 30 mantle may be estimated by combining published $N_2/^{36}Ar$ to $^{3}He/^{36}Ar$ ratios. This yields a 31 32 $N_2/^{3}$ He of 2.3 (±1.2) x 10⁶ (1 σ uncertainty). This is indistinguishable from the MORB estimate 33 of 3.7 (±1.2) x 10⁶. Invariant δ^{15} N across variable degrees of mantle enrichments and MORB-34 like $N_2/^{3}$ He for the high 3 He/ 4 He mantle are not consistent with nitrogen addition to plume 35 sources with elevated ${}^{3}\text{He}/{}^{4}\text{He}$ ratios. A δ^{15} N between -2 and 0‰ for plume sources, only marginally higher than MORB, could be a primordial feature of undegassed mantle 36 reservoirs. Nonetheless, nitrogen subduction may have contributed to a specific array of 37 mantle sources, as revealed by the few published data on basalts with low ${}^{3}\text{He}/{}^{4}\text{He}$ ratios. 38 39 Lavas from the Society plume with low ${}^{3}\text{He}/{}^{4}\text{He}$ ratios show an enriched mantle source, and 40 they have elevated $\delta^{15}N \ge +0.5\%$ and $N_2/^{3}He > 10^{7}$. For those, the addition of slabs with concentrations of ~ 0.1 ppm N to a mantle source can account for the integrated dataset. To 41 42 summarize, the published data suggest that nitrogen subduction may explain a sub-set of 43 published N isotope data on basalts, but that N recycling has an overall more limited impact 44 on mantle nitrogen than previously thought.

45

1. Introduction

Planetary formation and evolution have shaped the budget of volatile elements of 48 Earth's reservoirs. Nitrogen (N) is the main constituent of our atmosphere. Early 49 50 catastrophic degassing of the mantle, during a magma ocean phase, may have yielded an atmosphere with ~ 1 bar of N₂ partial pressure (Sossi et al., 2020). Modern N subduction 51 52 may overpower N₂ mantle degassing by a factor of ~ 20 (Busigny et al., 2011), contrasting with earlier suggestions of quantitative overturn of subducted N_2 , at least in a warm 53 subduction zone (Fischer et al., 2002; Hilton et al., 2002; Zimmer et al., 2004). Should modern 54 55 subduction fluxes from Busigny et al., (2011) be applied back in time, they would require 56 that N₂ from the ancient atmosphere was at least partially re-injected in Earth's mantle. This is ground for the concept of nitrogen "ingassing" or "regassing": the N budget of the modern 57 58 mantle would be accounted for by massive subduction of atmospheric N, erasing any 59 primordial signatures that the distribution of planetary N may have held (Barry and Hilton, 60 2016; Javoy, 1997).

61 The ¹⁵N/¹⁴N isotope ratios of various geological reservoirs may illustrate nitrogen 62 regassing. Variations of the ${}^{15}N/{}^{14}N$ isotope ratios are quantified with the δ notation, such as $\delta^{15}N = 1000 \text{ x} \left[\frac{15N}{14N} \right] \left(\frac{15N}{14N} \right)_{air} - 1 \right]$, and are given in permil. The modern convective 63 mantle is characterized by a $\delta^{15}N$ of ~ - 5‰ (Javoy and Pineau, 1991; Marty and 64 Zimmermann, 1999). It is somewhat comparable to ${}^{15}N/{}^{14}N$ observed in other differentiated 65 66 bodies such as Mars or the Angrite parent body (Abernethy et al., 2013; Grady and Wright, 2003), but distinct from solar and chondritic signatures. Solar wind and comets have $\delta^{15}N$ 67 signatures ~-387±8‰ and +850±150‰ respectively (Füri and Marty, 2015). Chondrites 68 69 show a more limited, but nonetheless large isotope range. Enstatite Chondrites (EC) have

70 average δ^{15} N of $-20\pm11\%$ (1 σ) while CI chondrites have δ^{15} N of $48\pm9\%$ (1 σ) (Alexander et al., 2012; Grady and Wright, 2003; Pearson et al., 2006). The negative δ^{15} N observed in bulk 71 EC is consistent with an enstatite chondrite model for Earth's origin (Javoy, 1998, 1997, 72 73 1995). Interestingly, enstatite chondrites are *even more* depleted in ¹⁵N than Earth's mantle at the 1σ level. Should the EC parent body be a major contributor of Earth's nitrogen, a 74 75 mechanism might have to be invoked to explain the raised $\delta^{15}N$ for Earth's mantle. Mantle N could result from mixing between various types of chondrites including a substantial EC 76 77 contribution (Javoy, 1997; Marty and Zimmermann, 1999; Piani et al., 2020). Alternatively, terrestrial N could have been delivered by EC parent bodies exclusively. In this scenario, the 78 δ^{15} N of bulk Earth is ~ -20‰ and planetary differentiation is required to fractionate 79 nitrogen isotopes to account for a mantle $\delta^{15}N$ of ~ -5‰. Core/mantle N isotope 80 fractionations could account for the observations, although the exact value of the 81 metal/silicate ¹⁵N/¹⁴N fractionation factor remains debated (Dalou et al., 2019; Li et al., 82 2016). 83

84 One complication for attempts at constraining the nitrogen origin on Earth is the 85 composition of air. Modern air is made of 78% N_2 . In terms of absolute quantity, air could host about as much nitrogen as the entire Earth's mantle (Marty, 2102). Air has a δ^{15} N of 86 0‰, heavier than the modern mantle by ~ 5‰. This heterogeneity reflects a nitrogen 87 88 isotope disequilibrium between Earth's mantle and surface (Boyd and Pillinger, 1994; 89 Cartigny and Marty, 2013). A mixture of chondritic parent bodies, and/or the expression of 90 metal/silicate fractionations, alone, may not explain the isotope imbalance between the 91 mantle and air. A possible explanation to all the data involves plate tectonics, rather than 92 planetary differentiation. In mantle-surface exchange scenarios, the $\delta^{15}N$ value of -5% of

93 Earth's mantle results from the addition of surface nitrogen with $\delta^{15}N > 0\%$ into a mantle with a starting δ^{15} N $\leq -20\%$ (Cartigny et al., 1997; Javoy, 1998; Javoy et al., 1986, 1984; Palot 94 95 et al., 2012). In this hypothesis, the bulk of the Earth would be composed of material similar 96 to enstatite chondrites, but a large proportion of the nitrogen now present in the atmosphere 97 and crust was added by carbonaceous chondrites and/or comets (Halliday, 2013; Javoy, 1997; Marty et al., 2016). The two reservoirs would exchange via subduction, eventually 98 leading to the present isotope imbalance. The $\delta^{15}N$ disequilibrium between air and the 99 100 mantle would reflect a snapshot of two reservoirs that have not reached complete 101 homogenization yet.

102 The subduction hypothesis has the merit to offer explanations to both the mantle δ^{15} N and the isotope imbalance. It is consistent with hypotheses based on modern N fluxes 103 (Busigny et al., 2011; Goldblatt et al., 2009) and indirectly supported by experimental studies 104 105 showing that recycled nitrogen may be stable as NH₄⁺ in potassium-bearing minerals at high pressure and temperature (Watenphul et al., 2010, 2009). However, the subduction 106 107 hypothesis has requirements that do not seem to be met by observations. By nature, 108 exchange models require a secular decrease in atmospheric N₂ partial pressure and δ^{15} N, and an increase in the mantle N concentration and δ^{15} N with geological time. It was 109 110 suggested that surface nitrogen must have had $\delta^{15}N > 20\%$ in the Archean, so that it can 111 balance a negative $\delta^{15}N$ for an enstatite-like Earth's mantle (Javoy, 1997). Similarly, a N₂ partial pressure in the Archean could have been higher than present-day by a factor of 2 112 (Busigny et al., 2011; Goldblatt et al., 2009). However, available geological evidence do not 113 114 substantiate the notions of high δ^{15} N or high N₂ partial pressures at the Earth's surface in the Precambrian (Ader et al., 2016; Marty et al., 2013; Pinti et al., 2001). If anything, both δ^{15} N of 115

Archean rocks and N₂ partial pressures in Archean air might have been *lower* than in presentday (Avice et al., 2018; Marty et al., 2013; Pinti et al., 2001; Stüeken et al., 2021), at odds with
the requirements of the subduction hypothesis.

The goal of this study is to discuss the merits and the limitations of the subduction 119 hypothesis, but mostly from the point of view of N isotope signatures of mid-ocean ridge 120 121 basalts (MORB) and ocean island basalts (OIB). Compiled data from the literature are used 122 to show that basalts tapping both the convective mantle and high ${}^{3}\text{He}/{}^{4}\text{He}$ plumes have 123 invariant $\delta^{15}N$ across a vast range of mantle enrichment. A mass balance suggests that 124 subducted slabs have N concentrations lower than the rest of the mantle by a factor of 3 or more. Published N isotope data are inconsistent with subducted nitrogen overwhelming the 125 126 convective mantle, which relaxes the need for substantial exchange between the Earth's 127 surface and mantle over geological times. Alternative set of circumstances to explain the N isotope imbalance are discussed. 128

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2. Basalt geochemistry

Basalts erupted in various geodynamical settings sample multiple mantle reservoirs. 131 132 Mid-ocean ridge basalts (MORB) sample the convective mantle over \sim 45,000 kilometers of active ridges. Ocean island basalts (OIB) tap deeper mantle sources, with extreme 133 134 geochemical signatures associated with mixtures of primordial and recycled components 135 (Kurz et al., 1982; Zindler and Hart, 1986). Upon eruption on the seafloor, basalts are quenched. Glassy rims preserve magmatic vesicles enriched in volatiles, essential to 136 137 constrain the gas budget of mantle reservoirs. The noble gas systematics for MORB and OIB 138 bring powerful constraints on the origin of Earth's volatile and on the mantle-atmosphere

systems, as presented in various review articles (Graham, 2002; Moreira, 2013; 139 Mukhopadhyay and Parai, 2019). Briefly, MORB have average ³He/⁴He of 8±1 R_A, where R_A 140 is air ${}^{3}\text{He}/{}^{4}\text{He}$. OIB show much larger variations, with ${}^{3}\text{He}/{}^{4}\text{He}$ typically between ~ 5 and 141 142 >20 R_A. Basalts from Iceland, Loihi and Galapagos have ${}^{3}\text{He}/{}^{4}\text{He}$ typically > 30 R_A (Füri et al., 2010; Hilton et al., 1999; Kurz et al., 2009, 1982). Elevated ³He/⁴He ratios likely represent 143 144 melts of relatively undegassed regions of the mantle, with low time-integrated (Th-U)/He 145 ratios, compared to MORB (Kurz et al., 1982). The convective mantle likely underwent catastrophic degassing early in Earth's history, followed by slow continuous degassing that 146 147 continues to the present day (Allègre et al., 1987; Moreira et al., 1998; Sarda et al., 1988).

148 On average, about $\sim 10\%$ of the convective mantle is made of recycled oceanic crust (Sobolev et al., 2007). This notion is coined the "marble-cake mantle" (Allègre and Turcotte, 149 150 1986). The recycled crust essentially acts as means to replenish the mantle with surface-151 derived components, which is helpful in models relying on volatile subduction: recycled 152 crust is a likely candidate as the carrier of surface-derived volatile in basalt sources. The elemental ratio K₂O/TiO₂ is an easy-to-measure proxy of recycled components in a mantle 153 source. Low $K_2O/TiO_2 < 0.09$ are characteristics of depleted mantle sources (Langmuir et al., 154 155 1992; Reynolds et al., 1992; Shen and Forsyth, 1995), hosting limited amounts of recycled components. Higher K₂O/TiO₂ ratios reflect larger contributions of subducted components 156 157 in mantle sources (Jackson and Dasgupta, 2008). They are typically associated with high La/Sm (Schilling et al., 1983), radiogenic ⁸⁷Sr/⁸⁶Sr ratios (Jackson and Dasgupta, 2008), and 158 159 a diverse range of incompatible elements signatures (Bach et al., 1994; Dosso et al., 1999; Le Roex et al., 1989; Le Roux et al., 2002; Schilling et al., 1983). The range in trace element 160 signatures illustrate the compositional variability of enriched mantle sources (Willbold and 161

Stracke, 2006). At order-zero however, K₂O/TiO₂ ratios act as a generic tracer of subducted
components in a mantle source (Jackson and Dasgupta, 2008; Michael and Cornell, 1998;
Workman and Hart, 2005).

165 Nitrogen recycling in a basalt source may be quantified using δ^{15} N, N₂/³⁶Ar and N₂/³He ratios of a glass. If mantle nitrogen is of recycled origin, trends can be predicted between 166 δ^{15} N and K₂O/TiO₂ ratios, as a function of various nitrogen concentrations in recycled slabs. 167 168 Because mantle ³He is not recycled in origin (Porcelli et al., 2002), $N_2/^3$ He ratios are also 169 anticipated to increase across addition of nitrogen in enriched MORB sources. However, air 170 contamination during eruption or sample handling is the main impediment on determining mantle δ^{15} N, N₂/³⁶Ar and N₂/³He ratios. A measurement strategy has been to crush basalts 171 under ultra-high vacuum and determine simultaneously $\delta^{15}N$, ${}^{40}Ar/{}^{36}Ar$, $N_2/{}^{36}Ar$ and 172 173 sometimes ³He/⁴He and N₂/³He ratios (Marty, 1995; Marty and Humbert, 1997; Marty and 174 Zimmermann, 1999). Data would be plotted in spaces featuring an isotope or elemental noble gas ratio of interest versus an unambiguous tracer of air contamination. So far, $\delta^{15}N$ 175 176 and $N_2/{}^{36}$ Ar would be plotted against the measured argon isotope ratio 40 Ar/ 36 Ar, so mantle δ^{15} N and N₂/³⁶Ar could be determined by extrapolation (Marty, 1995; Marty and Humbert, 177 1997; Marty and Zimmermann, 1999). In the following, I summarize the results obtained in 178 179 previous work with respect to δ^{15} N mantle estimates from basalts that underwent variable degrees of air contamination. I subsequently address whether the nitrogen systematics in 180 181 MORB and OIB show any consistency with K_2O/TiO_2 .

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3. MORB data

A nitrogen isotope dataset including a total of 50 MORB is available in supplementary table 1. The data source is Marty and Humbert (1997), Marty and Zimmermann (1999) and Barry and Hilton (2016). Nitrogen isotope data for three popping rocks are also used, from Javoy and Pineau (1991) and Labidi et al., (2020). The latter study was selected as nitrogen isotope ratios were measured together with Δ_{30} values, an independent measure of air contamination for nitrogen in natural samples (Labidi and Young, 2022).

192 On Fig. 1, MORB K_2O/TiO_2 data are shown against the magnesium oxide MgO as a tracer of magmatic differentiation. Small symbols are for global MORB, compiled using the PetDB 193 194 database (www.earthchem.org/petdb, Lehnert et al., 2000). Larger symbols reflect the set of 195 basalts discussed in this study, for which $\delta^{15}N$ data are available in the literature (supplementary table 1). Most MORB show K_2O/TiO_2 ratios varying between 0.02 and 0.40, 196 197 independent of the degree of basalt differentiation (Fig. 1). The low end of the K_2O/TiO_2 198 range is associated with a depleted mantle reservoir, while the high end of the range reflects 199 contributions from enriched slabs. Recycled components have K_2O/TiO_2 ratios ~ 0.5, 200 inherited from the composition of the igneous oceanic crust (Kelley et al., 2003) and/or 201 various types of recycled sediments (Plank and Langmuir, 1998).

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203 **3.1.** The ¹⁵N/¹⁴N ratio

Basalts from mid-ocean ridges tend to show negative $\delta^{15}N$ (Cartigny et al., 2001; Javoy and Pineau, 1991; Marty and Humbert, 1997; Marty and Zimmermann, 1999). Basalts with air-like ${}^{40}Ar/{}^{36}Ar$ show a ~10‰ range in $\delta^{15}N$ (Fig. 2). This may reflect the assimilation of hydrothermal nitrogen after it experienced $\delta^{15}N$ fractionation (Marty and Zimmermann, 208 1999). This is consistent with the observation of 36 Ar/ 22 Ne ratio of hydrothermal waters for 209 basalts with air-like 40 Ar/ 36 Ar ratios (Peron et al., 2019). At elevated mantle-like 40 Ar/ 36 Ar 210 ratios, basalts show a consistent depletion for 15 N/ 14 N akin to the signatures observed in 211 peridotitic diamonds (Cartigny et al., 2014), with a δ^{15} N ~ $-4\%_0$. This is interpreted as the 212 signature of the convective mantle tapped by mid-ocean ridge basalts (Marty and 213 Zimmerman, 1999).

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215 **3.2.** the $N_2/^{36}$ Ar ratio

The $N_2/{}^{36}$ Ar global basalt dataset is shown in Fig. 3. Data are from the same references 216 as Fig. 2. At atmospheric 40 Ar/ 36 Ar ratios of ~300, N₂/ 36 Ar is also atmospheric, i.e., 2.5 x 10⁴. 217 218 At mantle-like 40 Ar/ 36 Ar values of > 10,000, N₂/ 36 Ar ratios are higher, up to 4 x 10⁶. The available data are too scattered to allow identifying a trend. A global $N_2/{}^{36}Ar - {}^{40}Ar/{}^{36}Ar$ 219 220 correlation is apparent only when logarithm scales are used for the plot (Fig. 3B). Despite 221 the scatter and the few outliers, the trend indicates at first order that the N_2 and Ar overprints by air-derived components are concomitant, masking elevated N₂/³⁶Ar ratio of 222 223 the MORB source.

Taking the N₂/³⁶Ar - ⁴⁰Ar/³⁶Ar correlation has global significance, and assuming the ⁴⁰Ar/³⁶Ar of the convective mantle is ~25,000±2,000 (Moreira et al., 1998; Mukhopadhyay, 2012; Péron et al., 2019), a N₂/³⁶Ar ratio of $2.0^{+1.0}_{-1.2} \times 10^6$ is obtained for the convective mantle. This ratio is robust, since nitrogen and argon are not fractionated during basalt degassing, on account of a similar solubility with respect to CO₂-rich magmatic vesicles (Libourel et al., 2003; Marty, 1995). One potential issue however is that the trend on Fig. 3B is driven by extractions on one basalt from the mid-Atlantic ridge, CH98 DR11, which yielded 231 some of the highest 40 Ar/ 36 Ar ratios ever reported for MORB of 42,335 ± 9713 (Marty and 232 Humbert, 1997). Whether this basalt may represent an appropriate endmember to drive the 233 N₂/ 36 Ar – 40 Ar/ 36 Ar relation and thus characterize the entire convective mantle is unclear.

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3.3. The N₂/³He ratio

The N₂/³He data are shown against the argon isotope ratio 40 Ar/ 36 Ar in Fig. 4. Data 236 are the MORB in Marty and Zimmerman (1999), as well as the so-called "popping" rock by 237 Javoy and Pineau (1991). In this space, mixings are not on straight lines. The curvature of 238 mixing relationships is defined by the $[^{3}He/^{36}Ar]_{air}/[^{3}He/^{36}Ar]_{mantle}$ ratio. The $^{3}He/^{36}Ar$ air 239 value is 2.5×10^{-7} , considerably lower than the upper-mantle value of ~ 5.0×10^{-1} 240 (Moreira et al., 1998; Péron et al., 2019; Raquin et al., 2008), thus the 241 [³He/³⁶Ar]_{air}/[³He/³⁶Ar]_{mantle} ratio is different from unity by 6 orders of magnitude. This 242 243 results in air-mantle mixings on extremely curved hyperbolae (Fig. 4). As a result, any basalt with a ${}^{40}\text{Ar}/{}^{36}\text{Ar} > 500$ plots on the near-horizontal branch of the N₂/ ${}^{3}\text{He} - {}^{40}\text{Ar}/{}^{36}\text{Ar}$ mixing 244 hyperbola (Fig. 4). In other words, a basalt with a ${}^{40}\text{Ar}/{}^{36}\text{Ar} > 500$ shows a N₂/ ${}^{3}\text{He}$ ratio 245 246 broadly similar to the uncontaminated basalt endmember. The popping rock $2\pi D43$ yields a $N_2/^{3}$ He of 3.0±0.1 x 10⁶ (5 orders of magnitude below the air value of ~10¹¹) at 40 Ar/ 36 Ar 247 248 ratios \sim 5,000 (Javoy and Pineau, 1991), which is considered a sound representation of its 249 mantle source. A similar estimate was recently obtained in Marty et al., (2020), but with no 250 ⁴⁰Ar/³⁶Ar measurement.

MORB analyzed by Marty and Zimmerman (1999) have an average $N_2/{}^{3}$ He of 1.4±0.6 x 10⁶ (95% confidence, n=30) which at face value appears lower than the popping rock value by a factor of ~ 2 (Fig. 4A). Helium is 2 to 10 times more soluble than N_2 in basaltic melts

(Libourel et al., 2003 and references therin). Magmatic degassing often occurs under a 254 Rayleigh distillation, where vesicles are continuously nucleated and immediately lost from 255 melts (Cartigny et al., 2001; Marty and Zimmermann, 1999). Thus, measured elemental 256 257 ratios of ordinary MORB can be considerably different from the starting compositions, leading to confusion with regard to the true N₂/He ratio of a parental melt. To reconstruct 258 the starting $N_2/^{3}$ He value, the 4 He/ 40 Ar* tracer is particularly useful (40 Ar* only takes into 259 account the fraction of ⁴⁰Ar that is not air-derived, Staudacher et al., 1989). Helium is 260 fractionated from argon by degassing solubility rules. The starting ${}^{4}\text{He}/{}^{40}\text{Ar}^{*}$ is set at ~1.5. 261 as observed in popping rocks and constrained by the U/K ratio of the mantle (Moreira et al., 262 1998). In the MORB from Marty and Zimmermann (1999), ⁴He/⁴⁰Ar* vary over more than 263 one order of magnitude, suggesting volatile ratio reflect considerable fractionation. 264 265 Following Marty and Zimmermann (1999), reconstructed $N_2/^{3}$ He ratios are on average 3.7 266 $(\pm 1.2) \ge 10^6$ (n=30, 95% conf), indistinguishable from the popping rock value of 3.0 $(\pm 0.1) \ge 10^6$ 10⁶ (Fig. 4B). In this work, I adopt this ratio as the estimate of the convective mantle. 267

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269 4. **Ocean island basalts**

A nitrogen isotope dataset including a total of 44 OIB is available in supplementary table 2. The data source is Marty and Humbert (1997), Sano et al., (2001), Marty and Dauphas (2003), and Halldorson et al., (2016). Note that only 5 out of the 42 basalts characterized in Halldorson et al., (2016) were used in the data compilation. The five basalts were selected on the basis of their 40 Ar/ 36 Ar > 500. The other 37 samples with 40 Ar/ 36 Ar < 500 from Halldorson et al., (2016) are nonetheless plotted on Fig. 2. The OIB dataset is broken down in two groups: lavas with ${}^{3}\text{He}/{}^{4}\text{He} \leq 7.5 \text{ R}_{A}$ and with ${}^{3}\text{He}/{}^{4}\text{He} \geq 8 \text{ R}_{A}$. A total of 26 lavas from Society with ${}^{3}\text{He}/{}^{4}\text{He} \leq 7.5 \text{ R}_{A}$ were investigated for ${}^{5}\text{N}$, N₂/ ${}^{3}6\text{Ar}$ and ${}^{40}\text{Ar}/{}^{3}6\text{Ar}$ (Marty and Dauphas, 2003). Out of those, 13 have ${}^{40}\text{Ar}/{}^{3}6\text{Ar} >$ 279 500, including only 5 with measured N₂/ ${}^{3}\text{He}$ ratios. On the other side of the spectrum, 18 OIB 280 with ${}^{3}\text{He}/{}^{4}\text{He} \geq 8 \text{ R}_{A}$ from Iceland, Hawaii and Galapagos were investigated for ${}^{5}\text{N}$, N₂/ ${}^{3}6\text{Ar}$ 281 and ${}^{40}\text{Ar}/{}^{3}6\text{Ar}$. Out of those, 12 basalts have ${}^{40}\text{Ar}/{}^{3}6\text{Ar} \geq 500$ and simultaneous measurements 282 of ${}^{5}\text{N}$, N₂/ ${}^{3}6\text{Ar}$, ${}^{40}\text{Ar}/{}^{3}6\text{Ar}$, including 8 samples with measured N₂/ ${}^{3}\text{He}$ ratios.

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284 **4.1**¹⁵N/¹⁴N ratios

Nitrogen isotope measurements were made on volatile fractions showing ⁴⁰Ar/³⁶Ar 285 286 of up to ~3,300 for Iceland, (Marty and Dauphas, 2003), 2635±5 for Galapagos (Marty and 287 Humbert, 1997) and ~ 700 for Loihi (Sano et al., 2001). The Galapagos, Hawaii and Iceland mantle sources are characterized by ⁴⁰Ar/³⁶Ar of ~10,000±2,000 (Mukhopadhyay, 2012; 288 289 Péron et al., 2016; Trieloff et al., 2000), so δ^{15} N values have to be taken with caution. At the highest 40 Ar/ 36 Ar, δ^{15} N range between +0.6‰ and -1.9‰ (Fig. 2). For Society, data from 290 Marty and Dauphas (2003) show 40 Ar/ 36 Ar up to 9995±550. At the highest 40 Ar/ 36 Ar, δ^{15} N 291 are observed between +0.4 and \sim +3.6% (Fig. 2B). 292

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294 4.2 The N₂/³⁶Ar ratio

If extrapolating the data for basalts with high ${}^{3}\text{He}/{}^{4}\text{He}$ at a ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ of ~10,000, the N₂/ ${}^{36}\text{Ar}$ backed out from the trend on Fig. 3 is $0.7^{+0.5}_{-0.3} \times 10^{6}$. Although not statistically different from the convective mantle, this estimate allows somewhat lower N₂/ ${}^{36}\text{Ar}$ for the plume mantle, as suggested originally by Dauphas and Marty (1999). Under the assumption

of a unique $\ln[^{40}Ar/^{36}Ar] - \ln[N_2/^{36}Ar]$ trend and $^{40}Ar/^{36}Ar > 10,000$, data on Society basalts 299 would yield a somewhat higher $N_2/{}^{36}$ Ar than Iceland (Fig. 3B). 300

301

302 4.3 The $N_2/^3$ He ratio

The dataset on Galapagos and Iceland basalts, from Marty and Dauphas, (2003), does 303 not allow compiling N₂/³He ratios (supplementary Table 2). For Iceland basalts, Marty et al., 304 (2020) published a N₂/³He estimate of ~ 3 x 10⁶ for a DICE glass. The data is presented 305 without a 40 Ar/ 36 Ar measurement and therefore cannot be plotted on Fig. 4, but it is 306 307 consistent with a MORB-like N₂/³He for the Icelandic mantle source. Other Iceland basalts with 40 Ar/ 36 Ar between 591 and 1334 from Halldorson et al., (2016) show N₂/ 3 He of 2.7±3.6 308 $x10^{6}$ (95% conf., n=5). After correction from fractional degassing, N₂/³He averages at 309 $3.7\pm2.9\times10^6$ (95% conf., n=5). The one Loihi basalt with ${}^{40}\text{Ar}/{}^{36}\text{Ar} \sim 700$ shows an 310 uncorrected $N_2/^{3}$ He of 3.1×10^{6} , which becomes 2.5×10^{6} after correction (Sano et al., 2001). 311 Uncorrected N₂/³He values on basalts from the Society hotspot are up to $\sim 10^9$, three 312 orders of magnitude higher than the MORB mantle (Fig. 4A). After correction for fractional

degassing following the method of Marty and Zimmermann (1999), the $N_2/^{3}$ He range to 314 315 values up to 10^8 .

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5. Discussion 317

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5.1. MORB data do not support nitrogen regassing

The published dataset for ordinary MORB reveals that $\delta^{15}N$ and $N_2/^{3}He$ do not vary 319 systematically with K_2O/TiO_2 ratios (Fig. 5 and 6). The $2\pi D43$ popping rock is itself an 320 321 enriched MORB with a K_2O/TiO_2 estimated at ~0.38 (Sarda and Graham, 1990) or ~0.19

322 (Cartigny et al., 2008). This sample shows MORB-like δ^{15} N and N₂/³He signatures (Javoy and Pineau, 1991, Marty et al., 2020 Fig. 5). Three other popping rocks have $\delta^{15}N \sim -3\%$ 323 324 associated with near-zero Δ_{30} values, suggesting the extracted N₂ is unaffected by air contamination (Labidi et al., 2020; Labidi and Young, 2022). Those popping rocks have high 325 $K_2O/TiO_2 \sim 0.35$ (Jones et al., 2019). To account for the data, a mantle component with 326 327 $K_2O/TiO_2 \sim 0.02$ is taken to mix with recycled slabs of indeterminate lithologies but high 328 $K_2O/TiO_2 \sim 0.5$. An average $K_2O/TiO_2 \sim 0.5$ is an approximation consistent with observations in extreme mantle endmembers (Jackson and Dasgupta, 2008) and in protoliths susceptible 329 330 to be subducted (Kelley et al., 2003; Plank and Langmuir, 1998).

331 The flat relationship between δ^{15} N and K₂O/TiO₂ (Fig. 5) is not simple to reconcile with 332 recycling, if the mantle and slabs have distinct δ^{15} N signatures as suggested in e.g., Barry and Hilton (2016). One may suggest a mixing hyperbola is at play and all MORB happen to be on 333 334 the flat portion of the mixing curve in Fig. 5. By design, the curvature of mixing relationships in Fig. 5 is defined by the $[14N/TiO_2]_{slabs}/[14N/TiO_2]_{mantle}$ ratio. Mixing hyperbolae are valid 335 336 only if N/TiO₂ ratio of the two reservoirs (slabs and mantle) are different, i.e., if slabs have 337 either substantially higher or substantially lower N concentrations relative to the mantle. 338 Below, I explore in detail the viability of the two endmember scenarios.

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340 5.1.1 Scenario 1: slabs have high N concentrations

In a scenario 1, N/TiO_{2 slab} > N/TiO_{2 mantle}, i.e., slabs have high [N]. This is testing the possibility that the mantle prior to subduction had low [N] and thus low N₂/³He. For this reservoir, I take a δ^{15} N of ~-20‰, akin the average value of enstatite chondrites. This 344 scenario embodies the notion of nitrogen regassing: recycling would increase [N], N₂/³He, 345 δ^{15} N together with K₂O/TiO₂.

I take a $N_2/^{3}$ He of $3x10^{5}$ for the mantle prior to slab addition. This ratio is a factor of 10 346 347 lower than the observed ratio for the modern MORB mantle. Taking an N concentration of ~0.27±0.16 ppm N for the MORB source (Marty and Dauphas, 2003), a low $N_2/^{3}$ He by a factor 348 of 10 yields a concentration of ~ 0.03 ppm N for the mantle prior to the addition of slabs. 349 Values even lower would make no difference. I take TiO₂ concentration of 0.13 wt% for the 350 351 depleted mantle (Workman and Hart, 2005), resulting in a N/TiO₂ of \sim 2 x 10⁻⁵. For recycled components, I take $N_2/^{3}$ He = 10¹¹ (Sano et al., 2001) and [TiO₂] = 0.4 wt%. The latter is not 352 fundamentally different from $[TiO_2] \sim 0.35$ and 0.60 wt% for igneous crust and marine 353 sediments, respectively (Kelley et al., 2003; Plank and Langmuir, 1998). Other values for 354 355 slabs $N_2/^{3}$ He and TiO₂, within a reasonable range, do not change the main result: when a mixing scenario fits the K₂O/TiO₂ – δ^{15} N data, recycled nitrogen must have an average δ^{15} N 356 357 of -4% and slabs must have N concentrations ≥ 10 ppm (Fig. 5A).

This scenario is associated with an array of limitations. Firstly, recycled N with negative 358 359 δ^{15} N is inconsistent with published compositions of metasediments and metagabbros with average $\delta^{15}N \sim +3\%$ (Busigny et al., 2011), even in the Archean (Ader et al., 2016). A [N]_{slabs} 360 \geq 10 ppm is higher than the N concentrations in fresh MORB of ~1.1 ppm (Marty, 1995). The 361 altered oceanic crust shows [N] up to ~12 ppm, only for the shallowest 1,000 meters of 362 altered basalts (Busigny et al., 2019). Horizons under 1,500 meters under the seafloor show 363 [N] < 2 ppm (Busigny et al., 2019). It is not clear how the recycled oceanic crust could 364 preserve an average [N] as high as 10 ppm *after* subduction. 365

366 The most important limitation is that scenario 1 fails to account for the invariant $N_2/^{3}$ He at varying K_2O/TiO_2 (Fig. 5B). The curvature of mixing relationships in Fig. 5B is 367 defined by the [³He/TiO₂]_{slab}/[³He/TiO₂]_{mantle} ratio. Because ³He is not recycled (Porcelli et 368 al., 2002), the [³He/TiO₂]_{slab}/[³He/TiO₂]_{mantle} ratio by necessity is << 1. This always results in 369 hyperbolic mixtures in Fig. 5B, so that homogeneous $N_2/^{3}$ He at varying K_2O/TiO_2 cannot be 370 371 fit. Slab components with high [N] cause sharp increases in $N_2/{}^{3}$ He at varying K_2O/TiO_2 , 372 which is not observed. Overall, there is no viable scenario where Earth's convective mantle 373 is overwhelmed by recycled N and at the same time homogeneous δ^{15} N and N₂/³He at varying K_2O/TiO_2 ratios are accounted for. 374

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5.1.2 Scenario 2: slabs have low N concentrations

In a scenario 2, I explore the possibility of N/TiO_{2 slab} < N/TiO_{2 mantle}, i.e., slabs have low [N]. In this scenario, mixing hyperbolae are the inverse of scenario 1, so the starting mantle (prior to the initiation of subduction) inevitably has $\delta^{15}N \sim -4\%_0$. It is assigned a [N] of 0.3 ppm, a N₂/³He ratio of 3x10⁶, and a N/TiO₂ ~ 2x10⁻⁴. Subducted nitrogen is fixed at $\delta^{15}N \sim$ +3%0 by observations in metagabbros and metasediments (Bebout et al., 2013; Bebout and Fogel, 1992; Busigny et al., 2019, 2011, 2003; Haendel et al., 1986).

The main result is that N/TiO₂ for slabs must be $\leq 3x10^{-5}$, at least one order of magnitude lower than the mantle, for the mixing curve on Fig. 6 to fit the data. Taking [TiO₂] = 0.4 wt% for recycled components (Kelley et al., 2003; Plank and Langmuir, 1998), it results that [N]_{slabs} ~ 0.1 ppm N. A [N]_{slabs} ~ 0.1 ppm N is not unreasonable: it is lower than N concentrations in the altered oceanic crust, consistent with \geq 90% nitrogen losses from the slabs – likely occurring underneath sub-arc mantle sources (Füri et al., 2021; Labidi et al.,

389	2021). The addition of 10 to 20% slabs (with $[TiO_2]_{slabs} = 0.4$ wt% and $K_2O/TiO_2 = 0.5$) to a
390	depleted mantle (with $[TiO_2]_{depleted mantle} = 0.13 \text{ wt\%}$ and $K_2O/TiO_2 = 0.02$) returns K_2O/TiO_2
391	ratios between 0.12 and 0.19, covering most of the enriched-MORB range (Fig. 1). Taking
392	$[N]_{slabs} \sim 0.1$ ppm, adding 10 to 20% slabs to a mantle source would cause only a $\sim 3\%$ and
393	~6% increase of bulk [N] or $N_2/^3$ He respectively, well below the measurement uncertainties.
394	To summarize, scenario 2 suggests nitrogen subduction is not recorded in most MORB
395	because the concentration of nitrogen in slabs is too low compared to the average mantle. It
396	results that the observed $\delta^{15}N$ \sim –5‰ and $N_2/{^3}He$ \sim $3x10^6$ may reflect mantle signatures
397	pre-dating the onset of subduction. A summary of this analysis is shown on <mark>Fig. 7</mark> .
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400	5.2 Nitrogen in plumes
401	Elevated $\delta^{15}N$ values in plumes may reflect subducted nitrogen with positive $\delta^{15}N$
402	accumulated in mantle sources (Barry and Hilton, 2016; Bekaert et al., 2021; Dauphas and
403	Marty, 1999; Marty and Dauphas, 2003). Here, published data are separated between basalts
404	sampling (1) low 3 He/ 4 He mantle sources and (2) high 3 He/ 4 He mantle sources.
405	

5.2.1 the case of low ³He/⁴He basalts

Basalts from Society do show $\delta^{15}N > 0.5\%$ clearly distinct from MORB (Fig. 2B), with N₂/³He ratios corrected from fractional degassing being between 10⁷ and 10⁸ (Fig. 4). However, Society is all but a primordial plume. Lavas show low ³He/⁴He ratios, down to ~6 R_A (Marty and Dauphas, 2003), enriched K₂O/TiO₂ ~0.45 (Hemond et al., 1994, Jackson and Dasgupta, 2008), and extreme radiogenic isotope signature (Chauvel et al., 1992). Nitrogen 412 isotopes and K_2O/TiO_2 data were not acquired on the same Society basalts. Given that enriched K₂O/TiO₂ signatures appear homogeneous among basalts from Society (Hémond et 413 414 al., 1994), a possible Society field may be obtained by combining the N isotope data from 415 Marty and Dauphas (2003) to major element data from Hemond et al., (1994). Nitrogen subduction associated with enriched slabs can account for the resulting field, shown on Fig. 416 417 **5** and **6**. Society appears to be a plume with geochemical signatures fully consistent with 418 nitrogen subduction. A similar conclusion was reached for free gases with low ³He/⁴He from 419 the Eifel region, Germany : using the new Δ_{30} systematic to account for air contamination, 420 the source of the mantle-derived gases in this particular region was suggested to incorporate subducted nitrogen (Labidi et al., 2020). 421

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5.2.2 the case of high ³He/⁴He basalts

Lavas from Galapagos, Loihi and Iceland tell a different story than Society. They show $\delta^{15}N$ between -2% and 0% at their highest ${}^{40}Ar/{}^{36}Ar$ ratios (Fig. 2). Those $\delta^{15}N$ values have to be taken with caution, since measurements were done at ${}^{40}Ar/{}^{36}Ar$ between \sim 700 and \sim 3,300 (supplementary table 2), while the sources of the three plumes have ${}^{40}Ar/{}^{36}Ar$ of \sim 10,000±2,000 (Mukhopadhyay, 2012; Péron et al., 2016; Trieloff et al., 2000). Nonetheless, considering the shape of the mixing curve on Fig. 2, measured $\delta^{15}N$ at ${}^{40}Ar/{}^{36}Ar > 1,000$ are probably not far off the true values for the plume sources.

The N₂/³He ratios for the Galapagos, Loihi and Iceland basalts are not well known (supplementary table 2). Only one Loihi sample with a 40 Ar/ 36 Ar ratio of ~700 has a published N₂/ 3 He of 2.5x10⁶ (Sano et al., 2001). For Iceland and Galapagos, a rough N₂/ 3 He reconstruction can be done by combining published N₂/ 36 Ar with 3 He/ 36 Ar ratios from the literature. Taking N₂/³⁶Ar = $0.7^{+0.5}_{-0.3} \times 10^6$ according to the N₂/³⁶Ar - ⁴⁰Ar/³⁶Ar correlation (Fig. 3), and ³He/³⁶Ar of 0.3 for Iceland (Colin et al., 2015), a N₂/³He estimate of 2.3 (±1.2) x 10⁶ is obtained (1 σ uncertainty). If a ³He/³⁶Ar of 0.8 is used (Peron et al., 2016, Mukhopadyay, 2012), a N₂/³He estimate of 1.6 (±0.9) x 10⁶ (1 σ uncertainty) would be obtained. These estimates seem indistinguishable from the MORB mantle. This is also consistent with an actual N₂/³He measurement on a DICE glass performed recently, but with no ⁴⁰Ar/³⁶Ar data (Marty et al., 2020).

Halldorson et al. (2016) suggested a much higher $N_2/^3$ He ratio of 10¹⁰ for Iceland, 442 extrapolated from N₂/⁴⁰Ar* data. Such a massive N enrichment in Iceland was considered 443 unwarranted (Hirschmann, 2018), as it relies on assuming *all* N₂ to be mantle-derived in 444 445 basalts with atmospheric ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ ratios. Instead, one may take the measured N₂/ ${}^{3}\text{He}$ (corrected from fractional degassing) of the few basalts with 40 Ar/ 36 Ar > 500 in Halldorson 446 et al., (2016). This results in an average $N_2/^{3}$ He of $3.7\pm2.9\times10^{6}$ (95% conf., n=5), consistent 447 with the reconstructed N₂/³He of 2.3 (\pm 1.2) x10⁶ and the N₂/³He estimate of 3.7 (\pm 1.2) x 10⁶ 448 for the MORB mantle. 449

450 Hydrothermal gases from the Yellowstone stratovolcano yield similar results. Near-451 zero δ^{15} N and MORB-like N₂/³He were shown to be associated with the plume signature using the Δ_{30} approach (Labidi and Young, 2022). A picture of MORB-like N₂/³He but near-452 453 zero δ^{15} N for the high ³He/⁴He mantle seems to emerge as a global feature. It may be tempting to describe the nitrogen budget of the high ${}^{3}\text{He}/{}^{4}\text{He}$ mantle as being influenced by 454 recycled slabs, overprinting the potentially primordial δ^{15} N of solar or enstatite chondrite 455 456 parent bodies (Barry and Hilton, 2016). Although this is based on a few samples and therefore might change with future work, the $N_2/^3$ He of MORB and of the high 3 He/ 4 He 457

458 mantle appear indistinguishable, and it is unclear how this may reflect nitrogen recycling in one or in both reservoirs. One possibility involves the true primordial mantle having low 459 $N_2/^{3}$ He (< 10⁶). Mixing with a slab showing a high $N_2/^{3}$ He (>10⁶) would result in MORB-like 460 461 $N_2/^{3}$ He (Bekaert et al., 2021). The $N_2/^{3}$ He similarity with MORB would be the fortuitous result of mixing between two distinct components in just the right proportions to yield 462 463 convective mantle values. The basalt data do not support this circumstance. DICE 10 and 11 (Iceland) have low K_2O/TiO_2 , of ≤ 0.06 (Brandon et al., 2007), which argues for minimal 464 contributions of recycled components in their mantle source. Both the Loihi glass from Sano 465 et al., (2001) and the Galapagos sample with the highest ⁴⁰Ar/³⁶Ar ratios from Marty and 466 Humbert (1997) have K_2O/TiO_2 of ~0.20 (Geist et al., 2006; Nishio et al., 2007), indicating a 467 higher contribution of enriched components in their mantle sources, yet they all show 468 469 invariant δ^{15} N between -2 and 0‰ (supplementary table 2). If confirmed with new data in 470 future work, an invariant $\delta^{15}N$ (and N₂/³He?) at varying K₂O/TiO₂ for OIB probably indicates 471 that like with MORB, recycled components intermingled with the high ³He/⁴He mantle may not modify the plume N isotope signatures. A δ^{15} N between -2% and 0% for the high 472 473 ³He/⁴He mantle, if truly statistically distinct from MORB, would require an explanation 474 without the need to invoke slab recycling. A summary of this analysis is shown on Fig. 7.

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5.3. Revisiting the deep N cycle

The MORB mantle is made of roughly ~10% recycled slabs (Allègre and Turcotte, 1986;
Hamelin et al., 2011; Sobolev et al., 2007). The composition of plume basalts with high
³He/⁴He also require the occurrence of *some* recycled components in mantle sources (Farley)

et al., 1992; Hilton et al., 1999; Jackson et al., 2020). Yet, outside of extreme mantle enrichment such as seen in Society islands, basalt data do not seem in favor of substantial nitrogen subduction. The absence of an overwhelming recycling signature for nitrogen in MORB and most OIB has implications for the deep N cycle. The lack of recycled nitrogen may reflect a low slab/mantle nitrogen concentration ratio, as illustrated by the mass balance done in section 5.1.2: for MORB δ^{15} N to be accounted for, [N]_{slabs} must be < [N]_{mantle} by at least a factor of ~ 3.

488 The nitrogen behavior in subduction zones controls the slab/mantle N concentration ratio. In metamorphic rocks, nitrogen is hosted in the structures of minerals such as micas 489 490 and illites, as NH₄⁺ substituting for potassium (Bebout et al., 1992, Busigny et al., 2003; 491 Nieder et al., 2011). Nitrogen is thought to be quantitatively retained within minerals during 492 metamorphism, supporting efficient nitrogen recycling in the mantle (Bebout et al., 2013; 493 Busigny et al., 2003). In modern subduction zones, slab-fluid temperatures are between 750 494 and 950 °C (Plank et al., 2009). However, the rocks studied in Busigny et al., (2003) and in Bebout et al., (2013) reached a peak temperature of ~630 °C (Busigny et al., 2003), well 495 496 below temperatures relevant to slab devolatilization. Observations on metamorphic rocks 497 are invaluable, but may only apply to fore-arc devolatilization and may not constrain sub-arc slab fluid losses. 498

Experimental evidence suggest that cold subduction zones would allow nitrogen to remain in slabs even past the region of sub-arc melting (Jackson et al., 2021; Mallik et al., 2018). In those slabs, recycled nitrogen would remain stable as NH₄+ in potassium-bearing minerals throughout fluid losses (Watenphul et al., 2010, 2009). Under higher temperatures relevant to hot subduction zones, laboratory experiments show a reversal of the nitrogen

partition coefficient, such that slab-nitrogen would be quantitatively lost during 504 devolatilization and mineral breakdown (Jackson et al., 2021). Füri et al., (2021) and Labidi 505 et al., (2021) showed that the mantle wedges of two distinct subduction zones are enriched 506 507 in N by \sim 1 to 2 orders of magnitude relative to the average MORB mantle. In the case of the Central American hot subduction zone, the N enrichment in the mantle wedge is indicative 508 of near-quantitative nitrogen losses from the slab (Labidi et al., 2021). Overall, new 509 510 experimental and observational studies provide evidence that nitrogen losses during 511 devolatilization are substantial. In warm subduction zones, devolatilization would be nearly 512 quantitative, effectively preventing substantial N transfer to the deep mantle.

513 The perspective of limited nitrogen recycling may seem puzzling, partly because the recycling of other volatiles in basalt sources is observed. For example, the budget of xenon 514 515 in MORB and OIB sources is dominated by 80-90% of a surface-derived component, 516 independently of basalt enrichments (Parai et al., 2019; Parai and Mukhopadhyay, 2021). 517 This may reflect xenon concentrations to be far higher in slabs than in the rest of the mantle. Thus, even minimal contributions of slabs, like in the sources of depleted MORB, would drive 518 519 the xenon budget to be dominated by surface-derived components. These circumstances are 520 unique to xenon. The krypton isotope signatures of high ³He/⁴He basalts from plumes requires a substantially more limited regassed contribution than xenon (Péron et al., 2021). 521 The case for argon recycling is debated: mantle sources of high ³He/⁴He basalts have 522 40 Ar/ 36 Ar of ~ 10,000 (Mukhopadhyay, 2012; Péron et al., 2016), which is lower than 523 524 ⁴⁰Ar/³⁶Ar estimates of the MORB mantle by at least a factor of 2. This may reflect the signature of a less degassed mantle reservoir (Allègre et al., 1987) or evidence for ³⁶Ar 525 recycling in the sources of high ³He/⁴He basalts (Holland and Ballentine, 2006). A scenario 526

527 where 36 Ar recycling preferentially affects plume sources leaves unexplained the relatively high ³He/³⁶Ar of plumes relative to MORB (³He/³⁶Ar data in Moreira et al., 1998, 528 529 Mukhopadhyay, 2012, Peron et al., 2016). In contrast with ³⁶Ar subduction, neon recycling 530 was suggested to affect the MORB mantle more than high ³He/⁴He plumes: OIB with the most 531 primitive ³He/⁴He ratios show solar ²⁰Ne/²²Ne ratio (Williams and Mukhopadhyay, 2018). The recycling of surface-derived neon into the MORB mantle would have lowered its 532 20 Ne/ 22 Ne ratio by a limited but measurable amount, from ~ 13.4 to ~ 12.5 (Williams and 533 Mukhopadhyay, 2018). Note that alternative hypotheses offer explanations for the MORB 534 535 ²⁰Ne/²²Ne ratio without resorting to neon subduction (Moreira and Charnoz, 2016; Péron et 536 al., 2016). The carbon budget also shows somewhat limited regassing signatures. The 537 $CO_2/^{3}$ He ratios of depleted MORB is ~5.0 x 10⁸ (Marty and Zimmerman, 1999, Graham and Michael, 2021). Enriched MORB have higher $CO_2/^{3}He$, on average ~ 6.0 x 10⁹ (Graham and 538 Michael, 2021, Marty and Zimmerman, 1999, Peron et al., 2019). The relationship between 539 $CO_2/^{3}$ He and enrichment likely results from carbon recycling as an illustration of the marble-540 cake mantle (Marty and Zimmermann, 1999). The $CO_2/^3$ He ratio of Icelandic basalts is ~6.7 541 x 10⁸ (Colin et al., 2015), as low as values observed depleted MORB. The low $CO_2/^{3}$ He in 542 543 Iceland was suggested to argue against carbon recycling in the high ${}^{3}\text{He}/{}^{4}\text{He}$ Iceland source (Colin et al., 2015). Other volatiles such as sulfur, water and halogens illustrate various 544 degrees of recycling in mantle reservoirs (Bekaert et al., 2021). This brief literature survey 545 546 shows that various volatiles show a spectrum of behaviors in subduction. This work suggests 547 that nitrogen may not be tied to the species showing the highest recycling efficiencies.

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5.4 What consequences for exchange scenarios?

Nitrogen subduction is not recorded in the composition of the convective mantle. This 551 may appear to be in conflict with modern fluxes of nitrogen between Earth's reservoirs, 552 553 seemingly requiring nitrogen subduction to be much higher than N₂ degassing (Busigny et al., 2011). Scenarios extrapolating modern fluxes to deep time predict the ancient 554 atmosphere showed elevated N₂ concentration relative to modern air, possibly even 555 556 accounting for the faint young sun paradox (Goldblatt et al., 2009). When articulated to 557 specifically explain the N isotope imbalance between Earth's reservoirs, nitrogen regassing models posit that mantle and air δ^{15} N had an even larger nitrogen isotope disequilibrium in 558 559 the past (Javoy, 1997). Secular evolutions for [N] and δ^{15} N are anticipated, but they have not 560 been observed. The N_2 partial pressure of the atmosphere appears to not have substantially 561 changed over geological time, or if anything, to have *increased* (Avice et al., 2018; Marty et al., 2013; Nishizawa et al., 2007; Som et al., 2016). The δ^{15} N of air appears to have remained 562 563 broadly constant over time, as attested by $^{15}N/^{14}N$ ratios from hydrothermal fluid inclusions 564 (Avice et al., 2018; Marty et al., 2013; Nishizawa et al., 2007). Ancient sediments are inconsistent with an isotope evolution of surface nitrogen outside of brief (but extreme) 565 excursions (Ader et al., 2016; Stüeken et al., 2015; Thomazo et al., 2011). If anything, the δ^{15} N 566 of ancient sediments has been recently suggested to be *negative* prior to metamorphism in 567 one formation from Greenland (Stüeken et al., 2021), at odds with the requirements of 568 569 *positive* δ^{15} N for old surface-derived N. On the mantle side, most diamonds with fibrous and peridotitic paragenesis also appear to reflect broadly invariant $\delta^{15}N$ of ~ -4% through 570 geological times (Boyd and Pillinger, 1994; Cartigny et al., 2014, 1997; Javoy et al., 1984; 571 Palot et al., 2012; Stachel et al., n.d.). 572

This leads to a conundrum: modern subduction fluxes require nitrogen exchange 573 between two isotopically distinct reservoirs, but no observational record of that interaction 574 is preserved. Fluxes of nitrogen subduction are by design derived from modern subduction 575 576 zones (Busigny et al., 2011). In present day, subduction zones are dominated by relatively 577 low temperature gradients compared to Proterozoic and Archean subduction zones (Martin 578 and Moyen, 2002). However, most of Earth's history has been dominated by hot subduction 579 zones (Antonelli et al., 2021; Keller and Schoene, 2018; Martin and Moyen, 2002). I speculate that extrapolating fluxes from warm subduction zones (rather than average modern 580 581 subduction fluxes) would probably relieve the need for substantial N exchange between 582 mantle and air, and essentially allow the N isotope imbalance to persist with time (Labidi et 583 al., 2020). The corollary to this principle is that the N isotope disequilibrium between Earth's 584 reservoir observed today would be a relatively ancient feature.

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587 **5.5 Why is plume nitrogen not isotopically solar?**

In the ³He/⁴He mantle, solar ²⁰Ne/²²Ne ratios indicate that at least some of the Earth's 588 parent bodies must have dissolved gases of the solar nebula (Williams and Mukhopadhyay, 589 2018). This would have occurred in a magma ocean stage, requiring that molten parent 590 bodies were somehow put in contact with nebular gases. Because only a few high ³He/⁴He 591 592 basalts show solar 20 Ne/ 22 Ne ratios (and not MORB), the plume mantle is the only reservoir 593 sampled today that would have recorded interactions with solar gases. In this context, the 594 absence of solar nitrogen with $\delta^{15}N \sim -387\pm 8\%$ is noted as problematic (Barry and Hilton, 2016; Williams and Mukhopadhyay, 2018). Chondritic addition and/or subduction could 595

both be culprits for nitrogen-neon decoupling. In the latter case, recycled nitrogen would
have replaced any solar components inherited from planetary formation (Barry and Hilton,
2016; Williams and Mukhopadhyay, 2018).

599 One can calculate how much solar N would be dissolved altogether with solar Ne. I estimate the highest amount of solar neon present in the OIB mantle using a ³He/²²Ne of the 600 plume mantle ~ 2 (Peron et al., 2016, Mukhopadhyay, 2012) and $^{20}Ne/^{22}Ne$ anywhere 601 between 12.5 and 13.5 (Williams and Mukhopadhyay, 2018). I take the [³He] concentration 602 of the MORB source is 10⁻¹⁰ ccSTP/g ³He (Moreira et al., 1998), and 10 times higher in the 603 plume endmember, i.e. 10^{-9} ccSTP/g ³He. This results in ~ 10^{-8} ccSTP/g Ne as the 604 concentration of solar neon in Earth's plume mantle, or $\sim 10^{-13}$ mol/g Ne. Knowing solar gas 605 N/Ne ~ 1 (Anders and Grevesse, 1989; Lodders, 2003) and respective solubilities of gaseous 606 607 species (Libourel et al., 2003 and references therein), the dissolution of $\sim 10^{-13}$ mol/g of solar Ne would result in $\sim 10^{-14}$ mol/g of solar N, or 0.007 ppt of solar N. This is 8 orders of 608 609 magnitude lower than observables on Earth, and ~ 11 orders of magnitude lower than 610 chondritic precursors making up the bulk Earth. Chondrites contain 400 to 3000 ppm N (Alexander et al., 2012; Pepin, 1991), so that solar gases are unlikely to impact the budget of 611 612 N of any planetary reservoir made of any realistic parent body. This simple mass balance 613 shows that subduction is not needed to explain the absence of solar nitrogen in deep mantle, 614 if it may be genetically linked with any chondritic parent body.

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5.6. Speculation about the origin of Earth's nitrogen

620 Some rare diamonds from Earth's mantle record extremely low $\delta^{15}N$, consistent with an EC parent bodies (Palot et al., 2012). One may then ask, why is the δ^{15} N of both MORB and 621 OIB mantle both different from enstatite chondrite, if not because of subduction? Substantial 622 623 future work is needed to determine what set of circumstances may allow the Earth's N 624 isotope imbalance to have been set during planetary differentiation, once accretion was 625 complete. Recent studies have investigated the nitrogen behavior during planetary 626 formation, with a focus on the thermodynamics of accretion, differentiation, and magma 627 ocean degassing (Bernadou et al., 2021; Boulliung et al., 2020; Grewal et al., 2021; Sossi et al., 2020). Evidently, the content of N in modern Earth's reservoirs could easily have been set 628 629 by a competition between metal/silicate equilibria and magma ocean degassing. As pointed out by Boulliung et al., (2020), N³⁻ would substitute with O²⁻ ions, leading to the formations 630 631 of X– N³⁻ complexes dominated by Si-N bonds (see also Libourel et al., 2003). Under this 632 speciation, nitrogen becomes substantially more soluble than dissolved N₂ (Bernadou et al., 633 2021; Boulliung et al., 2020; Libourel et al., 2003). Isotopic fractionation is set by distinct 634 average bonding strengths of an element between two phases. The obviously distinct 635 bonding environments between N³⁻ in a silicate melt and gaseous N₂ may result in ¹⁵N being preferentially partitioned in gaseous N₂. Depending on the magnitude of the isotopic 636 637 fractionation, partial degassing of a magma ocean, once Earth's accretion was complete, could conceivably set the isotope difference between mantle and atmospheric N. This 638 639 suggestion has recently received experimental interest (Dalou et al., 2022). The notion of 640 magma ocean degassing causing ¹⁵N depletions in residual nitrogen, in silicate melts with low fO_2 , seems viable (Dalou et al., 2022). In this context, it is possible that the plume $\delta^{15}N$ 641

values between air and MORB reflect the signature of mantle reservoir that underwent less
degassing during a magma ocean phase (and therefore less ¹⁵N depletion) than the more
degassed convective mantle.

645 The $\delta^{15}N$ of Earth's mantle is higher than the enstatite chondrites average $\delta^{15}N$ of $-20\pm11\%$ (1 σ , Grady et al., 1986), at least at the 1 σ level. This difference may have been set 646 by heterogeneous accretion. Carbonaceous chondrites could have contributed positive $\delta^{15}N$ 647 to an EC-like Earth during either the main stages of accretion or via the addition of a late 648 649 veneer (Marty and Zimmermann, 1999; Piani et al., 2020). However, it is not clear whether 650 a substantial addition of carbonaceous chondrites, especially during late accretion, would allow maintaining the EC-Earth similarity for a vast array of nucleosynthetic anomalies 651 (Dauphas, 2017). 652

653 Heterogeneous accretion may not be required to explain the $\delta^{15}N$ of Earth's mantle, 654 should planetary nitrogen undergo isotope fractionation(s) during Earth's formation and differentiation. Metal/silicate fractionations could raise the mantle $\delta^{15}N$ from a starting 655 656 composition similar to EC. although there is debate as to what the true metal/silicate isotope 657 fractionation is for N (Dalou et al., 2019; Li et al., 2016). Isotope fractionation associated with volatile losses described in Young et al., (2019) for other elements could also be 658 659 relevant. They are not mutually exclusive with metal/silicate fractionation, and their combined effect on δ^{15} N, N₂/³He and N₂/³⁶Ar need to be investigated experimentally and 660 with first-principle calculations. 661

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665 **6.** Conclusion

MORB and OIB nitrogen isotope data were compiled from the literature. After filtering 666 667 out air-contaminated basalts, and correcting N₂/³He from fractional degassing, δ^{15} N and $N_2/^{3}$ He estimates can be obtained. MORB have $\delta^{15}N \sim 4\%$ and $N_2/^{3}$ He are $\sim 10^{6}$ on average. 668 669 Both , $\delta^{15}N$ and $N_2/^{3}He$ appear invariant across vastly different degrees of mantle source 670 enrichments. Notably, popping rocks have some of the highest K₂O/TiO₂ observed in MORB, but show δ^{15} N and N₂/³He indistinguishable from MORB. The invariant δ^{15} N and N₂/³He are 671 672 fit with slabs containing ~ 0.1 ppm N at most. Slabs are required to show [N] ≤ 0.1 ppm N. mixed in a mantle with ~0.3 ppm N, for invariant δ^{15} N and N₂/³He at varying K₂O/TiO₂ to be 673 674 accounted for. OIB are less well characterized than MORB for the nitrogen systematics. 675 Extremely enriched mantle sources such as seen at the Society plume, where basalts show 676 low ³He/⁴He ratios, are consistent with nitrogen subduction: erupted basalts have elevated δ^{15} N and N₂/³He ratios. On the other hand, OIB with high ³He/⁴He ratio have δ^{15} N between – 677 2 and 0‰, and reconstructed $N_2/^{3}$ He that appear similar to MORB, across varying K_2O/TiO_2 . 678 679 This is not consistent with nitrogen subduction. Overall, published data argue against 680 nitrogen recycling to overwhelm the modern mantle, for at least high ${}^{3}\text{He}/{}^{4}\text{He}$ OIB and MORB 681 sources. Instead, mantle nitrogen with $\delta^{15}N \sim -4\%$ for MORB and between -2 and 0% for OIB, with $N_2/^3$ He ~ 10⁶, appear to be intrinsic features of Earth's interior, mostly 682 683 disconnected from Earth's surface.

This conclusion has implications on the origin of Earth's N: δ^{15} N differences between the mantle and parent bodies similar to enstatite chondrites (or solar gases) may have to be explained without resorting to nitrogen subduction. It may reflect the contribution of carbonaceous chondrites to Earth's nitrogen budget. Alternatively, nitrogen isotope 688 fractionation during planetary formation may have been at play. Subsequent magma ocean 689 degassing under the restricted condition of low fO_2 could potentially yield the $\delta^{15}N$ 690 disequilibrium between the MORB mantle and air. These two reservoirs would then remain 691 broadly unchanged, on account of a limited exchange via subduction. These hypotheses will 692 be largely testable with experimental and theoretical work.

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700 Captions





 K_2O/TiO_2 ratios shown against magnesium oxide concentrations for mid-ocean ridge basalts. Worldwide704MORB data are compiled using the PetDB database (Lehnert et al., 2000). Large symbols are for basalts with705known N isotope composition. For popping rocks, data are combined from Javoy and Pineau (1991), Jones et706al., (2019), Cartigny et al., (2008), Sarda and Graham (1989) and Labidi et al., (2020). For ordinary MORB, data707are from Marty and Zimmermann (1999), Marty and Humbert (1997) and Barry and Hilton (2016). None of the708basalts with published N isotope composition have MgO low enough to indicate titanomagnetite on the liquidus709(MgO ≤ 4%), so their K₂O/TiO₂ are likely good tracers of the mantle source enrichments.



712 Figure 2

713 Published $\delta^{15}N$ data shown against ${}^{40}Ar/{}^{36}Ar$ ratios, for MORB and OIB. Data are compiled in Table 1 714 and 2, and are from the literature as discussed in the main text (Barry and Hilton, 2016; Halldórsson et al., 715 2016; Javoy and Pineau, 1991; Marty and Dauphas, 2003; Marty and Humbert, 1997; Marty and Zimmermann, 716 1999; Sano et al., 2001). On Panel A, worldwide MORB and high ³He/⁴He basalts from Hawaii, Galapagos and 717 Iceland are shown. A mixing curve is drawn between air and the mantle. The curvature of the mixing 718 relationship depends on the $N_2/^{36}$ Ar taken for air and mantle. A large majority of the samples are consistent 719 with mantle endmembers (with ${}^{40}\text{Ar}/{}^{36}\text{Ar} > 5,000$) showing negative δ^{15} N. MORB tend towards a δ^{15} N of ~-720 4‰. High 3 He/ 4 He OIB with the highest 40 Ar/ 36 Ar have δ^{15} N between –2 and 0‰. On Panel B, low 3 He/ 4 He

721 lavas from Society are emphasized. They show distinctly high $\delta^{15}N$ at high $^{40}Ar/^{36}Ar$ ratios.



Figure 3 723

724 725 726 727 728 729 **Basalts N₂/³⁶Ar data plotted against ⁴⁰Ar/³⁶Ar ratios.** The data source is the same as for figure 2. On panel A and B, the same dataset is shown using linear or using logarithm scales, respectively.



732Basalts N2/3He data shown against 40 Ar/36Ar ratios. The data source is the same as for figure 2 and 3.733On panel A, raw N2/3He are plotted. On panel B, N2/3He is corrected for fractional degassing (see text). Only734samples with 40 Ar/36Ar > 500 are shown, thus avoiding the largely elevated N2/3He ratios associated with air735signatures, at 40 Ar/36Ar < 500.</td>





737 **Figure 5**

738 Nitrogen isotope data and $N_2/3$ He ratios for MORB and OIB shown against K_2O/TiO_2 ratios. Only 739 samples with high $\frac{40}{Ar}/\frac{36}{Ar}$ are used. A threshold of $\frac{40}{Ar}/\frac{36}{Ar} > 500$ was used. On panel A, 28 ordinary MORB, 740 3 popping rocks (including two duplicates of $2\pi D43$) and 4 OIB pass the filter, and are plotted. On panel B, the 741 same basalts are plotted, but only a fraction of them have published $N_2/^{3}$ He ratios. This results in only 10 742 ordinary MORB, 1 popping rock (three replicates of $2\pi D43$) and one OIB to be plotted. The reconstructed 743 $N_2/^{3}$ He field for OIB is shown (see text). For MORB, both $\delta^{15}N$ and $N_2/^{3}$ He ratios are invariant across a vast 744 range of mantle enrichment. High ³He/⁴He OIB show a comparable data distribution, although it is much less 745 well known. When $N_2/^{3}$ He ratios are not directly measured (e.g., DICE 10 and 11), or when K_2O/TiO_2 and 746 $N_2/^{3}$ He ratios are not measured on the exact same basalts (e.g., Society samples), fields are shown for 747 illustration. Mixing curves are shown, taking $[N]_{slabs}$ 1 and 10 ppm. Doing so allow a starting $\delta^{15}N$ of the mantle 748 to be similar to enstatite chondrites as done here for illustration, but is allowed to be virtually be any value, 749 including a CI-like or solar $\delta^{15}N$ of +48‰ and -387‰, respectively. This scenario requires improbable [N] and 750 δ^{15} N signatures for recycled components, and fails at explaining the constant N₂/³He ratios of basalts across 751 varying K_2O/TiO_2 .



754 **Figure 6**

755 Nitrogen isotope data and $N_2/^{3}$ He ratios for MORB and OIB shown against K_2O/TiO_2 ratios. Same 756 data as in figure 5. Here, a set of mixing curve is shown, taking $[N]_{slabs} \sim 0.1$ ppm and 1 ppm N. Doing so require 757 the starting δ^{15} N of the mantle to be similar to the modern value. The recycled components are taken with an 758 elevated δ^{15} N (Busigny et al., 2011). Doing so results in flat relationships in both panels. The near-vertical part 759 of the mixing hyperbolae happens to be consistent with the low ³He/⁴He Society basalts, that show elevated 760 δ^{15} N. This is at odds with OIB with high 3 He/ 4 He. Their marginally high δ^{15} N and MORB like N₂/ 3 He do not 761 require nitrogen addition via subduction.

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Figure 7 765

766 **Cartoon showing the constraints on the origin of N in MORB and plume sources**. The cartoon is largely 767 inspired by the illustration in Parai et al., (2019), redrawn for the purpose of this work. Panels A, and B illustrate 768 two snapshots in time. Panel A represents a tentative view of the solid mantle, immediately after the 769 solidification of the magma ocean. Panel B represents modern day.

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