Discussion


Pierre Cartigny *, Magali Ader

Laboratoire de Géochimie des Isotopes Stables, UMR CNRS 7047, Institut de Physique du Globe and Université Paris 7, 2 Place Jussieu, 75251 Paris Cedex 05, France

Received 23 April 2003; received in revised form 8 June 2003; accepted 30 July 2003

© 2003 Published by Elsevier B.V.

Keywords: nitrogen isotopes; Archean; recycling; mantle

1. Introduction

The Earth’s upper mantle is depleted in $^{15}$N isotope, with a $\delta^{15}$N value around $-5\%_o$ [where $\delta^{15}$N = ($^{15}$N/$^{14}$N$_{sample}$/$^{15}$N/$^{14}$N$_{Air}$ -- 1)1000], relative to atmosphere and crust. The $^{15}$N-depleted character first identified from recent (i.e. $<380$ Ma) diamonds ([1–3], see [4] for review) was confirmed by studies focusing on volatiles extracted from Mid-Ocean Ridge Basalts (MORB) vesicles [5–8]. Archean diamonds as old as 3.2 Ga ([9], for review see [10] and references therein) confirmed the negative $\delta^{15}$N values, showing that the $^{15}$N-depleted character of the Earth’s upper mantle is a long term feature [11,12]. If the nitrogen present within the external reservoirs of the Earth (i.e. atmosphere, sediments and crust) had been simply outgassed from the mantle, then one would expect them to display also negative $\delta^{15}$N values. However, the atmosphere, sediments and crust have all $\delta^{15}$N $\geq 0\%_o$. In addition, the fractionation of N-isotopes occurring during basaltic melt degassing at ridges is opposite to what would be required to achieve positive $\delta^{15}$N in vesicles ([8,13], see below and [1,14] for discussion). Accordingly, there is a so-called isotopic imbalance of nitrogen between the mantle and the external reservoirs of the Earth (Fig. 1) which cannot be accounted for by outgassing of the Earth’s mantle only.

Several models have been proposed to account for the nitrogen isotopic imbalance (see Fig. 1): (1) a heterogeneous accretion of the Earth’s volatiles (e.g. [15]), (2) core-mantle isotopic fractionation [7,13], (3) hydrodynamic escape and fractionation of the atmospheric nitrogen [6], and (4) the new model presented by Marty and Dauphas [16] who consider that the nitrogen now present in the different mantle reservoirs is dominantly recycled organic nitrogen. According to these authors, the nitrogen in the upper mantle, as sampled by diamonds and MORB, has a $\delta^{15}$N value around $-5\%_o$ because it contains nitrogen of organic origin recycled in the Archean which would have had a $\delta^{15}$N around $-5\%_o$. The nitro-
gen of the deeper mantle, as sampled by ocean island basalts (OIB, their study) and carbonatites from Kola [17], they suggest, would have positive N\textsuperscript{15}N values around +3 because nitrogen of organic origin recycled after 2.3 Ga has such values. According to Marty and Dauphas, the initial nitrogen content of the Earth’s mantle as a whole would be negligible (e.g. primordial nitrogen would contribute less than 10% of the present-day inventory of the upper mantle) because most of the primordial nitrogen would be sequestered into the core. In addition, these authors propose that two mantle domains (upper and deeper) would have distinct \(\delta^{15}N\) values because the change in recycled \(\delta^{15}N\) values through time would be almost concomitant with a change in the convection mode of the Earth’s mantle at about 2.3 Ga, allowing the nitrogen isotopic heterogeneity to survive.

The model developed by Marty and Dauphas [16] relies heavily on a sequence of assumptions that deserves closer examination. In the present comment, two of these assumptions are considered in detail and the consequences of the proposed model are criticised.

2. Assumption 1: Nitrogen isotope fractionation during degassing does not occur

In their model, Marty and Dauphas completely ignore isotopic fractionation associated with degassing and assume that the \(\delta^{15}N\) values measured in OIB are representative of the deeper mantle. They consider that the positive \(\delta^{15}N\) values of OIB (mean \(\delta^{15}N = +3.0 \pm 2.1\%\), mean \(\delta^{15}N = +4.0 \pm 2.1\%\) for samples with \(^{40}\text{Ar}/^{36}\text{Ar} > 1000\) [16]) characterise a reservoir different from MORB (mean \(\delta^{15}N = -5 \pm 2\%\) [16]). Whilst this conclusion may be correct for rare gas systematics, it is not necessarily the case for nitrogen.

During basaltic magma ascent, carbon supersaturates and the light volatile stable isotopes of carbon, nitrogen and hydrogen partition between the magma and exsolved phase (i.e. the vesicles). In particular, fractionation of carbon isotopes during degassing in MORB or OIB magmas (i.e. between CO\textsubscript{2} in vesicles and carbonate ions dissolved in the melt) is well established, for example, by calculation (e.g. [18]), by experimental measurements (e.g. [19–21]) or by empirical determinations (e.g. [22–25]). In consequence, \(\delta^{13}C\) values of both MORB and OIB depend on source characteristics and the scale and mode of degassing. It is unfortunate that despite the cumulative evidence, it is still sometimes assumed that MORB or OIB \(\delta^{13}C\) values demonstrate source characteristics, when [26] emphasised that such simplifications lead to serious internal inconsistencies.

Similarly, the fractionation of N-isotopes dur-
ing degassing also cannot be neglected as it would lead any N-isotopic variability being assigned to source heterogeneity. $^{15}$N values are strongly correlated with other indices of degassing (e.g. $^{13}$C, C/Ar ratio) in MORB vesicles demonstrating that N-isotopes do fractionate during degassing, variations being incompatible with mixing relationships [8]. Previously, Exley and coworkers [13] pointed out that "the wide range in $^{15}$N may reflect in part heterogeneities in the mantle ... [but] ... it is possible however that magmatic degassing processes have also affected N-isotope compositions" (see also [14] for other examples). Vesicles are depleted by about 1.5‰ relative to dissolved nitrogen and, therefore, residual nitrogen is enriched in $^{15}$N-isotope with increased degassing.

It is possible to model the evolution of $^{15}$N during degassing in OIB magmas. The equations and parameters used for the present computation are presented in Table 1. $^{13}$C and C/Ar values are from the literature but the N$_2$/Ar ratio and $^{15}$N value are those proposed by Marty and Dauphas for MORB (Table 1). The variations have been modelled using open-system degassing following [27] but if a two-stage model had been used [8,22] the conclusion would have been the same. Fig. 2 shows that $^{15}$N up to +3‰ can be produced from a source with $^{15}$N $\approx$ −5‰ (remaining fraction of nitrogen $\sim$ 0.5%). The values interpreted by Marty and Dauphas as reflecting the deep mantle isotopic composition could well result from degassing a magma having initial MORB-like $^{15}$N $\approx$ −5‰.

To demonstrate that positive $^{15}$N values in OIB are not a consequence of degassing, the authors would require the use of reliable degassing indices such as He/Ar ratio which, due to the

| Table 1 |
|---|---|
| Summary of the different solubilities $S_i$ (in cm$^3$ g$^{-1}$ bar$^{-1}$) and fractionation factors for C- and N-isotopes (in ‰) |
| Values |
| $^{13}$C (‰) | −5.0 |
| $^{15}$N (‰) | −5.0 |
| C/N$_2$ | 400 |
| N$_2$/Ar | 125 |
| C/Ar | 50000 |
| $\Delta_c$ | 3.5‰ |
| $\Delta_N$ | −1.6‰ |
| $S_c$ | 2.56 x $10^{-4}$ |
| $S_{N_2}$ | 5.12 x $10^{-5}$ |
| $S_{Ar}$ | 6.14 x $10^{-5}$ |

Initial volatile characteristics, $^{13}$C, $^{15}$N and molar C/N$_2$, C/Ar, N$_2$/Ar ratios are taken from Marty and Dauphas and the literature. The evolution of the concentration of i (C, N, Ar) in the magma or in the vesicles for open (i.e. Rayleigh distillation) system degassing is expressed as follows [28]:

$$C_{\text{melt}}^{i}/C_{\text{melt}}^{0} = C_{\text{ves}}^{i}/C_{\text{ves}}^{0} = \left( V' + \rho S_i T_{C_i} T_0 \right) \left( V' + \rho S_i T_{C_i} T_0 \right)$$

and

$$C_{\text{melt}}^{i}/C_{\text{melt}}^{0} = C_{\text{ves}}^{i}/C_{\text{ves}}^{0} = \left( V' + \rho S_i T_{C_i} T_0 \right) \left( V' + \rho S_i T_{C_i} T_0 \right),$$

respectively.

The isotopic composition ($\delta_i$) of i in the magma is related to its remaining fraction $f$ in the melt as follows [22,23]:

$$\delta_{\text{melt}} = \delta_{i} + \Delta_i \times \ln f,$$

where $\Delta_i$ is the equilibrium fractionation factor of i between the vesicles and the melt $\Delta_i = \delta_{\text{ves}} - \delta_{\text{melt}}$.

The open-system degassing is simulated by removing the gas phase in 0.01% increments.

---

Fig. 2. Illustration of the $\delta^{15}$N variations associated with $\delta^{13}$C, C/Ar-molar and N$_2$/Ar-molar ratios in melt and vesicles produced during open-system degassing of a basaltic magma. Parameters and equations used in the calculation are reported in Table 1. Grey fields illustrate the range in $\delta^{15}$N and N$_2$/Ar which can be produced during degassing.
great difference of He and Ar solubility ($S_{\text{He}}/S_{\text{Ar}} \approx 10$), itself strongly depends on degassing (e.g. [27,28]). However, He/Ar* ratios below the production ratio (i.e. $\approx 1.5$) are commonly observed among OIB (e.g. [29], see table 1 in [16]) which implies that some helium is clearly missing. The reason is not well understood yet, but is possibly pointing out to a loss of helium either in the magma chamber or during gas extraction or sample baking (see [30]). In other words, it is not possible to evaluate the respective roles of source heterogeneity and degassing on the $\delta^{15}$N signature of the OIB source from the authors sample set. Furthermore, because N$_2$ and Ar have similar solubilities [6,8,28,31], N$_2$/Ar ratios cannot actually be used as an index of degassing, but lower N$_2$/Ar ratios (down to 50) of OIB can be explained by degassing without having to call upon a source different from MORB (see Fig. 2). Additionally, the influence of degassing on the $\delta^{15}$N signature of plume-type magma cannot be constrained from the data on carbonatites, as no solubility data for noble gases in carbonatitic magmas are available.

Finally, it should be pointed out that previously published data by Marty and Humbert [6] on OIB, but not considered in the present work [16], show ubiquitous negative $\delta^{15}$N values for Galapagos and the McDonald Seamount. In particular, one of these samples (PL2-RC-01) referred to as plume-type by [6] yielded a negative $\delta^{15}$N value of $-1.9\%$ and a high $^{40}$Ar/$^{36}$Ar of 2635. Also, there are even in Marty and Dauphas’ present sample set negative $\delta^{15}$N values. In sample Dice10-11, for example, the nitrogen recovered during a crushing experiment shows a $\delta^{15}$N ranging between $-1.5\%$ and $+3.3\%$. Such an isotopic variation in a single sample is unlikely to reflect source heterogeneity and further points out to nitrogen stable isotope fractionation during degassing.

3. Assumption 2: Recycled nitrogen in the Archean had a mean $\delta^{15}$N value of $\approx -5\%$

The model developed by Marty and Dauphas relies heavily on the nitrogen isotopic composition of organic matter in the Archean. They consider that early Archean organic matter had a $\delta^{15}$N of $\approx -7\%$. Subsequent metamorphism would have led to a weak enrichment in $^{15}$N of about $+1$ to $+3\%$ (e.g. [36-38]). Thus the nitrogen recycled in the mantle in the Archean would have a mean $\delta^{15}$N of $\approx -5\%$.

Very little nitrogen data are available for the Archean, and whether cyanobacteria and/or chemosynthetic were the dominant available organisms remains unknown. Marty and Dauphas assume the dominant ecosystems were chemosynthetics. The authors then use an Archean $\delta^{15}$N of $\approx -7\%$ for their model on the basis that modern chemosynthetics present negative $\delta^{15}$N values down to $-12\%$. The available nitrogen data from the present day chemosynthetics, however, are far from being exclusively negative with $\delta^{15}$N up to $+4\%$. It is therefore difficult to understand how the value of $-7\%$ for Archean organic matter $\delta^{15}$N was derived, especially since chemosynthetics might not be the dominant organisms which would lead to higher $\delta^{15}$N values (see for example the discussion in [16] and references therein). The authors consider the two published studies on Archean organic matter [32,33] as supporting the $\delta^{15}$N value of $-7\%$ for Archean organic matter.

The two published studies on Archean organic matter [32,33] both show a range from negative to positive values of $\delta^{15}$N (see Fig. 3f). In the case of Pinti et al. [33], the nitrogen from Archean metasediments was extracted using a step-heating procedure. For all samples, the nitrogen released at low temperature had negative or near atmospheric $\delta^{15}$N (i.e. likely reflecting either modern atmospheric or organic contaminations). For all but one sample, the nitrogen extracted at high temperature showed positive $\delta^{15}$N (mostly between $+2$ to $+9\%$). The authors concluded that positive values reflect either fixation of nitrogen as atmospheric NH$_3$ dissolved in the ocean or trapping of hydrothermal effluents enriched in NH$_4^+$ [33]. Only one sample, that was the specimen least subject to metamorphism, shows a negative $\delta^{15}$N of about $-7\%$. This single negative $\delta^{15}$N value was interpreted by Pinti et al. as reflecting either pristine organic nitrogen or alternatively the incorpo-
ration of mantle volatiles from a hydrothermal vent environment [33].

In the second paper, Beaumont and Robert [32] extracted kerogen from early Archean to late Proterozoic cherts using HF/HCl attack technique and analysis of residue by sealed-tube combustion. The authors found that $^{15}$N values of kerogen from early Archean to Phanerozoic had increasing mean $^{15}$N values with time (Fig. 3a-e). Early Archean cherts (33 analyses from 12 samples are plotted on Fig. 3e) have $^{15}$N values ranging from $-6.2$ up to $+13.0\%$ with mean around $0\%$ (when metamorphism cannot be invoked, see below) considering the lowest $^{15}$N value around $-7\%$ as representative of early organic nitrogen is convincing. A further consideration, omitted by Marty and Dauphas, are the available data on nitrogen isotope compositions in bulk metasediments. Bulk metasediments integrate both the mean organic nitrogen $^{15}$N and $^{15}$N metamorphic enrichment. As noted earlier, according to Marty and Dauphas, pristine Archean organic matter has a $^{15}$N value $\sim 37$ with a metamorphic enrichment of $+1$ to $+3\%$ in $^{15}$N during metamorphism, a significant proportion of Archean metasediments should display negative $^{15}$N. Nitrogen isotope data obtained on the most metamorphosed samples by Pinti et al. were all positive $^{15}$N (Fig. 3f), this being supported by further recent studies (Fig. 3g). The recycling of metamorphic nitrogen with $^{15}$N value of $-5\%$ is therefore clearly unsupported by the available data.

4. Implications on our understanding of diamond formation

Most eclogitic diamonds have negative $^{15}$N values (Fig. 1 in Marty and Dauphas, but note that eclogitic and peridotitic $^{15}$N distributions have been interchanged). As presently subducted nitrogen is characterised by positive $^{15}$N values, it was argued that eclogitic diamond formation is mantle-related (e.g. [12]). However, based on O-isotopes [39,40] and S-isotopes [41,42], some eclogite nodules found in kimberlites are considered showing an internal $^{15}$N variation of more than $20\%$, from $-6.2$ up to $+13.0\%$. When compared with early Archean to late Proterozoic cherts, $^{15}$N values are unambiguously higher (Fig. 3).

Hence, the two studies on Archean (meta)sediments yielded negative $^{15}$N values down to $-7\%$, but also the positive $^{15}$N values are ubiquitous in both sample sets and early Archean cherts are clearly centred around $0\%$ ([32], Fig. 3e). As a single sample can show extreme $^{15}$N variations of more than $20\%$ from $-6.2$ up to $+13.0\%$ (when metamorphism cannot be invoked, see below) considering the lowest $^{15}$N value around $-7\%$ as representative of early organic nitrogen is unconvincing.

A further consideration, omitted by Marty and Dauphas, are the available data on nitrogen isotope compositions in bulk metasediments. Bulk metasediments integrate both the mean organic nitrogen $^{15}$N and $^{15}$N metamorphic enrichment. As noted earlier, according to Marty and Dauphas, pristine Archean organic matter has a $^{15}$N value $\sim 37$ with a metamorphic enrichment of $+1$ to $+3\%$ in $^{15}$N during metamorphism, a significant proportion of Archean metasediments should display negative $^{15}$N. Nitrogen isotope data obtained on the most metamorphosed samples by Pinti et al. were all positive $^{15}$N (Fig. 3f), this being supported by further recent studies (Fig. 3g). The cycling of metamorphic nitrogen with $^{15}$N value of $-5\%$ is therefore clearly unsupported by the available data.
to be Archean recycled oceanic crust (but note the contribution by [43]). This dichotomy is reconciled by Marty and Dauphas by postulating that isotopically light nitrogen (i.e. mean $\delta^{15}N \approx -5\%$) represents nitrogen recycled in the Archean. Their model would therefore reconcile the negative $\delta^{15}N$ values and subduction-related formation of the Archean eclogitic diamonds from Jwaneng and Kimberley [16]. In consequence, no mantle contribution would thus be required.

From the arguments developed earlier in the present comment (see Section 3), the existence of an isotopically light nitrogen recycled in the Archean appears unsubstantiated. In addition, the available data from Jwaneng eclogitic diamonds indicate formation ages ranging from the Archean and extending to the Proterozoic (i.e. 2900 to 1500 Ma; see table 2 in [10] and references therein). The model developed by Marty and Dauphas would thus predict the occurrence of some positive $\delta^{15}N$ values within Jwaneng eclogitic diamonds, which are not found (see [44]). Furthermore, eclogitic diamonds of Archean age from Kimberley [45] ought to have only negative $\delta^{15}N$ values. Within this dataset, positive $\delta^{15}N$ values occur [12]. Currently, there is no paradox, as increasing evidence shows that diamond formation is closely associated with metasomatic episodes during mantle-derived fluids or melts percolating e.g. recycled oceanic crust (see [46,47]). The origin of carbon and nitrogen in diamonds is thus likely decoupled from that of the eclogite-forming silicates, oxides and sulfides.

5. Concluding remarks

In the absence of constraint on degassing, we find no support for Marty and Dauphas’ requirement in separate nitrogen isotope reservoirs within MORB and OIB. We further find no support that Archean recycled nitrogen had mean $\delta^{15}N \approx -5\%$.

In the perspective of future studies, as initiated by Boyd and Philippot [48], we believe that the Earth’s atmosphere, sediments and crust secular $\delta^{15}N$ evolutions (if any) are probably best recorded in the continental crust and its sediments rather than present-day OIB and 370 Ma carbonatites.

Acknowledgements

Danièle Velde, Jeff Harris and Manuel Moreira are thanked for their comments on and improvements to a preliminary version of this comment. Gray Bebout and David Hilton are thanked for their constructive reviews. This is IPGP Contribution 1939.

References


