

# The nitrogen record of crust–mantle interaction and mantle convection from Archean to Present

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Received 19 June 2002; received in revised form 28 October 2002; accepted 28 November 2002

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## Abstract

Mantle fluids sampled by mid-ocean ridge basalts and by diamonds are depleted in the heavy isotope of nitrogen, <sup>15</sup>N, by about 3–5 parts per mil relative to atmosphere, suggesting a common nitrogen end-member since at least the Archean. In contrast, deep mantle material sampled by mantle plumes (Kola Devonian magmatic province, Iceland, Loihi Seamount, Hawaii, Society Islands) is enriched in <sup>15</sup>N by up to 8 parts per mil, as are post-Archean sediments. Several independent lines of evidence strongly suggest that mantle nitrogen is mostly recycled. Notably, the ratio between nitrogen and an incompatible lithophile element like potassium is nearly constant between the surface of the Earth and the different mantle reservoirs, whereas the ratio between nitrogen and a noble gas like <sup>36</sup>Ar varies over two orders of magnitude between these reservoirs. We propose that the large-scale N isotope heterogeneity of the mantle results from secular variation of the nitrogen isotope composition of recycled sediments, which is governed by specific metabolic paths having changed with the advent of oxygenated ocean. If this is the case, the contrast between mantle reservoirs reflects a profound change in the mantle convection regime through time. In the Archean, recycled material was stored in a mantle domain sampled by diamonds and by mid-ocean ridges. Starting from the Proterozoic, slabs reached deep, volatile-rich regions of the mantle which are now sampled by mantle plumes.  
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*Keywords:* nitrogen isotopes; mantle convection; Archean; recycling

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## 1. Introduction

The composition and the redox state of the at-

mosphere, hydrosphere, and biosphere might have been largely controlled by exchanges of matter between the surface of the Earth and the mantle [1]. Central to this problem is the evolution of the mantle convection regime through time. Magma generation, mantle degassing, and mantle stirring might have proceeded at a higher rate in a hotter Archean mantle, as suggested by the widespread occurrence of very magnesian komatiites in most Archean greenstone belts [2], as well as by the short survival rate of chemical heterogeneities in

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the Archean mantle [3]. The effect of a higher heat flow on mantle convection and crustal recycling is, however, controversial. Some authors have argued that formation of a thicker basalt crust in a hotter Archean Earth would have prohibited subduction [4]. Other authors have proposed that the Archean crust was formed by accretion and melting of subduction-related material [5], and that subduction occurred at a faster rate than today [6]. Late Archean Re–Os model ages of sulfide inclusions encapsulated in eclogitic diamonds from Kaapvaal craton localities call for subduction of oceanic crust operating at this time [7,8], as do convincing seismic images of late Archean subduction-related accretion [9]. Recent detailed mapping of the Isua supracrustal belt, West Greenland has been interpreted as evidence for modern-like plate tectonics, including subduction processes, at 3.8 Ga [10]. Models of mantle convection advocating periodic transitions between layered and global mantle convection regimes [11,12], together with geochronological evidence that the growth of continental crust has been episodic between quiescent periods of low crustal production and brief episodes of enhanced crustal growth, have led to the suggestion that the Earth history is punctuated by episodes of enhanced exchange between deep and shallow mantle regions [12,13]. Alternatively, it has been suggested that recycled material was able to penetrate into the deep mantle only recently ( $\leq 500$  Ma) [14].

Testing these models requires adequate tracers of crustal recycling from Archean to Present. Nitrogen isotopes are potentially important in this context because there exists a gross isotopic heterogeneity between nitrogen in the mantle sampled by diamonds and mid-ocean ridge basalts (MORB) which are depleted in  $^{15}\text{N}$  relative to atmospheric  $\text{N}_2$  (mantle  $\delta^{15}\text{N} \approx -5\%$ , where  $\delta^{15}\text{N} = [(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{AIR}} - 1] \times 1000$ ) [15–20], and nitrogen in sedimentary and crustal rocks which are enriched in  $^{15}\text{N}$  by a few parts per mil (Fig. 1). The discovery of positive  $\delta^{15}\text{N}$  values in fluid inclusions trapped in minerals from the Kola ultramafic complexes (Russia) which contain plume-like helium and neon could represent the first evidence of recycling of nitrogen into the deep mantle [21]. In this contribution, we explore

the potential of nitrogen isotopes to record secular changes in mantle–crust interactions. We first detail the present knowledge on the N isotopic composition of the different terrestrial reservoirs. We then present new data on ocean island submarine lavas that shed light on the N isotopic composition of the deep mantle. These data suggest that mantle nitrogen is mostly recycled in origin, and that the isotopic composition of sedimentary nitrogen might have varied with time in relation to changes in the environmental conditions at the Earth's surface. In this case the light N isotope end-member of the mantle could represent recycled N having a different composition in the past.

## 2. Nitrogen isotopic composition of the mantle

### 2.1. MORBs and diamonds

Eclogitic, peridotitic, and fibrous diamonds show a distribution of  $\delta^{15}\text{N}$  values ranging from  $-25\%$  up to  $+15\%$ , with a strong mode around  $-5\%$  (see [15–17] and refs. therein, Fig. 1). The  $\delta^{15}\text{N}$  distribution may be due to mixing between a light nitrogen end-member that could represent the primordial signature of the silicate Earth [22], and a heavy nitrogen component originally residing at the Earth's surface and progressively recycled into the mantle. However, the distribution of  $\delta^{15}\text{N}$  values in diamonds may also be due to isotope fractionation occurring during diamond growth. Indeed, it is similar in extent to the range of carbon isotopic variations observed in diamonds which, together with extremely variable nitrogen contents, has been attributed to fractionation processes [23]. The mantle source of fluid-forming diamonds acquired this specific light nitrogen isotope signature ( $-5\%$ ) as far back the Archean, as recorded in 3.3–2.9 Ga Re–Os, Sm–Nd and Rb–Sr model ages of Kimberley diamond inclusions [7,24].

Basalts erupted on the seafloor under considerable hydrostatic pressure contain  $\text{CO}_2$ -rich inclusions representing quenched gas bubbles having concentrated magmatic volatiles before eruption and being preserved from surface-derived contam-

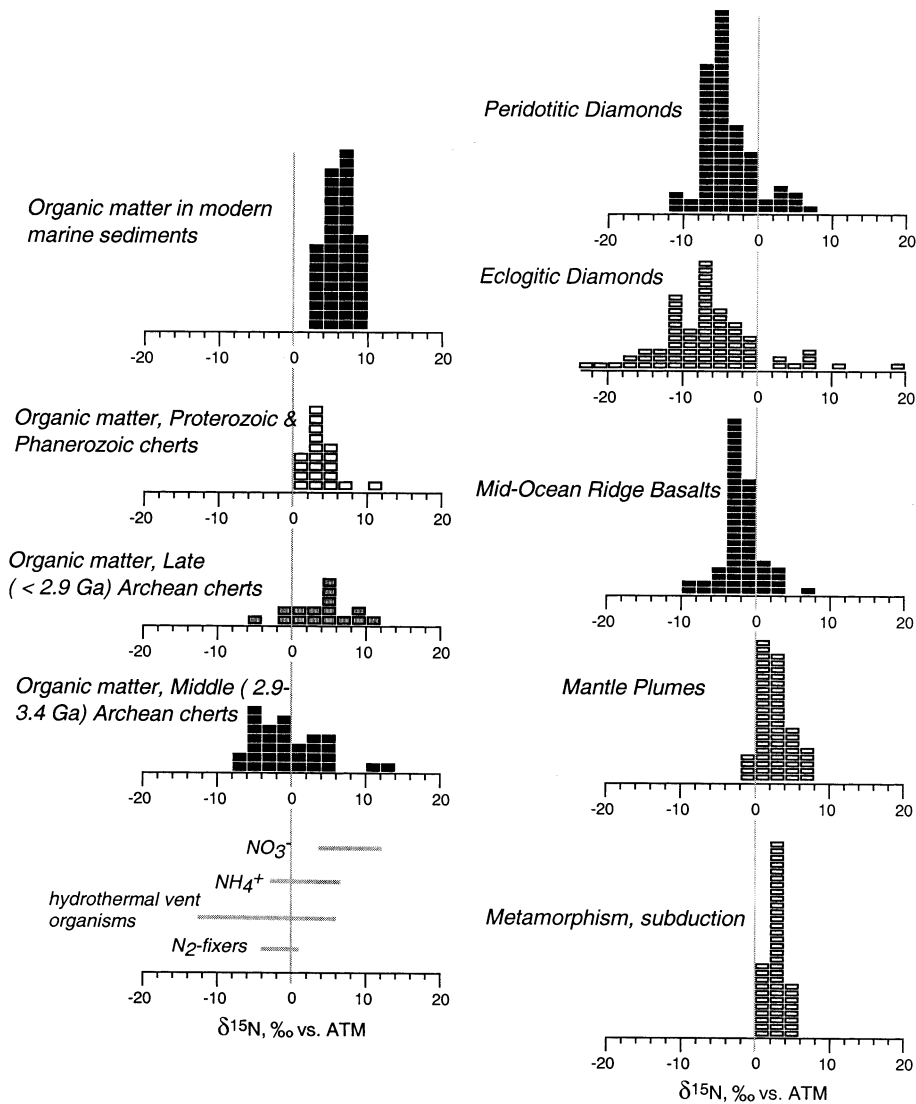


Fig. 1. Variations in the nitrogen isotopic composition of organic matter, sediments, metamorphic rocks and mantle-derived samples. Sources of data: organic matter in marine sediments: [37]; organic matter from Archean–Phanerozoic cherts: [57]; dissolved nitrate and ammonium: [36], [51] and refs. therein; hydrothermal vent organisms: [53,54]; diamonds: [15–17]; MORB: [19,20]; mantle plumes: [21], this work; metamorphic terranes in subduction zone: [39].

ination. Nitrogen and argon extracted by crushing of MORB glasses are correlated, and permit the identification of a mantle source nitrogen end-member depleted in  $^{15}\text{N}$  by 3–5 parts per mil on average [18,19]. The overall resemblance of the  $\delta^{15}\text{N}$  distribution for MORB and diamond data as well as comparable C/N ratios of MORB ( $535 \pm 224$  when corrected for fractional degassing

[20]) and of diamonds (200–500 after correction for fractionation due to diamond growth [23]) strongly suggest that both sets of mantle-derived materials have sampled a common volatile component.

The preservation of negative  $\delta^{15}\text{N}$  values in the MORB mantle requires this reservoir to be efficiently isolated from contribution of recycled ni-

Table 1  
Nitrogen and argon abundances and isotopic ratios of plume-related lavas

Hot spot	Sample	He 10 <sup>-12</sup> mol/g	<sup>3</sup> He/ <sup>4</sup> He R/Ra	±	Ar 10 <sup>-12</sup> mol/g	<sup>40</sup> Ar/ <sup>36</sup> Ar ±	N <sub>2</sub> 10 <sup>-10</sup> mol/g	δ <sup>15</sup> N ‰	±	N <sub>2</sub> / <sup>40</sup> Ar 10 <sup>4</sup>	N <sub>2</sub> / <sup>36</sup> Ar 10 <sup>4</sup>	
<i>Society</i>												
Teahitia	SO47-5DS	152	6.92	0.25	1035	905	23	1327	3.89	1.62	128	12
	SO47-9DS	9.9	6.37	0.25	51.6	329	11	42	0.58	1.64	81	2.7
	TH09-02	230	7.69	0.15	164	348	11	117	1.38	1.62	71	2.5
	TH09-05	1.29	7.52	0.15	40.0	299	9	38	1.35	1.64	96	2.9
	TH12-06	n.a.	n.a.	–	373	468	12	281	0.51	1.63	75	3.5
	TH14-02	12.9	6.73	0.07	161	490	14	152	-0.23	1.63	95	4.6
	TH14-03-4	205	6.27	0.06	312	9995	550	268	1.46	1.63	86	86
	TH14-03-5				590	2231	26	820	7.97	1.29	139	31
	TH14-05	504	6.50	0.07	233	2597	176	208	4.05	1.26	89	23
Mehetia	TH10-04	363	9.24	0.15	420	660	17	328	0.45	1.63	78	5.2
Cyana	SO47-81DS	0.18	1.26	0.06	20.0	417	28	22	5.31	1.64	111	4.6
	TH25-03-4	1.11	1.65	0.03	7.26	5175	2273	4.5	3.58	1.25	62	32
Rocard	SO47-34DS	n.a.	n.a.	–	713	1598	21	659	4.51	1.25	92	15
	TH21	0.05	6.29	0.31	17.2	384	11	13	2.85	1.63	77	3.0
Seamount no. 1	DTH02-01-1	0.53	3.44	0.10	19.3	4786	657	21	6.71	1.61	111	53
	DTH02-01-2	n.a.	n.a.	–	21.5	3156	294	26	6.13	1.77	119	37
	DTH02-01-3	n.a.	n.a.	–	22.0	6681	3304	19	0.40	1.80	88	59
	DTH02-01-4	n.a.	n.a.	–	29.1	1264	48	48	3.51	1.62	165	21
	DTH02-01-5	n.a.	n.a.	–	15.4	5134	913	12	2.28	1.27	76	39
	DTH02-02-1	0.61	1.26	0.04	20.4	7202	683	41	3.38	1.64	200	144
	DTH02-02-2	n.a.	n.a.	–	34.4	3130	390	26	4.18	1.23	76	24
		DTH03-02	7.0	8.31	0.07	10.0	360	10	11	1.33	1.30	115
Seamount no. 3	DTH04-01-1	0.48	1.27	0.04	43.8	592	24	28	5.77	1.64	65	3.8
	DTH04-01-2	n.a.	n.a.	–	56.6	777	22	37	3.46	1.66	65	5.1
	DTH04-01-3	n.a.	n.a.	–	37.4	1641	52	20	1.39	1.65	53	8.6
Seamount no. 4	DTH05-02	0.02	5.51	0.33	1.41	335	45	0.75	3.96	1.26	54	1.8
<i>Cook-Austral</i>												
MacDonald	TH28-07	210	11.16	0.13	17.6	299	13	7.9	2.63	1.65	45	1.3
	TH30-03	3.58	5.62	0.10	949	291	9	823	1.82	1.63	87	2.5
<i>Hawaii</i>												
Loihi	T4D3#3	n.a.	33	–	112	298	4	105	2.07	1.26	94	2.8
	T4D3#7	n.a.	n.a.	–	38.9	305	4	30	1.72	1.29	78	2.4
<i>EPR 15–19°S</i>												
	G324G	n.a.	<i>9.48</i>	<i>0.14</i>	7.21	422	12	14	3.08	1.25	187	7.9
	G296G	n.a.	<i>10.38</i>	<i>0.15</i>	2.39	1095	42	4	1.60	1.28	154	17
	G136D	n.a.	<i>8.21</i>	<i>0.25</i>	15.0	3825	84	32	1.40	1.26	210	80
	G178D	n.a.	<i>8.42</i>	<i>0.14</i>	3.02	618	11	3	1.55	1.26	93	5.7
<i>Iceland</i>												
Subglacial glass	DICE10-10#	n.a.	<i>16.6</i>	–	16.9	1669	119	12	0.23	1.81	74	12
	DICE10-10#	n.a.	–	–	18.9	3203	250	13	0.02	1.83	71	23
	DICE10-10#	n.a.	–	–	34.1	3302	226	26	0.12	1.86	78	26
	DICE11-10#	n.a.	<i>17.6</i>	–	27.4	940	66	18	-0.60	1.94	66	6.2
	DICE11-10#	n.a.	–	–	33.0	3004	218	25	-1.50	1.81	76	23
	DICE11-10#	n.a.	–	–	8.64	1574	127	6	3.26	1.79	70	11
Air			1			295.5			0		84	2.5
ASW						295.5			0		37	1.1

Gases were extracted by vacuum crushing. 100 strokes were applied, except for Icelandic samples for which # refers to the number of strokes. n.a.: not analyzed. He isotopic data in italics are from the literature. Loihi: [33]; Icelandic glasses: [34]; EPR: [35].

trogen since the time of diamond formation. This isolation would contrast with geochemical evidence (e.g., oxygen isotopes [25]) which indicates that some recycled material was added to the

MORB mantle, and that the MORB mantle has been open to geochemical contributions from other mantle reservoir(s) on a timescale of about 1 Ga [26,27]. In agreement with this possibility, the

present data are compatible with a limited contribution of presumably recycled  $^{15}\text{N}$ -rich nitrogen to the MORB mantle. Indeed, the heterogeneity of  $\delta^{15}\text{N}$  values of MORB glasses indicates that the upper mantle is isotopically heterogeneous for nitrogen, and the slightly heavier N isotope composition of MORBs when compared to diamonds (Fig. 1) suggests a progressive shift of the  $\delta^{15}\text{N}$  value of the mantle upon secular recycling of heavy nitrogen, and therefore progressive invasion of the MORB mantle by crustal material recycled in the plume source.

## 2.2. Mantle plumes

Devonian carbonatites and associated mafic minerals from the Kola Peninsula, Russia, contain numerous fluid inclusions having trapped plume-like noble gases ( $^3\text{He}/^4\text{He}$  ratios up to 24 Ra, steep  $^{20}\text{Ne}/^{22}\text{Ne}$ – $^{21}\text{Ne}/^{22}\text{Ne}$  correlation,  $^{40}\text{Ar}/^{36}\text{Ar}$  end-member value of 5000 [28]). These inclusions host nitrogen characterized by  $\delta^{15}\text{N}$  values between 0‰ and +6‰ [21]. In order to document the composition of oceanic island provinces, several well-characterized oceanic plumes have

been investigated for nitrogen and noble gas abundances and isotopic ratios following the method developed in the CRPG-CNRS, Nancy [19]. Society and Cook-Austral volcanic provinces have sampled mantle sources which are enriched in trace elements, radiogenic isotopes and  $^{18}\text{O}$ , and such enrichments are best explained by the contribution of up to 9% recycled crust containing a substantial proportion of pelagic sediments [29–31]. Radiogenic isotope systematics strongly suggest that this recycling leading to such enrichments took place  $\sim 2$  Ga ago [29,30].

Fresh submarine glasses from the Society Islands (Teahitia, Mehetia, Cyana, Rocard and small nearby seamounts [30]) and MacDonal (Cook-Austral) have variable  $^3\text{He}/^4\text{He}$  ratios ranging from 1.3 Ra up to 9.2 Ra (Mehetia) and 11.2 Ra (MacDonal Seamount), illustrating the diversity of the geochemical sources and processes involved (Table 1). All  $\delta^{15}\text{N}$  values are positive up to +8‰ and do not show any relationship with  $^3\text{He}/^4\text{He}$  ratios. Samples showing  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios close to the atmospheric value of 295.5 have most likely been contaminated by surface-derived (sediments, sea water, or local oceanic

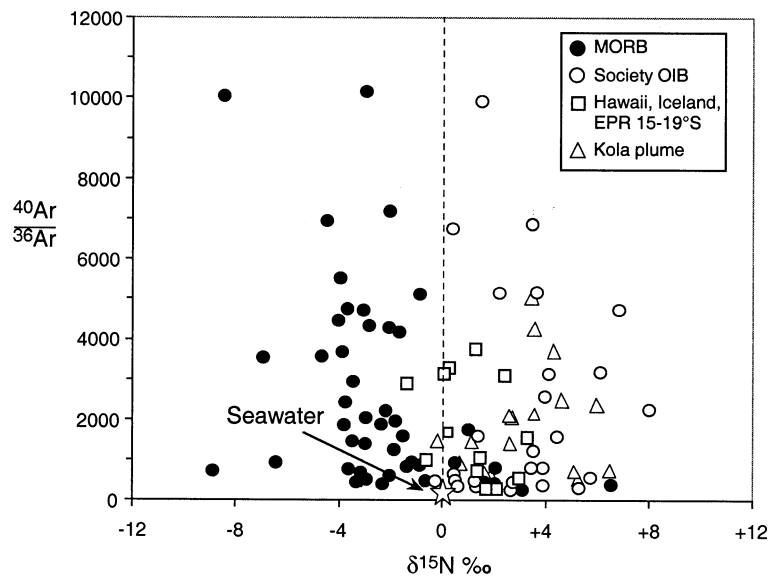


Fig. 2. Variations of  $\delta^{15}\text{N}$  values as a function of  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios in mantle-derived samples. Sources of data: MORBs [19,20]; plume-related samples: ocean island lavas, EPR: this work; Kola plume: [21]. MORB samples having  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios higher than 12000 are not represented, in order to focus the diagram on plume-related data.

crust) volatile elements. Notably, the majority of analyzed plume-related volcanic glasses showing positive  $\delta^{15}\text{N}$  values have  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios much higher than the atmospheric value, indicating extremely limited contamination by atmospheric argon (Table 1, Fig. 2). Some of the lavas presenting elevated  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios together with low  $^3\text{He}/^4\text{He}$  ratios (e.g., seamount samples, Table 1) could have experienced assimilation of old oceanic crust [32]. However, despite great differences in the nature and the thickness of the crustal setting, the distribution of  $\delta^{15}\text{N}$  values of oceanic plume samples (mean  $\delta^{15}\text{N} = +3.0 \pm 2.1\text{‰}$ ,  $n = 28$ , for all samples, mean  $\delta^{15}\text{N} = +4.0 \pm 2.1\text{‰}$ ,  $n = 13$ , for samples with  $^{40}\text{Ar}/^{36}\text{Ar} > 1000$ ) coincides with that of continental plume samples [21] (mean  $\delta^{15}\text{N} = +3.3 \pm 1.8\text{‰}$ ,  $n = 17$ ), demonstrating that plume-type nitrogen sampled either by the Kola plume or by Society and Cook-Austral plumes is most likely of mantle origin, deriving from deeply recycled material.

Further samples from typical plume provinces have been analyzed (Table 1), including submarine glasses from Loihi seamount, Hawaii [33], subglacial glasses from Iceland showing high (primordial)  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios together with high  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios [34], and MORB glasses from the East Pacific Rise (EPR) at 15–19°S showing plume-like He and Ne [35]. In all cases,  $\delta^{15}\text{N}$  values close to 0‰ or slightly positive were observed (Table 1, Fig. 2), which may indicate mixing between a plume-like  $^{15}\text{N}$ -rich component and a MORB-like  $^{15}\text{N}$ -depleted nitrogen end-member supplied by entrainment of upper mantle material, in full agreement with models derived from other trace element and radiogenic isotope systems for Hawaii and Iceland.

### 3. Discussion

#### 3.1. Evidence for nitrogen recycling in the mantle

The major cause of nitrogen isotopic variation is linked to the development of the biosphere. In the oceans, dissolved nitrate is the main form of nitrogen available for metabolism. Kinetic exchange of nitrogen isotopes during dissimilatory

denitrification of  $\text{NO}_3^-$  results in nitrate being enriched in  $^{15}\text{N}$  by 6–7 parts per mil relative to atmospheric nitrogen [36]. Residual nitrate enriched in  $^{15}\text{N}$  can be enzymatically reduced to  $\text{NH}_4^+$  and assimilated by organisms. Thus, marine phytoplankton which is a major source of the organic matter in sediments has mean  $\delta^{15}\text{N}$  values close to +7‰ [36] and marine sediments have positive  $\delta^{15}\text{N}$  values between +2‰ and +10‰ [37] (Fig. 1). Both thermal and biological degradation of organic matter results in the formation of significant quantities of  $\text{NH}_4^+$  that can be fixed by clay minerals in the sedimentary column by substitution to potassium [38]. Notably, high-grade metamorphic mineral assemblages such as those characterizing the amphibolite facies from paleo-subduction zones contain significant (typically a few tens to a few hundred ppm) quantities of ammoniacal nitrogen enriched in  $^{15}\text{N}$  by a few parts per mil [39] (Fig. 1).

There are several geochemical and petrological observations that support nitrogen recycling into the mantle. First,  $\text{N}_2$ -rich fluid inclusions have been observed in mantle xenoliths, and have been attributed to in situ breakdown of ammonium-bearing silicates (phlogopite, amphibole), providing direct evidence that nitrogen has been introduced as ammonium in some regions of the mantle, presumably by subduction [40]. Second, N and noble gas elemental and isotopic abundances in fluid inclusions trapped in continental xenoliths from SE Australia strongly suggest a contribution of volatile elements from sediments subducted during the Paleozoic [41]. Third, recent Ar–Pb ([42], see [43] for an alternative interpretation) and He–Ar [44] investigations suggest that argon can be recycled in limited amounts, contrary to what was previously proposed on the basis of volatile mass balance calculations at arcs (the so-called subduction barrier [45]). Because argon is not chemically bound to the silicate network as nitrogen (in the form of ammonium ion) is, one would expect nitrogen to be much more efficiently recycled than argon, resulting in elevated N/Ar ratios for the recycled component. Fourth, mass balance considerations suggest that nitrogen can be effectively recycled into the mantle during subduction since the amount of nitro-



gen released through arc volcanism is generally lower than the amount of sedimentary and crustal N carried by the subducting plate [46] (although in some cases like the Central American margin both fluxes are similar [47]). Finally, the nitrogen concentrations of the different mantle domains are small, of the order of 1 ppm or less (Table 2) whereas those typical of altered basalts (up to 200 ppm for spilitized submarine basalts) and of metasediments are two orders of magnitude higher. It follows that the isotopic composition of nitrogen in the sources of plumes (1–10% recycled sedimentary/crustal material) will be buffered by that of recycled nitrogen even if only a small fraction ( $\leq 10^{-2}$ ) of nitrogen survives further devolatilization beyond the amphibolite facies. Consequently, the  $\delta^{15}\text{N}$  values of plume-derived samples, which are comparable to those of oceanic nitrates, modern sediments, and high-grade metamorphic minerals from paleosubduction zones (Fig. 1), are best explained by the addition of sediments or altered oceanic crust to the source of plumes as are trace element concentrations, radiogenic isotopic compositions [29], and stable isotopic ratios [31] of oceanic island lavas.

### 3.2. Nitrogen recycling in the Archean?

Nitrogen subducted in the ancient mantle might have had a different isotopic signature. In the oxygen-depleted Archean ocean [1], the nitrogen cycle was probably dominated by chemical and metabolic reactions involving reduced forms of nitrogen. Hence there would have been no enrichment in  $^{15}\text{N}$  due to kinetic isotope fractionation associated with dissimilatory denitrification of  $\text{NO}_3^-$ . When nitrate dissolved in the oceans cannot meet the requirements of the biota in the euphotic zone, certain organisms like cyanobacteria and blue-green algae can directly fix  $\text{N}_2$  or assimilate  $\text{NH}_4^+$ , and these metabolic processes are able to produce negative  $\delta^{15}\text{N}$  values ranging from the atmospheric ratio down to  $-9\text{‰}$  [48–50]. Rau et al. [51] reported negative  $\delta^{15}\text{N}$  values for Cretaceous marine sedimentary sequences containing organic-carbon-rich beds ('black shales') that they attributed to a scarcity of dissolved nitrate resulting in phytoplankton assemblages being

dominated by  $\text{N}_2$ -fixing blue-green algae. Of interest in the Archean context are also metabolic paths characterizing seafloor chemosynthetic ecosystems which derive their energy from the oxidation of inorganic compounds produced during high-temperature seawater–rock interactions along hydrothermal vents [52]. The N isotopic composition of hydrothermal vent species is light, with  $\delta^{15}\text{N}$  values ranging from  $-12\text{‰}$  to  $+4\text{‰}$  [53,54]. Because chemosynthesis might have been the main form of biosynthesis prior to photosynthetic life, the N isotopic composition of Archean organic matter and sediments could have been significantly lighter than that of their Proterozoic–Phanerozoic counterparts [55]. Two recent studies have provided new insights into the nitrogen isotopic composition of Archean organic matter. Pinti et al. [56] identified among a suite of Archean sediments a light N end-member with a  $\delta^{15}\text{N}$  value of  $-7.4\text{‰}$  that they considered to be the pristine signature of organic matter at that time. Beaumont and Robert [57] found that the  $\delta^{15}\text{N}$  values of kerogens extracted from Precambrian cherts vary from essentially negative  $\delta^{15}\text{N}$  values (down to  $-6.2\text{‰}$ ) in the Middle Archean towards positive values in the Late Archean and the Proterozoic, the latter being indistinguishable from the nitrogen isotopic compositions of Phanerozoic samples and in the range of values found in modern sediments (Fig. 1). These authors proposed that the secular change of the nitrogen isotopic composition recorded in cherts was a consequence of the increase in the partial pressure of oxygen during the Late Archean–Early Proterozoic, which allowed the development of modern metabolic nitrogen paths involving oxidized nitrogen compounds. Metamorphism might erase the original light N isotope signature at the time of deposition by favoring retention of  $^{15}\text{N}$  over  $^{14}\text{N}$  [58], but we think that this effect is probably limited. Available data for metamorphic rocks in subduction zones [39] show that the  $\delta^{15}\text{N}$  values are in the range expected for sediments, suggesting that the effect of metamorphism, if any, could be of the order of 1–3‰.

Recycling of isotopically light nitrogen derived from Archean organic matter could account for the  $^{15}\text{N}$ -depleted nitrogen component seen in dia-

monds and in MORB. In the Archean, recycling of nitrogen was probably effective, as Archean sediments contain ammonium of probable biogenic derivation at concentrations comparable to those of modern sediments [59], and because subduction was already active at that time [7,10]. In order to test this possibility, we need to compare the behavior of nitrogen with that of an incompatible, non-volatile element like potassium, and to an incompatible, extremely volatile element like argon.

### 3.3. Nitrogen–argon–potassium systematics

About half of potassium originally trapped in the mantle now resides in the continental crust, as the result of time-integrated extraction of incompatible elements during partial melting of mantle material. A fraction of potassium extracted from the mantle is recycled during oceanic crust subduction since the process of incompatible element extraction at arcs is not 100% efficient. This process is evidenced by the diversity of MORB compositions, including the so-called E-MORBs

which present variable enrichments in incompatible elements like potassium. As discussed previously, there is little doubt that incompatible elements are recycled in the source of mantle plumes (e.g., [60]). In order to compare the behavior of nitrogen and potassium, we compute the N/K ratios of the different terrestrial reservoirs using: (i) estimates for the K contents of these reservoirs [61], and (ii) our own evaluation of the respective nitrogen contents. The measured N contents of mantle-derived lavas are of little relevance for the latter since they represent residual N after magma degassing. A way to turn around this problem is to use the  $N_2/^{40}\text{Ar}$  ratios of the different mantle reservoirs, which are fairly well characterized for MORB and plume samples [20,21,62]. The problem is therefore to estimate the  $^{40}\text{Ar}$  contents of the terrestrial reservoirs. For the MORB mantle, we use the classical approach based on the  $^3\text{He}$  content of the MORB mantle (see Table 2 caption). For the plume source, we assume a closed system condition and compute how much  $^{40}\text{Ar}$  has accumulated from the decay of  $^{40}\text{K}$ . For the continental crust, we use previous

Table 2  
Potassium, argon and nitrogen in Earth

	MORB source	Plume source	Continental crust	Atm.	Atm.+cont. crust	Silicate Earth
K (ppm)	$60 \pm 15$	$370 \pm 90$	$16\,000 \pm 4000$	–	–	$240 \pm 60$
$^{40}\text{Ar}$ (mol/g)	$(8 \pm 4) \times 10^{-11}$	$(1.3 \pm 0.3) \times 10^{-9}$	$(6 \pm 2) \times 10^{-9}$	–	–	$(0.9 \pm 0.2) \times 10^{-9}$
$N_2/^{40}\text{Ar}$	$124 \pm 40$	$74 \pm 34$	$300 \pm 200$	83.6	$88 \pm 7$	$80 \pm 20$
N/K (molar, $10^{-3}$ )	$13^{+11}_{-6}$	$21^{+25}_{-11}$	$9^{+6}_{-4}$	–	$36^{+12}_{-7}$	$22 \pm 5$
$N/^{36}\text{Ar}$ (molar, $10^4$ )	$846^{+417}_{-324}$	$74^{+40}_{-35}$	–	2.47	–	–
N (ppm)	$0.27 \pm 0.16$	$2.7 \pm 1.4$	$50 \pm 25$	–	–	$1.9 \pm 0.7$
$\delta^{15}\text{N}$ (‰ vs. Atm.)	$-5 \pm 2$	$+3 \pm 2$	$+4 \pm 2$	0	–	–
N ( $10^{20}$ mol)	–	–	$0.4 \pm 0.2$	2.8	$3.2 \pm 0.2$	$5.5 \pm 1.9$

The data compiled in this table were derived without resorting to any structural model for the mantle. The potassium concentrations of the different reservoirs are from [61], with an assigned uncertainty of 25%. The  $^{40}\text{Ar}$  concentration in the MORB source was derived using the observed  $^3\text{He}$  flux at mid-ocean ridges of  $1000 \pm 300$  mol/yr [72], a partial melting rate of  $10 \pm 2\%$ , a mid-ocean ridge lava production rate of  $20 \pm 4$  km<sup>3</sup>/yr, the MORB mean  $^3\text{He}/^4\text{He}$  ratio of  $8 \pm 1$  Ra, and the radiogenic  $^4\text{He}/^{40}\text{Ar}$  mantle ratio of  $2.0 \pm 0.5$  [73]. For the plume source, we assumed that this reservoir behaved as a closed system for 4.5 Ga, allowing the radiogenic  $^{40}\text{Ar}$  accumulation due to the decay of  $^{40}\text{K}$ . Knowing the  $^{40}\text{Ar}$  concentrations in the MORB and plume sources, it is then straightforward to compute elemental ratios involving nitrogen using the observed mean  $N_2/^{40}\text{Ar}$  ratios ([20], and this work). For the silicate Earth, we assumed a mean  $N_2/^{40}\text{Ar}$  ratio of  $80 \pm 20$  from the range of limited variations in the other major terrestrial reservoirs. The  $N/^{36}\text{Ar}$  ratios were computed with  $^{40}\text{Ar}/^{36}\text{Ar}$  values of  $35\,000 \pm 10\,000$  for the MORB source (using the popping rock Ne–Ar isotope correlation from [73] with  $^{20}\text{Ne}/^{22}\text{Ne}$  varying from 12.5 to 13.8) and of  $5000 \pm 1000$  for the plume source (considering that the Kola plume Ne–Ar isotope correlation [28] is representative of the plume source). The nitrogen inventories for the crust and the atmosphere are from [63], and that of crustal argon is from [74]. When possible, uncertainties were propagated in the calculations using Monte Carlo simulations. The stated uncertainties are 95% confidence intervals.



estimates from [63]. The results of this exercise indicate that the MORB mantle source, the plume mantle source, and the external reservoirs have comparable N/K ratios of  $13 \times 10^{-3}$ ,  $21 \times 10^{-3}$ , and  $9 \times 10^{-3}$ , respectively, all estimates having uncertainties of about a factor of 2 (Table 2). The comparable N/K ratios of mantle and crustal reservoirs provide strong evidence that nitrogen has a behavior comparable to that of potassium during cycling between the Earth's surface and the mantle.

In contrast, the ratio between nitrogen and  $^{36}\text{Ar}$ , a non-radiogenic noble gas isotope, varies by one to two orders of magnitude among the different terrestrial reservoirs. Indeed the N/ $^{36}\text{Ar}$  ratios of the MORB, plume, and atmospheric reservoirs are  $846_{-324}^{+417} \times 10^4$ ,  $74_{-35}^{+40} \times 10^4$ , and  $2.5 \times 10^4$ , respectively (Table 2). The much lower N/ $^{36}\text{Ar}$  ratio of the atmosphere could be due to preferential retention of nitrogen in the mantle relative to argon. This possibility is substantiated by the N/ $^{36}\text{Ar}$  end-member ratio of the extensively degassed MORB mantle which is one order of magnitude higher than the N/ $^{36}\text{Ar}$  value characterizing the less degassed mantle plume source. The problem is therefore to find an adequate phase which might retain nitrogen preferentially. Under oxygen fugacity conditions relevant to the upper mantle (which might not have been drastically different in the Archean [64]), the only nitrogen-bearing phases that are potentially stable are those accommodating ammonium ions such as amphibole and phlogopite, and these phases are readily destabilized during partial melting [40]. Alternatively, mantle conditions more reducing than today could have played a role in fractionating the N/Ar ratio during magma degassing [62]. However, experimental data on volatile element partitioning between basaltic melt and vapor do not support this possibility as the solubility of nitrogen in basaltic melts is very similar to that of argon in a large range of oxygen fugacities extending from IW-1 to QFM [65], and it is unlikely that the mantle oxygen fugacity could have been lower than IW in the Archean [64]. In the absence of a viable mechanism for fractionating the N/Ar during mantle degassing, we rather propose that the higher N/ $^{36}\text{Ar}$  ratio of the MORB

mantle relative to the plume source was established by nitrogen recycling, the effect of this being more apparent in the volatile-depleted MORB reservoir than the volatile-rich plume reservoir.

It must be noted that a recycled origin for nitrogen in the mantle implies that, before the advent of plate subduction, the mantle N/ $^{36}\text{Ar}$  ratio had to be lower than the present-day value. This possibility is consistent with: (i) N/ $^{36}\text{Ar}$  values of primitive meteorites ( $10^4$ – $10^6$  [66]) lower than the end-member ratio of the MORB mantle, and (ii) preferential trapping of nitrogen relative to noble gases in the core, as nitrogen is siderophile [67] and noble gases are not [68].

### 3.4. Implications for mantle convection through time

As discussed above, several lines of evidence point to a recycled origin for mantle nitrogen sampled by present-day plume-related lavas as well as by MORBs, despite differences in the respective N isotopic compositions. A solution of these contrasting observations is that the isotopic composition of recycled nitrogen has changed with time. Nitrogen metabolized in the Archean might have lacked the  $^{15}\text{N}$  enrichment characterizing modern organic matter [55–57], because the reduced oxygen fugacity at the Earth's surface did not allow the stability of nitrate in the oceans, or because ancient organic matter was dominated by metabolism based on chemosynthesis around submarine hydrothermal vents which are known to produce organics (microbial mats) depleted in  $^{15}\text{N}$  [55]. Nitrogen trapped in Proterozoic and Phanerozoic sediments and kerogens from cherts was enriched in  $^{15}\text{N}$  as are present-day marine sediments [57]. This isotopic fractionation records either the increase in the availability of nitrates in the oceans resulting in modern-like metabolic paths, or the transition from chemosynthesis to photosynthesis, or both. It is tempting to link these profound changes in the nitrogen biocycle processes to the 'Great Oxygenation Event' having taken place presumably around the Archean–Proterozoic transition [1].

The implications of this model for mantle con-

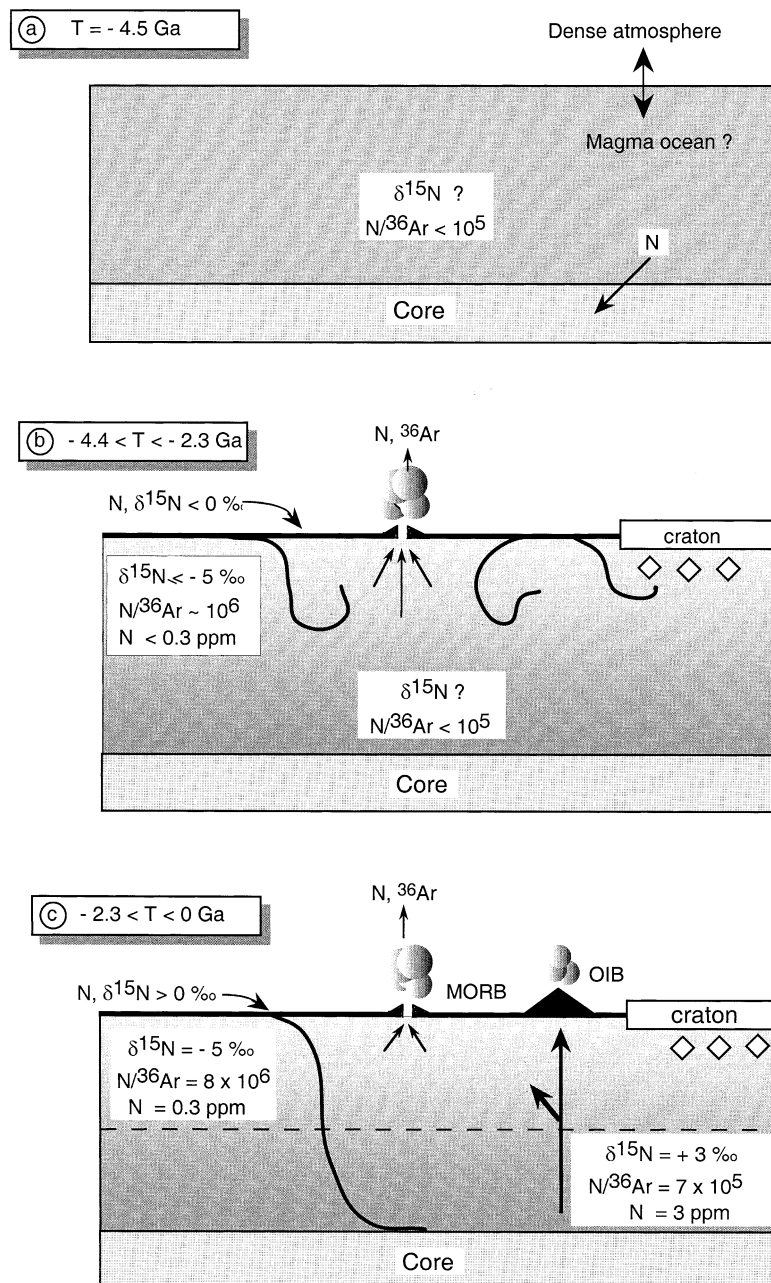


Fig. 3. The geological nitrogen cycle from Archean to Present. (a) 4.5 Ga ago, nitrogen was preferentially partitioned into the core relative to argon, lowering the  $\text{N}/^{36}\text{Ar}$  ratio below  $10^5$ . Knowledge of the initial isotopic composition of mantle nitrogen is not required by the present model. Some remnant of a light N component could still be present in the mantle and could account for the very light N isotopic compositions rarely observed in diamonds [15] or in other mantle-derived minerals [75] (if these compositions are not due to isotopic fractionation). (b) In the Archean, light nitrogen was progressively recycled, mostly in the upper regions of the mantle, and the deep mantle was isolated from downgoing slabs. (c) From the Proterozoic to Present, recycled material transporting nitrogen enriched in  $^{15}\text{N}$  was able to reach the deepest regions of the mantle.

vection are important (Fig. 3). The nitrogen isotope record suggests that there might have been a major change in the mantle convection regime between the late Archean (based on the 2.9 Ga Re–Os age of sulfide inclusions in Kimberley eclogitic diamonds [7]) and  $\sim 2$  Ga, the residence time of recycled crust and sediments in the mantle source of the Society lavas [29] and more generally the typical residence time of recycled material in the source of plumes [69]. In the Archean,  $^{15}\text{N}$ -depleted nitrogen was recycled in large mantle domains and was well mixed due to a high convection rate that might have been 10 times faster than today [3]. A hotter mantle would have prohibited penetration of slabs in the deepest regions of the mantle [12]. Alternatively, subduction of younger and hotter plates in a hotter mantle would have resulted in slab melting and stirring [5] before reaching considerable mantle depth. Both processes might have allowed preservation of deep mantle domains from either contribution of recycled material, or mantle melting and subsequent degassing. The observation that plume-related material contains more primordial noble gases than do MORBs [70] suggests independently that there exist some deep regions of the mantle that have been less involved than the MORB mantle in mantle convection. In the Proterozoic and Phanerozoic, subducted material became enriched in  $^{15}\text{N}$  due to changing environmental conditions at the Earth's surface. This material was able to make its way towards deep regions of the mantle now sampled by plume-related magmas. The possibility of a causal link between the oxygen fugacity at the Earth's surface and the mantle convection regime, as recently proposed [71], is substantiated by the present study.

#### 4. Concluding remarks

The model presented in this contribution makes it possible to address an intriguing problem that was raised by Cartigny et al. [16]. Eclogitic diamonds from Jwaneng and Kimberley, whose genesis presumably involved subduction fluids, present generally negative  $\delta^{15}\text{N}$  with a distribu-

tion similar to that of peridotitic diamonds of purely mantle origin. From this similarity, Cartigny et al. [16] concluded that eclogitic diamonds have trapped nitrogen from the mantle and not from subduction fluids, despite independent evidence that Kimberley eclogitic diamonds have recorded Archean subduction [7]. This paradox is resolved if isotopically light nitrogen represents nitrogen recycled in the Archean as we propose here.

Finally, an inventory of potassium, argon and nitrogen (Table 2) indicates that the amount of nitrogen stored in the silicate Earth is comparable to that contained in the atmosphere. Therefore, unless drastic variations in the amount of nitrogen stored in the mantle occurred in the past, the isotopic composition of atmospheric nitrogen is unlikely to have varied by more than a few parts per mil.

#### Acknowledgements

This work is dedicated to the memory of the late Dr. Stuart Boyd whose expertise in nitrogen isotope geochemistry and illuminating discussions greatly helped us to shape our ideas. This research was supported by several grants from INSU-CNRS. Samples were kindly made available by BRGM-Ifremer. We are grateful to F. Albarède, M. Chaussidon and R.N. Clayton for comments, and to D. Hilton, D. Pinti and F. Robert for their constructive reviews. **[BARD]**

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