Quantification and isotopic analysis of nitrogen in rocks at the ppm level using sealed tube combustion technique: A prelude to the study of altered oceanic crust

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Abstract

The present paper reports recent improvements in sealed tube combustion technique used for the determination of N isotopic composition in various rocks characterized by low N contents (i.e. few ppm). Nitrogen is extracted from samples by combustion in quartz tubes sealed under vacuum. The nitrogen gas purified using Cu, CuO and CaO, is quantified as dinitrogen N_2 by capacitance manometry in ultra-high vacuum line. Nitrogen isotopic analysis is performed on a triple-collector static vacuum mass spectrometer, allowing measurement of nanomole quantity of N_2. Nitrogen amount and isotopic composition of the analytical blanks are low and describe Gaussian distribution with mean values of 0.65 ± 0.30 nmol N and $-3.7‰ \pm 2.7‰$, respectively (2σ). Systematic analyses of international and internal standards demonstrate that this technique provides accurate and precise results. The precision on N content and isotopic composition are better than $\pm 8\%$ and $\pm 0.5‰$ respectively, even for samples containing less than 2 ppm N. The sealed tube combustion technique is shown to apply successfully to rocks of various lithologies such as metagabbros, metaperidotites and altered basalts. It is thus suitable for studying oceanic crust in a perspective to better constrain N exchanges between Earth mantle and surface reservoirs. The investigation can also be extended to analysis of small size samples, particularly when little sample exists and when high spatial resolution is required.
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1. Introduction

Nitrogen has two stable isotopes, ^{14}N and [15]N. Because N isotopes are neither radiogenic nor radioactive, N isotopic composition of natural samples is only modified after mixing and/or fractionation related to physico-chemical processes. In Earth Sciences, N isotopes system has been applied to various environments. For instance, it was used successfully to trace (i) hydrocarbon production and migration during sediment diagenesis process (e.g. Williams et al., 1992), (ii) devolatilization and fluid–rock interactions attending metamorphism (Haendel et al., 1986; Bebout and Fogel, 1992; Bebout, 1997; Mingram and Bräuer, 2001; Busigny et al., 2003a), and (iii) to reconstruct paleoecological and paleodepositional history (Lajtha and Michener, 1994). One of the most exciting and debated issue of N geochemistry studies concerns global geodynamic cycle (e.g. Javoy, 1998; Pinti, 2002; Cartigny and Ader, 2003; Marty and Dauphas, 2003;

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Kerrich and Jia, 2004). Nitrogen of the Earth mantle is depleted in ^{15}N relative to surface reservoirs (atmosphere, hydrosphere and crust). Because of these different isotopic compositions, N is potentially a powerful tracer of exchanges between mantle and exosphere. Surface material recycled to the mantle via subduction zones should have positive $\delta^{15}N$ value ($\delta^{15}N_{sample}$ (‰) = [($^{15}N / ^{14}N)_{sample} / (^{15}N / ^{14}N)_{standard} - 1] \times 1000$, 1000, where the standard is atmospheric N_2), very distinct from the negative $\delta^{15}N$ values measured in most mantle rocks. Constraining exchanges between mantle and exosphere requires systematic studies of rocks forming oceanic lithosphere (i.e. sediments, basalts, gabbros and peridotites). Contrasting with growing literature data on sediments and metasediments (e.g. Haendel et al., 1986; Bebout and Fogel, 1992; Mingram and Bräuer, 2001; Busigny et al., 2003a), N isotopes system in (meta)mafic and (meta)utramafic rocks remains poorly studied — a consequence of the difficulty to determine precisely and accurately N content and isotopic composition in rocks containing only few ppm of N. To date, only fresh basalts were investigated either by crushing (e.g. Javoy and Pineau, 1991; Marty and Zimmermann, 1999; Cartigny et al., 2001) or pyrolysis techniques (Sakai et al., 1984; Exley et al., 1987; Marty et al., 1995) but data on altered basalts, gabbros and serpentinized peridotites are still lacking. A previous work has been conducted on metamafic and meta-ultramafic rocks metasomatized in an accretionary complex (Bebout, 1997). However, this study demonstrated that N, which occurred mainly as ammonium (NH_4^+) in micas, was likely added from nearby devolatilizing metasediments and did not reflect primary signature of rocks (Bebout, 1997).

Conventional methods for bulk analyses of N in rocks or minerals are based either on the decomposition of samples in acid solutions (Haendel et al., 1986; Williams et al., 1992; Mingram and Bräuer, 2001; Bräuer and Hahne, 2005), or on combustion or pyrolysis techniques under vacuum (Kendall and Grim, 1990; Bebout and Fogel, 1992; Boyd et al., 1994; Boyd, 1997). Elemental analyser coupled to a mass spectrometer (EA-MS) has been used as a rapid and simple alternative to these conventional methods (e.g. Jia et al., 2003) but a comparative study recently illustrated that EA-MS may not be able to extract all lattice bounded N and still requires improvement (Bräuer and Hahne, 2005). Sealed tube combustion is likely the most standard technique and can be considered as reference. It can be used systematically for cross-calibration of other techniques like Kjeldahl digestion, EA-MS, stepheating or pyrolysis (Minagawa et al., 1984; Bräuer and

Hahne, 2005; Ader et al., submitted for publication). The sealed tube combustion method was originally developed for organic biogeochemical studies in order to analyze $\delta^{15}N$ and $\delta^{13}C$ simultaneously (e.g. Minagawa et al., 1984). Bebout et al. modified this technique to investigate N isotopes in silicates minerals and wholerock samples (Bebout and Fogel, 1992; Bebout, 1997; Sadofsky and Bebout, 2000; Bebout and Sadofsky, 2004; Idleman et al., 2004). The minimum N concentration that may reliably be analyzed is ~10 ppm (Bebout and Sadofsky, 2004), which is still insufficient for analysis of basalts, gabbros and peridotites. This minimum concentration is practically imposed by the use of dual-inlet mass spectrometry, requiring fairly large amount of N for isotopic analysis (>1 μmol N; for details see Bebout and Sadofsky, 2004). This problem can be overcome by means of static vacuum mass spectrometry, which allows N analysis at the nanomole level (e.g. Boyd and Pillinger, 1990; Boyd et al., 1994; Boyd, 1997). The only drawback of the method is a slight loss of precision on the isotopic measurement compare to dual-inlet mass spectrometry. Boyd (1997) described a technique involving sealed tube pyrolysis and static mass spectrometry, which was used to measure N in single micas crystals. The present contribution reports recent progresses of this previous experimental procedure. Combustion was preferred rather than pyrolysis because it provides more reproducible results for low N quantities (~10 nmol; Ader, 1999). The main goal of the present work is to provide a sealed tube combustion technique characterized by low analytical blanks in order to allow isotopic measurements of samples containing only few ppm of N. Accuracy and precision of the technique are evaluated by several tests performed on international and internal standards. The sensitivity of the technique is estimated from replicate analyses of rock samples containing very low N content. A body of evidence indicates that N is successfully extracted and isotopically analyzed in various rock types, including metasediments, metagabbros, altered basalts and metaperidotites.

2. Experimental section

2.1. Sealed tube combustion

This technique is based on a combustion of the samples (either as separate mineral or rock powder) in tubes sealed under vacuum, followed by a chemical separation of the different gas products using CuO, Cu and CaO (Kendall and Grim, 1990; Boyd et al., 1994, 1995). The temperatures and degassing times of

the analytical protocol have been optimised in order to improve the sensitivity and reproducibility of the measurements. The replacement of diffusion pumps by turbomolecular pumps on the vacuum line also contributed to decrease significantly analytical blank size. A detailed description of the protocol is given below.

Quartz glass tubes (OD 6 mm, ID 4 mm, 250 mm in length) are closed at one end and heated for 1 h at 1200 °C in a muffle furnace to remove any modern organic matter. Subsequently, ~15 mg of CaO granules (0.5–1 mm) prepared following Boyd et al. (1994) and 120 mg of Cu and CuO wires (0.7 mm in diameter) are loaded in the quartz tubes and degassed at 650 °C for 48 h on a vacuum line (Fig. 1a). The tubes are then sealed under vacuum and heated in a muffle furnace at 950 °C for 6 h followed by a step at 600 °C for 2 h in order to pre-purify the reagents.

The samples (1 to 50 mg) are embedded in platinum foils previously cleaned by heating for 1 h at 1200 °C in air in a muffle furnace. They are loaded in the side arm of the preparation line (Fig. 1b). At the same time, the quartz tubes containing the reagents are opened to air, quickly connected to the preparation line and heated at 650 °C for 12 h under vacuum. The next step is repeated three times in order to further purify reagents: the preparation line is isolated from the pumps and flooded with O_2, generated by the heating at 900 °C of the CuO together with the tubes containing the
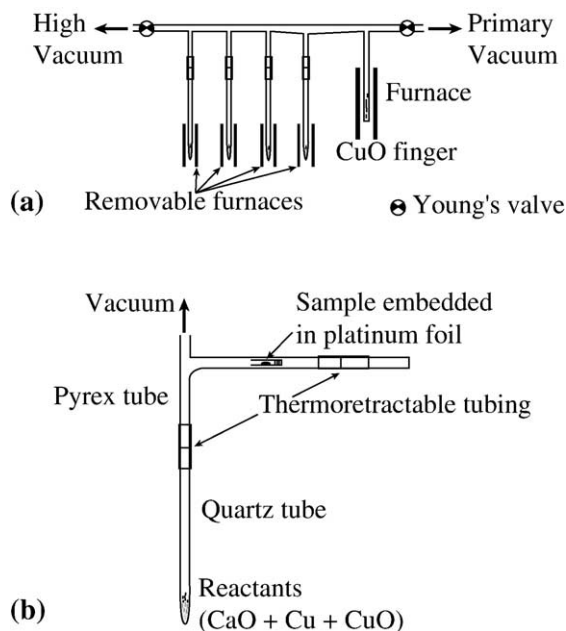

(a)

(b)

Fig. 1. Schematic diagram of the vacuum line used for the preparation of sealed tubes. (a) Front view of the preparation line. (b) View in profile showing one of the sample preparation vessels.

reagents. After 1 h, O_2 is re-adsorbed by cooling the CuO and the tubes to 450 °C and the line is evacuated.

When the line is evacuated to pressure lower than 10^{-6} Torr, the samples are dropped on the top of the reagents (Fig. 1b) and degassed at 450 °C during 12 h. The line is then isolated from the pumps and saturated with O_2 pressure generated with CuO heated to 900 °C for 1 h. This step allows removing all organic contamination and adsorbed atmospheric nitrogen of the samples. O_2 is then re-adsorbed by cooling the CuO to 450 °C and the line is evacuated. At pressure lower than 10^{-6} Torr, the tubes are sealed to give evacuated ampoules of ~5 cm length. Those ampoules are heated in a programmable muffle furnace at 950 °C for 6 h, and 600 °C for 2 h for the following reasons: (i) sample combustion under oxygen pressure at 950 °C, (ii) nitrous oxide reduction by copper and (iii) trapping of carbon dioxide by CaO at 600 °C. The tubes are then slowly cooled to room temperature allowing water to react with CaO.

Ampoules are loaded into ultra-high vacuum line for 48 hr and opened with a tube cracker (for a detailed description of tube-cracking device and ultra-high vacuum line, see Ader et al., submitted for publication). Combustion gases are transferred using a molecular sieve cooled to liquid nitrogen temperature. Nitrogen is further purified using a CuO/Cu mixture heated at 450 °C and quantified as dinitrogen N_2 by capacitance manometry with a precision better than 8% (2σ). This precision was determined from the replicated analyses of several homogeneous powders. The amount of extracted N usually ranges from 10 to 300 nmol.

Depending on the protocol (pyrolysis or combustion) and the time of reaction, N is extracted at various temperatures. In the present work, several samples' combustions have been performed at temperature of 1050 and 1100 °C for 6 h. They show results indistinguishable from combustions at 950 °C, suggesting that N is efficiently extracted at temperature ≥ 950 °C. This temperature is slightly lower than the one determined by vacuum step-heating technique to extract N from various igneous silicate minerals ($T\sim 1200$ °C; Boyd et al., 1993). This can be explained by the fact that the authors used a pyrolysis technique (i.e. no oxygen pressure) and heating duration lower than 40 min, requiring higher temperature to achieve full release of fixed reduced-N species such as ammonium (NH_4^+). Similarly, Bebout and Sadofsky (2004) showed that N extraction from silicate minerals could be fully achieved at temperature of ~1200 °C. They used a sealed tube pyrolysis at high temperature (>1000 °C) for 30 min, followed by a combustion step at 850 °C for

1 h. Together with the present results, it suggests that N can be efficiently released from minerals either (i) by pyrolysis at high temperature (~1200 °C) for a short time (~30 min) or (ii) by combustion at lower temperature (~950 °C) for longer duration (~6 h).

2.2. Mass spectrometry

After the quantification, the gas is introduced and isotopically analyzed in a static mass spectrometer (modified from VG-type, Micromass™). The mass spectrometer includes a Nier-type ion source, a flight tube of 8 cm radius across a Hall probe-stabilized magnetic field and three single Faraday cup collectors. The ion source settings are adjusted to obtain a long $^{28}N_2$ half-life of ~1 h in the mass spectrometer, trap current and filament intensity being 120 μA and 0.4 A, respectively.

Nitrogen isotopes are measured at masses 28, 29 and 30. The major isobaric interferences are carbon monoxide and hydrocarbon. The interference of carbon monoxide is monitored at masses 30 ($^{12}C^{18}O$) and 12. Furthermore, the occurrence of CO traces in the gas would induce a significant drop of the $^{28}N_2$ half-life and would be immediately identified. Potential atmospheric contamination is monitored using $m/z = 40$ (Ar). Variations in the isotopic composition of nitrogen are expressed in the usual δ notation (in ‰): $\delta^{15}N_{sample} = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1] \times 1000$, where the standard is atmospheric N_2. The precision on $\delta^{15}N$ measurement is better than $\pm 0.5‰$ (2σ), estimated from the reproducibility of international standards (IAEA-N1 and -N2; Boyd et al., 1995). It is worth noting that no correction is applied on the N isotopic measurement and determination of m/z 12, 30 and 40 are only used to check the purity of the gas.

2.3. Blank level

The nitrogen blank of the present procedure has been evaluated by analyzing several sealed tubes ($n = 40$) prepared as described above but without sample powder (Fig. 2). The blank amount is comprised between 0.39 and 0.95 nmol N (Fig. 2a), with mean value at 0.65 ± 0.30 nmol (2σ). Among this blank, the quartz tube contribution represents less than 15% (0.1 nmol). The contribution of the tube-cracking is negligible. Blanks prepared with and without platinum foil are similar, suggesting that platinum contribution is also negligible. The main contributor to blanks seems to be the reagents (i.e. CaO, Cu and CuO). Although CaO may contribute up to 50% to the blank, its use is
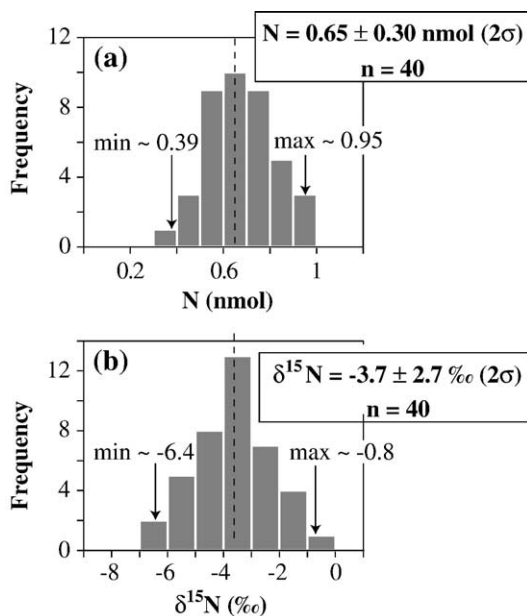

Fig. 2. Distribution of the (a) nitrogen amount and (b) isotopic composition of the analytical blanks.

necessary to fully trap CO_2 and H_2O, and thus avoid any isobaric interference (such as CO or C_2H_5) on N isotopes measurement (N_2). The use of a constant quantity of reagents allows to obtain reproducible amount of blank, as illustrated by Fig. 2a. In order to test if the sample powder would bring any further contamination (e.g. air adsorption, modern organic matter), five samples for which nitrogen had been extracted first time were re-analyzed. For all of the samples, the measured nitrogen amount ranges from 0.70 to 0.74 nmol. This quantity is indistinguishable from the blank prepared without sample powder (0.65 ± 0.30 nmol), indicating that nitrogen had been entirely extracted during the first analysis. It is worth noting that nitrogen amounts were almost constant at ~0.72 nmol for sample weights ranging from 15.62 to 31.93 mg. This supports that N atmospheric contamination brought by sample powder is negligible. Such a low "powder blank" is obtained because of (i) sample degassing at 450 °C under vacuum for 12 h, and (ii) saturation of the line with O_2 pressure in order to replace adsorbed atmospheric nitrogen by oxygen and induce combustion of N-bearing modern organic matter.

The blank $\delta^{15}N$ values vary from $-6.4‰$ to $-0.8‰$ (Fig. 2b), and define a Gaussian distribution with a mean value at $-3.7 \pm 2.7‰$ (2σ). It is within the range of known isotopic compositions of mantle rocks (e.g. Javoy et al., 1986) and not strongly different from crustal material, being usually between 0 and +10‰ (Williams et al., 1992; Bebout and Fogel, 1992; Boyd,

1997; Ader et al., 1998; Mingram and Bräuer, 2001; Busigny et al., 2003a,b). This is important because for this blank isotopic composition, the blank amount is not large enough to require any correction of isotope ratios for samples with more than 40 nmol N. In contrast, a correction of isotopic ratio from blank contribution is necessary for sample size lower than 40 nmol. Such a correction can be applied to samples using the blank mean values. Sample nitrogen amount and $\delta^{15}N$ can be determined from mass balance approach as:

$$N_{sample} = N_{measured} - N_{blank} \tag{1}$$

$$\delta^{15}N_{sample}$$
$$= \left(N_{measured} \cdot \delta^{15}N_{measured} - N_{blank} \cdot \delta^{15}N_{blank}/N_{sample}\right) \tag{2}$$

where N_{sample}, $N_{measured}$, N_{blank}, $\delta^{15}N_{sample}$, $\delta^{15}N_{measured}$ and $\delta^{15}N_{blank}$ are nitrogen amount and isotopic composition of the sample, the measured values and the mean blank, respectively. The uncertainty on sample N content is determined from minimum and maximum blank amount, respectively of 0.39 and 0.95 nmol N (Fig. 2a). The uncertainty on sample isotopic composition is calculated as the sum of the analytical precision ($\pm 0.5‰$) and the uncertainty on blank $\delta^{15}N$. The uncertainty on blank $\delta^{15}N$ is estimated using both extreme values of blank $\delta^{15}N$ ($-6.4‰$ and $-0.8‰$, Fig. 2b) and the maximum amount of blank (i.e. 0.95 nmol, Fig. 2a).

The blank amount of the present protocol can be compared to previous works based on similar analytical procedures. A sealed tube combustion using only slightly purified Cu, CuO and CaO, produced blank amount ranging from 200 to 400 nmol N (Bebout and Fogel, 1992), being three orders of magnitude higher than our blanks (0.65 ± 0.30 nmol). A similar procedure, however replacing the use of CaO by cryogenic trap, gave blank amount lower than 50 nmol N (Sadofsky and Bebout, 2000; Bebout and Sadofsky, 2004). Recent development of sealed quartz tube method, employing Cu and CuO (but no CaO), and metal high vacuum extraction line yields blanks of only 1 to 2 nmol N (Idleman et al., 2004). Pyrolysis method in sealed tubes containing CaO (but no Cu and CuO) produced blank of the order of 1.4 nmol N (Boyd, 1997), which are still slightly higher compare to those of the present work. These examples illustrate that the procedure of purification of Cu, CuO and CaO presented herein is drastic and provides very low blanks. Contrasting with blank amount, blank isotopic compositions are not reported in previous studies and can thus not be compared to present results.

3. Results and discussion

3.1. Accuracy

The accuracy of sealed tube combustion technique was preliminary evaluated through replicate analysis of international standards, for which N content and isotopic composition are known. International standards analyzed herein are IAEA-N1 and IAEA-N2, the first being used as internal reference material and the second being compared to the first. These standards are dried ammonium salt $(NH_4)_2SO_4$, that are oxidized to N_2 through sealed tube combustion. Nitrogen isotopic compositions of IAEA-N1 and -N2 standards have been estimated in previous studies (Gonfiantini, 1984; Gonfiantini et al., 1995; Böhlke and Coplen, 1995). The $\delta^{15}N$ weighted average calculated from previous studies data gives $+0.46‰ \pm 0.14‰$ ($n=43$) and $+20.32‰ \pm 0.26‰$ ($n=43$) for IAEA-N1 and -N2, respectively. In the present work, $\delta^{15}N$ values of IAEA-N2 were found at $+20.17‰ \pm 0.36‰$ ($n=30$), which compare well with previous data. This result indicates that sealed tube combustion technique coupled with static mass spectrometry provides accurate measurement of N isotopic composition.

Although the use of international standards such as IAEA-N1 and -N2 is essential to preliminary validate a method of N isotopic measurement, this approach is not sufficient for workers who want to analyze crustal and mantle rocks. Indeed, IAEA-N1 and -N2 are ammonium salts that can be destabilized at relatively low temperature ($\sim 300\ °C$). In contrast, crustal and mantle rocks usually contain various NH_4-bearing minerals that could resist, at least partially, to high temperature treatment (e.g. muscovite, biotite, feldspar). The efficiency of extraction of N fixed in minerals should be tested using other standards more similar to crustal and mantle rocks. In order to provide an internal standard material that could easily be exchanged for interlaboratory calibration, we crushed and analyzed several times a metasedimentary rock from the Moine Succession (Scotland). Nitrogen content and isotopic composition of this sample were measured in a previous study dealing with Precambrian ammonium biogeochemistry (Boyd and Philippot, 1998). N contents and $\delta^{15}N$ were estimated at 323 ppm and $+14.8‰$, respectively ($n=1$; Boyd and Philippot, 1998). The sample, labelled MS#5, is a garnet-bearing mica-schist, coarsely banded (cm scale) showing alignment of micas parallel to foliation plane. Mineralogical assemblage includes quartz (50%–60%), plagioclase (30%–35%), garnet (2%–5%), white mica (2%) and biotite (2%–10%). In the present work,

approximately 60 g of the sample MS#5 were crushed to a thin powder (<160 μm) and then homogenized. Variable weights of sample were analyzed using sealed tube combustion method (Table 1, Fig. 3). Fig. 3b shows that MS#5 is isotopically homogeneous at the precision level (i.e. ±0.5‰). The good reproducibility of N content and $\delta^{15}N$ measurements obtained for a large range of sample weight suggests that N was efficiently extracted. Nitrogen content and $\delta^{15}N$ average 244 ± 22 ppm and +14.9‰ ± 0.5‰ (2σ), respectively. The $\delta^{15}N$ value is indistinguishable from previous estimate determined by Boyd and Philippot (1998) while N content is slightly lower. The small discrepancy in N content cannot result from an incomplete extraction of the N because, in such a case, N isotopic composition of the former and the present studies would have been different owing to isotopic fractionation between fixed and released N (see for instance Haendel et al., 1986). In contrast, this discrepancy arises from the fact that Boyd and Philippot selected a piece of rock containing a higher quantity of biotites, which are particularly enriched in nitrogen. Therefore, the good agreement in $\delta^{15}N$ further validates N isotopic measurement using sealed tube combustion technique.

The efficiency of N extraction using sealed tube combustion can also be illustrated by comparing N content measured from this technique to other independent methods such as infrared spectrometry. In two companion papers, two methods were presented to determine N concentration in muscovite and biotite (Busigny et al., 2003b, 2004) directly from infrared spectrometry. Both papers reported several mica single grains N contents estimated (i) initially from infrared spectrometry and (ii) subsequently from sealed tube combustion technique. Fig. 4 plots the results obtained
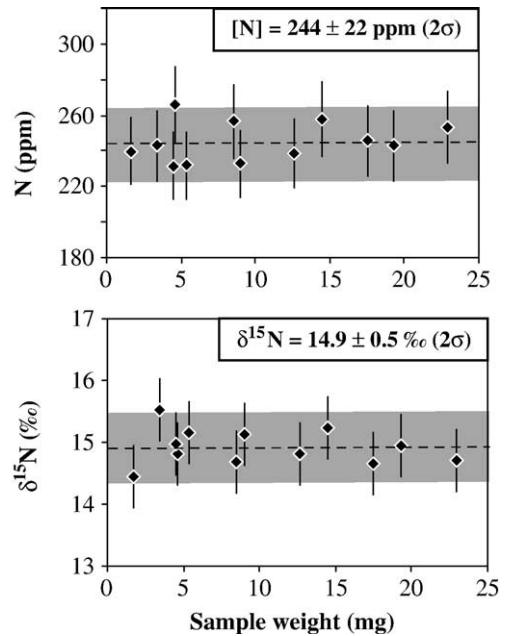

Fig. 3. Nitrogen content (a) and isotopic composition (b) of replicate analyses of a garnet-bearing mica-schist from the Moine Succession (Scotland). Results are plotted versus sample weights used for analyses.
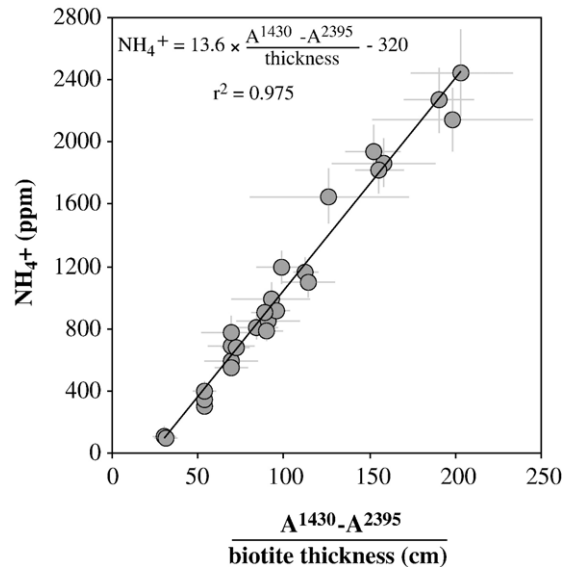

Fig. 4. Ammonium content of biotite estimated from sealed tube combustion data versus NH_4 infrared absorbance normalised to biotite thickness. The perfect agreement between both independent methods illustrates the efficiency of N analysis by sealed tube combustion technique. The absorbance difference "$A^{1430} - A^{2395}$" corresponds to the sum of NH_4 bending absorption band and absorbance of superimposed network vibration. The correlation does not intersect the origin of the plot as a consequence of the use of an absorbance difference rather than a "direct" baseline-corrected absorbance (for details, see Busigny et al., 2004).

Table 1
Replicate analyses of the mica-schist MS#5

Sample weight (mg)	Extracted N (nmol)	N content (ppm)	$\delta^{15}N$ (‰)
1.67	29	239.9	14.5
3.45	60	242.9	15.5
4.54	76	231.6	15.0
4.64	89	265.8	14.8
5.40	90	231.8	15.2
8.52	157	256.5	14.7
8.96	150	232.7	15.1
12.63	216	238.7	14.8
14.52	268	257.8	15.2
19.33	336	242.8	14.9
17.52	308	245.5	14.7
22.93	415	253.0	14.7
Mean value		244.9 (±22.3, 2σ)	14.9 (±0.5, 2σ)

for biotite. It reports NH_4 content determined from sealed tube combustion versus NH_4 infrared absorbance normalised to biotite thickness. Each point corresponds to a single biotite grain. The good linear correlation suggests that N initially detected by infrared measurement was entirely extracted by subsequent combustion, further supporting the efficiency of N extraction by sealed tube combustion.

3.2. Analytical precision

A mean of assessing the analytical reliability is through the analysis of multiple preparations of individual samples. Such replicate analyses take into account not only the external precision of the technique, but various parameters such as the nature of the sample and variations due to chemical separation and handling. In addition, the reproducibility of replicate measurements of powdered rock takes into account any heterogeneity of the powder. Two types of replicate analyses were achieved: (i) one on a sample of very low N content (~2 ppm) providing an opportunity to test the sensitivity of the sealed tube combustion technique and (ii) another one performed on a number of samples of various lithologies in order to test any potential "matrix" (i.e. mineralogical) effects.

The low N content sample, which was selected, has a very positive $\delta^{15}N$ value (~+9‰) that can be easily distinguished from the blank $\delta^{15}N$ (~−3.7‰). This sample, labelled ETF-7, is a metaperidotite from the Erro–Tobbio massif (western Alps). Several analyses of ETF-7 ($n=12$) were performed on various weights ranging from 3.85 to 42.03 mg. N contents and $\delta^{15}N$ values corrected from the blank contribution are plotted as a function of sample weight in Fig. 5. They are strongly variable for low sample weights (<15 mg) but tend to be very similar for weights higher than 20 mg (Fig. 5). The variations reflect an effect of blank contribution, being important and negligible, respectively. Nitrogen content and $\delta^{15}N$ value of the sample ETF-7 can be estimated at 2.0 ± 0.1 ppm and $+9.4‰ \pm 0.5‰$, respectively, when data considered are limited to weights higher than 20 mg. The sealed tube combustion is thus suitable for analysis of low N content samples (i.e. few ppm) if prepared sample weight is higher than 20 mg.

Table 2 reports the results of multiple replicate measurements of various rock types (metasediments, metagabbro, altered basalt and metaperidotite). The sample weights range from 0.68 to 49.75 mg for highest and lowest N content samples, respectively (Table 2). Ni-
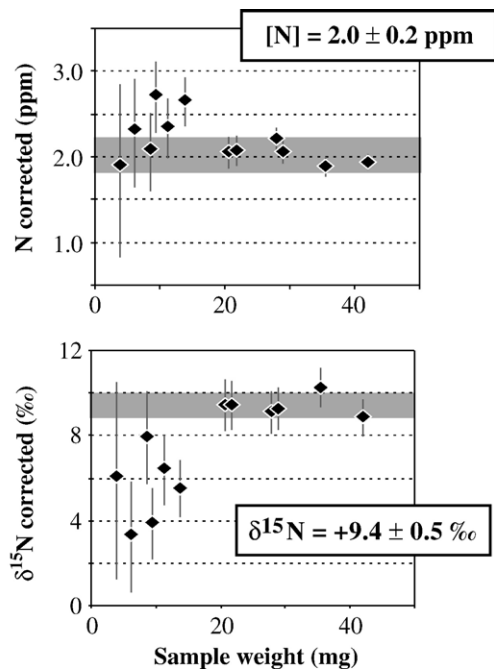

Fig. 5. Nitrogen content and isotopic composition corrected from the blank contribution versus sample weight for replicate analyses of the metaperidotite ETF-7.

trogen content and $\delta^{15}N$ value vary over a large range from 1.9 to 1682 ppm and +3.4‰ to +10.3‰, respectively. Nitrogen content standard deviation of replicate analyses of the seven samples ranges from 0.4% to 7.5%, with a mean value of $\pm 4.2\%$. The $\delta^{15}N$ standard deviation varies from 0.2‰ to 0.5‰ (Table 2), with a mean value of $\pm 0.36‰$ (1σ). This indicates that the capacity to replicate isotopic composition of any sample is at least as good as the analytical precision (i.e. $\pm 0.5‰$). These results illustrate that the sealed tube combustion technique can be applied successfully to a large variety of lithologies, the precision of the technique being better than 8% for N content and 0.5‰ for $\delta^{15}N$.

3.3. A prelude to the study of N in oceanic lithosphere

The preliminary results reported in Table 2 provide an opportunity to depict first order observations on N content and isotopic composition in the different components of oceanic lithosphere. Notably, it brings a first estimate on the global flux of subducting N. Nitrogen contents of metasedimentary rocks show a large range of variation from 195 to 1637 ppm, which compare well with previous data (e.g. Bebout and Fogel, 1992; Mingram and Bräuer, 2001; Busigny et al., 2003a). They are about two orders of magnitude higher than N contents of mafic and

Table 2
Reproducibility of N analyses for different types of lithology (1σ uncertainties)

Sample	Location	Rock type	Weight (mg)	$\delta^{15}N$ (‰)	N (ppm)
SL98-3P	Assiete	Metasediment	3.82	3.5	1596
			1.29	3.9	1632
			0.68	3.7	1682
Average				3.7	1637
				(± 0.2)	(± 44)
98SE9	Finestre	Metasediment	3.80	4.7	537
			3.47	4.2	510
			3.19	4.4	522
			2.74	4.2	521
Average				4.4	523
				(± 0.2)	(± 11)
90-25B	Cignana	Metasediment	3.57	4.9	203
			2.42	5.1	181
			3.15	4.4	201
Average				4.8	195
				(± 0.4)	(± 12)
09-02	Buchet	Metagabbro	30.96	7.2	4.0
			31.82	7.3	4.6
			35.52	7.7	4.5
Average				7.4	4.4
				(± 0.3)	(± 0.3)
ETF7	Erro–Tobbio	Metaperidotite	20.66	9.4	2.1
			21.75	9.5	2.1
			27.86	9.1	2.2
			28.95	9.3	2.1
			35.44	10.3	1.9
			42.03	8.9	1.9
Average				9.4	2.0
				(± 0.5)	(± 0.1)
16R-1	EPR	Altered basalt	45.24	4.2	2.7
			40.88	3.3	2.8
			49.75	3.3	3.0
Average				3.6	2.8
				(± 0.5)	(± 0.2)

All samples were collected in Western Alps (Europe) except one altered basalt (16R-1) collected in the Guatemala basin at the east of East Pacific Rise (EPR).

ultramafic rocks, which vary from 2.0 to 4.4 ppm (Table 2). Because the mass flux of subducted sedimentary rocks ($\sim 1.8 \times 10^{15}$ g/yr; Plank and Langmuir, 1998) is approximately 30 times lower than that of subducted basalts and gabbros ($\sim 6.0 \times 10^{16}$ g/yr; Peacock, 1990), the contribution of mafic rocks to the total flux of subducting N may be relatively important. It may represent as much as one third of the total subducting N flux and should likely be considered in future studies attending to global N recycling to subduction zones. We want to emphasize that systematic measurements of N content in oceanic lithosphere are required to determine precisely the different contribution of each specific component. Future studies should concentrate on fresh rock sampled at mid-ocean ridges, and rocks altered on oceanic seafloor and/or metasomatized during subduction-related metamorphism.

Nitrogen isotopic composition of samples analyzed herein are clearly enriched in ^{15}N relative to atmosphere (Table 2). Metasediments and altered basalt have similar $\delta^{15}N$ values of $\sim +4.0$‰ while metagabbro and metaperidotite show higher $\delta^{15}N$ values of $+7.4$‰ and $+9.4$‰, respectively. Because $\delta^{15}N$ values of subducting rocks is either increased (Haendel et al., 1986; Bebout and Fogel, 1992; Mingram and Bräuer, 2001) or unchanged (Busigny et al., 2003a) during metamorphism, it is expected that N recycled to the deep mantle will have markedly positive $\delta^{15}N$ values. Such positive $\delta^{15}N$ values are significantly distinct from the negative values of the mantle (~ -5‰; e.g. Javoy et al., 1986) and should allow tracing efficiently recycled component in mantle rocks.

4. Conclusion

The present contribution describes progress on the development of the "standard" sealed tube combustion technique coupled with static mass spectrometry. This procedure allows N isotopic analysis of rocks containing less than 2 ppm N, for sample weight higher than 20 mg. The precision on N content and isotopic composition are better than $\pm 8\%$ and ± 0.5‰, respectively. Systematic measurement of analytical blanks indicates that they are low and average 0.65 ± 0.30 nmol N (2σ) with $\delta^{15}N$ at -3.7‰ ± 2.7‰ (2σ). Among this blank, reagents (CaO, Cu and CuO) are identified as the main contributors although they are purified before N extraction from samples. The sealed tube combustion sensitivity can thus be improved if (i) reagents are efficiently purified and (ii) the amount of reagents is decreased to a minimum.

The sealed tube combustion technique described herein can contribute to study geochemical systems in which N concentrations are particularly low and for which analyses of small samples are required (e.g. where little sample exists, or where high spatial resolution is useful). It should however be noted that this technique is time-consuming and may not represent the simplest and more precise method to analyze samples with relatively large amount of nitrogen (i.e. >100 ppm).

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