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Isotope-ratio-monitoring gas chromatography methods for high-precision isotopic analysis of nanomole quantities of silicate nitrogen

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Abstract

We have developed a system for analyzing nanomole-sized quantities of silicate-derived N_2 by carrier-gas methods, through combination of a metal high-vacuum extraction line fabricated at Lehigh University and a commercially available continuous-flow, gas chromatography interface (the Finnigan Gas Bench II). This work involves heating of samples to 950–1050 °C (depending on the material being analyzed), with Cu metal and Cu oxide reagents, in evacuated and sealed 6 mm (o.d.) quartz tubes. Uncertainties (expressed as 1σ for ≥ 3 replicate analyses of both internal silicate standards and unknowns) are generally less than 5% for N concentrations and on the order of 0.15‰ $\delta^{15}N$ for samples with >5 ppm N. At current blank levels (minimum overall system blank of 3.8 ± 0.2 nmol N_2 with a $\delta^{15}N_{air}$ value of -7.3 ± 0.4‰, mean $\pm 1\sigma$), uncertainty in $\delta^{15}N$ increases to ~0.6‰ for samples with 1–2 ppm N. Practical minimum sample size, taking into account blanks and other factors affecting N_2 transfer, is now ~10 nmol, two orders of magnitude smaller than that previously possible in our laboratory using dual-inlet microvolume methods (~1 μmol). These methods, which can be employed in any laboratory able to undertake continuous flow techniques (with a dynamic-vacuum, isotope ratio mass spectrometer), afford increased spatial resolution in some studies and open up many new avenues of investigation previously impeded by the absence of sufficiently N-rich materials.

Keywords: Nitrogen isotopes; Carrier gas; Mass spectrometry; Oceanic basalt

1. Introduction

The nitrogen (N) isotope system has shown exciting potential to trace interactions among Earth's major reservoirs, in particular providing a tracer for the transfer of organic components through a wide range of biogeochemical processes. Whereas the application of N isotopes has been extensive in studies of the biosphere (see Boyd, 2001), applications of $^{15}N/^{14}N$ ratios to trace the transfer of organic components into the deeper Earth have lagged behind, partly related to the small quantities of N in many silicate materials (commonly <100 ppm, rarely >1000 ppm) and other analytical difficulties. Some of the most extensive use of N isotopes for study of the deeper Earth has been on mantle-derived materials, including diamonds and mantle-derived igneous rocks. Many of the laboratories pursuing such work have

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been those employing highly sensitive static mass spectrometry capable of analyzing into the picomole range with precision near ±0.5‰; a number of these labs also devote attention to studies in cosmochemistry (for discussions of precision, see Humbert et al., 2000; Cartigny et al., 2001). Another category of research has been to couple the study of N cycling with analyses of noble gases in order to assess deep Earth degassing and extents of crustal recycling at convergent margins, and in broader considerations of Earth and extraterrestrial volatiles evolution (e.g., Hilton et al., 2002; Snyder et al., 2003). The great potential of the N isotope system as a tracer of flux of organic components into the solid Earth has been extremely under-explored, with only a few laboratories conducting research aimed at transfer of N into the crust and mantle via organic processes, diagenesis, and low- to high-grade metamorphism and melting. An additional recent frontier involving N isotopes has concerned the possibility of changes in sedimentary/organic cycling related to changes in oxygenation levels in Earth's oceans and atmosphere: this work has involved analyses of N isotopic compositions in Precambrian paleosoils and sediments metamorphosed to varying degrees (e.g., Beaumont and Robert, 1999; Papineau et al., 2005; Brauer and Hahne, 2005).

Until recently, most of our work on N isotopes has involved sealed-tube extraction techniques and off-line cryogenic purification methods (i.e. using separate glass vacuum lines) and dynamic-vacuum, dual-inlet, viscous-flow mass spectrometry (Bebout and Fogel, 1992; Sadofsky and Bebout, 2000; Bebout and Sadofsky, 2004). These methods involve heating of mineral separate and whole-rock samples to 910–1250 °C in sealed quartz tubes with CuO_x and Cu metal, with or without CaO (Bebout and Fogel, 1992; Sadofsky and Bebout, 2000). The N_2 gas samples analyzed in our laboratory using these methods are in the size range of 1–50 μmol, a size range that can be handled using the variable volume (bellows) and microvolume (cold finger) inlets on a viscous-flow mass spectrometer (Finnigan MAT 252 at Lehigh Univ.). These methods yield highly accurate and precise $\delta^{15}N$ and N concentration data for samples with relatively high N concentrations (see Sadofsky and Bebout, 2000; Bebout and Sadofsky, 2004). However, large amounts of sample are needed for materials with <100 ppm N, as N_2 samples ≥1 μmol in size are needed to guarantee viscous flow conditions in the mass spectrometer capillary. For $\delta^{15}N$ values of samples with >100 ppm N, 1σ precision for 2–10 duplicate analyses typically approaches 0.1‰, and N concentration data have <5% uncertainty (data for muscovites and biotites in Sadofsky and Bebout, 2000). Blanks for these methods are <0.025 μmol N_2, affording analyses of N_2 samples to ~1.0 μmol. The precision of these analyses is typically higher than that obtainable by static mass spectrometry, with the latter methods commonly producing data with 1σ precision of 0.2–0.5‰. The requirement of sufficient pressure to achieve viscous-flow conditions and a practical limit on maximum sample sizes that can be fused without tube rupture restrict this technique to samples containing greater than ~10 ppm N (for samples containing ~10–100 ppm N, $1\sigma \leq 0.30$‰).

It has been obvious for some time that more routine applications of gas chromatography–isotope ratio monitoring techniques (Merritt and Hayes, 1994; Brand, 1996), ultimately involving laser ablation techniques, constitute one necessary analytical frontier for N-isotope analyses of silicates (see recent studies employing element analyzer (EA)-GC-IRMS methods; Kyser et al., 2000; Jia et al., 2003; discussion by Brauer and Hahne, 2005). In this paper, we describe a system we have developed for analyzing nanomole-sized quantities of silicate-derived N_2 by carrier-gas methods, through combination of a metal high-vacuum extraction line fabricated at Lehigh University and a commercially available continuous-flow, gas chromatography interface (Finnigan Gas Bench II; Bebout et al., 2004). This methodology can be employed in any laboratory with a standard dynamic-vacuum, isotope ratio mass spectrometer equipped with differential pumping (i.e., able to undertake carrier-gas work). The use of sealed-tube combustions circumvents fractionation problems that appear more prevalent with the shorter-duration heating used in element-analyzer systems (see Brauer and Hahne, 2005), and affords relatively rapid through-put of samples of up to 8–10 samples/day, including standards.

2. Description of methods

Toward analyses of smaller N_2 samples, we have coupled a Finnigan Gas Bench II carrier-gas system (hereafter referred to as the GBII) with a metal, low-blank vacuum extraction/purification line built at Lehigh. The design of the system, including the interface built for the transfer of small samples of N_2 into the GBII in an He stream, is illustrated schematically in Fig. 1. This interface handles the awkward transition from the high-vacuum section of the system (the metal high-vacuum line) and the section of the system that "sees" both high-vacuum and considerable He flow depending on the gas transfer mode. The critical components of the interface are a Valco type W

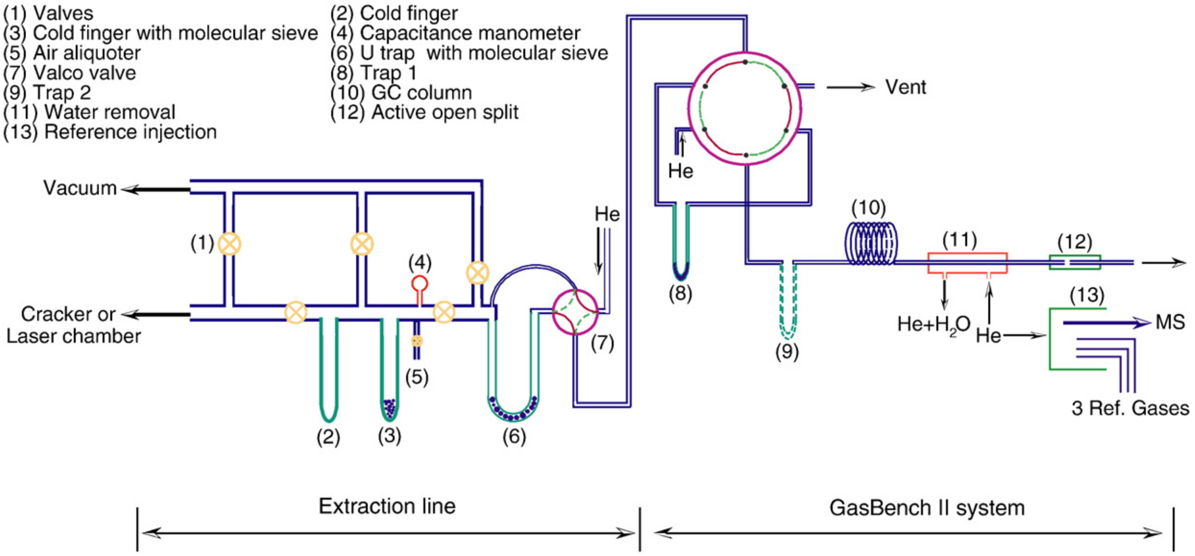

Fig. 1. Schematic illustration of the Lehigh University high-vacuum line and interface with the Gas Bench II, and critical components of the GBII on the right.

4-port, 2-position switching valve (Valve 7; rated for high-vacuum use) for manipulation of the He gas stream, and a U-trap (6) containing 5 Å molecular sieve. The system is similar in a number of ways to those constructed by Young et al. (1998) for analyses of nanomole quantities of O_2, in their case liberating silicate O by UV-laser heating in the presence of F_2 (also see Ono et al., 2006, for description of methods for analyzing S at nanomole levels by laser fluorination isotope-ratio-monitoring gas chromatography–mass spectrometry). We have modified the configuration of the GBII somewhat to allow the use of one or two U-traps (8 and 9 above), the first (8; 1/16-inch ss tubing w/ 5 Å sieve inside coating) for transferring N_2 from our extraction system into the GC, and the second (9; uses a section of 5 Å molecular sieve capillary GC column) initially included as a means of cryofocussing the N_2 before release into the GC (this trap was later removed). In the GBII system, we have used a PLOT (Porous layer open tubular) fused silica chromatographic column (Varian MD-03-14-1), with a 5 Å molecular sieve coating, held at 40 °C for effective separation of the various components of the sample gas. Tank He (ultrahigh purity, grade 5.0) flows through a liquid-nitrogen trap, upstream of our system, to further purify it to the point where its contribution to our blank is quite low (∼5% of our current total analytical blank of ∼3.8 nmol; discussion below).

The GBII system partially emulates dual-inlet mode in that it is possible to bracket measurement of the sample gas with multiple analyses of reference gas during an analytical run. The system is capable of analyzing multiple aliquots of gas from unknowns; however, on our system, we have removed the aliquoting loop attached to the main Valco valve to allow the addition of a U-trap (8 on Fig. 1) for transfer of the N_2 samples from our vacuum line into the GBII. The reference N_2 tank has been calibrated by analyses of other calibrated tank reference gases, and by analyses of various non-silicate and silicate standards previously calibrated by dual-inlet analyses using the methods described in Bebout and Sadofsky (2004).

Here, we provide a description of the analytical protocol, beginning with the treatment of the samples prior to sealing the quartz tubes, and including the analyses with the GBII system. Powdered samples (1–250 mg) are loaded, along with varying amounts of the Cu/CuO_x reagent, into 6 mm (o.d.) quartz tubes that are previously combusted in atmosphere at 550 °C for 2 h to remove organic and other contaminants. Samples are evacuated overnight, heated with heat tape to ∼100 °C, then sealed under vacuum. The tubes are then heated to 950–1050 °C in a programmable furnace, held at these peak temperatures for at least 3 h, then cooled slowly, particularly through the 700–500 °C temperature range, to ensure proper speciation of gases as H_2O, CO_2, and N_2 (see Bebout and Fogel, 1992).

Included here is a brief description of the overall extraction and analytical method, which is undertaken

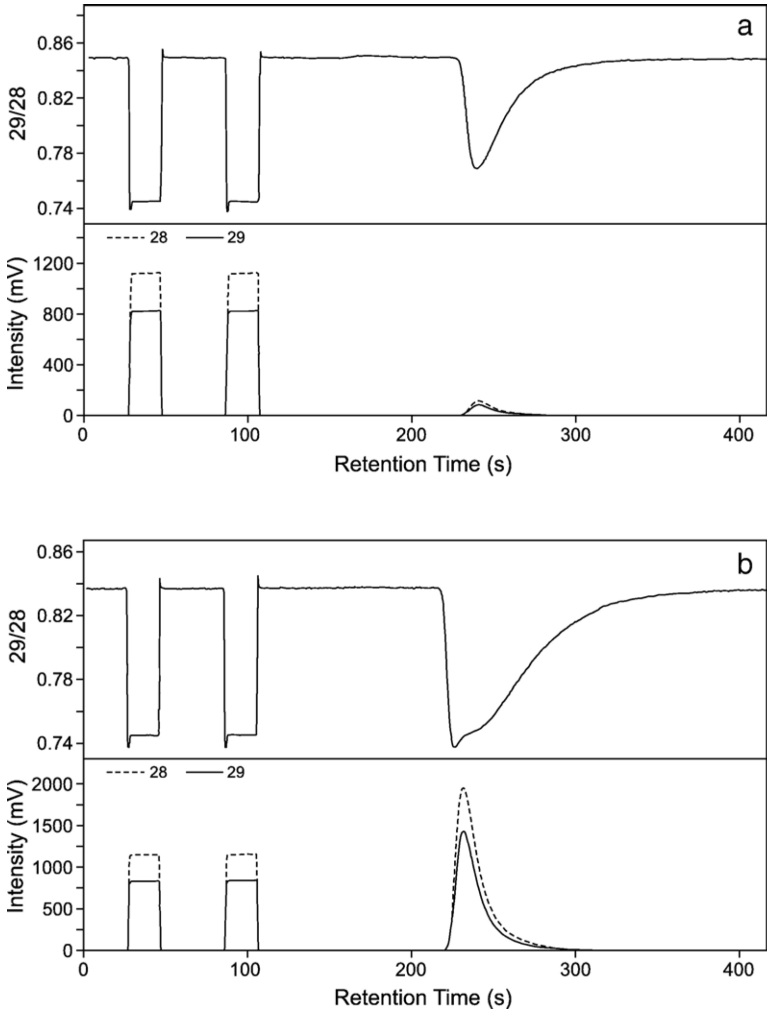

Fig. 2. Representative Gas Bench II analysis, showing peaks for reference gas and for the unknown. (a) Analysis of "internal blank", without the tube cracked, but including all other volumes of the system. (b) Analyses of ~35 nmol N_2 sample extracted from an altered oceanic basalt (data from Li et al., in press).

using optimized transfer times and He flow rates. After loading of the sealed tube onto the tube cracker, and at least 1 h of evacuation, the tube is cracked and the released gas is expanded into the volume with traps (2) and (3). First, condensable gases, presumably mostly H_2O and CO_2, are frozen into trap (2) using liquid nitrogen (10 min). Then, the remaining gas (presumably mostly N_2, but some Ar and other very minor contaminants) is frozen into trap (3) containing 5 Å molecular sieve (15 min). The gas in trap (3) is then expanded and measured with the capacitance manometer (4), then transferred into trap (6), monitoring the pressure with the capacitance monitor to ensure full transfer (10 min transfer). After isolating the volume with trap (6) from the high-vacuum extraction line, the gas is expanded, then entrained into the He stream to transfer it into trap (8) using liquid nitrogen (10 min). Once the gas trapped in trap (8) is expanded, isotopic analyses are undertaken using the GBII system software (unless trap 9 is in use as an additional means of cryofocussing). Delay times are optimized for capture of the N_2 peak, and the GC column effectively separates the N_2 from any O_2, Ar, and CO present in the gas sample. Once a sample tube is cracked, the sample extraction and analysis takes approximately 50 min.

Representative chromatograms for analyses of blanks and N_2 from silicate minerals are provided in Fig. 2. Fig. 2a shows the chromatograph for an analysis of the total instrument blank (performed without cracking a tube onto the extraction line), and Fig. 2b is for an analysis of N_2 (~35 nmol) resulting from sealed-tube heating of a fuchsite (Cr-rich white mica) standard.

3. Results

The development of our methods involved testing of a number of steps in the cryogenic transfer of the N_2 sample, and entrainment of the N_2 sample into and through the vacuum/He transfer interface and GBII system before introduction into the ion source on the MAT 252. In addition to testing on aliquots of standard gases and atmosphere (the latter introduced through a capillary (5) shown on Fig. 1), we have focused attention on reduction of the total analytical blank for sealed-tube methods, analyses of a number of silicate internal laboratory standards, and tests of yields from low-N samples by heating of samples over a range of temperatures.

3.1. Efficiency of transfer of small N_2 samples in the new system

As a part of the initial testing, we optimized transfer times required to quantitatively move small samples of N_2 among the various sections of the system, with the expectation that incomplete transfer would result in preferential transfer of the isotopically light N_2 into the GBII and mass spectrometer. When transfers involved the section of the extraction line containing the capacitance manometer, we were able to use the manometer to document full transfer. We also tested for incomplete transfer by performing repeat analyses of the gas remaining after the initial transfer and analysis of individual samples. These experiments produced N_2 amounts comparable to system blank levels and smaller than the "reagent blank" described below, indicating that the N_2 was efficiently transferred in the initial extraction.

We also tested for the optimal He gas flow rate required to prevent N_2 back-diffusion into the system and to efficiently and, as rapidly as possible, transfer the N_2 from trap to trap without flow of N_2 through the traps at liquid nitrogen temperature. The optimal flow rate, for our system, as measured in the waste capillary coming out of the GBII, is ~15 ml/min. As noted above, we experimented with a second trap (trap 9) mounted just upstream of the GC column in the GBII. Freezing into this second trap resulted in no significant further focusing of the N_2 peak.

3.2. The nature of the total analytical (system) blank

We have experimented at length with determining the size and characteristics of the analytical blanks in this work. Peak m/z 28 beam intensities, calibrated against intensities for laboratory standards, indicate that the total system blanks (including the reagents, heated to 950 °C) from 6 mm O.D. sealed tubes are in the range of 4–15 nmol N_2, depending largely on the amounts of Cu metal and CuO_x reagents used in the combustions. Blanks at the higher end of this range correspond to the use of 1 g Cu metal and 1.5 g CuO_x, while those near 4 nmol can be achieved by the use of 1 g of CuO_x only (no Cu metal). Reducing the CuO_x to 0.5 g lowers the blank by ~30%; however, there is a loss of uniformity in the blank abundance and isotopic composition that produces poor precision in the corrected data for unknowns. At present, we are operating with a total experimental blank on the order of 3.8 ± 0.2 nmol N_2, $\delta^{15}N$ value of $-7.3 \pm 0.4‰$ (mean $\pm 1\sigma$ for both concentration and isotopic composition), reflecting the use of 1 g CuO_x. This blank is approximately an order of magnitude smaller than that we can achieve for our dual-inlet, sealed-tube analyses (Sadofsky and Bebout, 2000; Bebout and Sadofsky, 2004). It is similar to the blanks reported in recent applications of EA-GC-IRMS to silicate N isotopic analyses (Kyser et al., 2000; K. Kyser, personal communication, 2005; Jia et al., 2003), and somewhat higher than the blank of 0.6 nmol reported by Busigny et al. (2005). We have found the blank for our system to be reproducible in both size and isotopic composition, which allows precise correction of data for small samples of unknowns.

The total experimental blank appears to be derived from several sources. From a series of tests designed to measure the contribution from various sections of the extraction system, including experimentation with empty quartz tubes, sealed at high vacuum and combusted, then cracked onto the extraction line (producing a blank of ~1.7 nmol of N_2 with $\delta^{15}N = -8.6‰$), we have determined that the largest contribution comes from the cracked tube/reagent blank (~2.1 out of a total of ~3.8 nmol, over 50% of the total blank). Additional pretreatment of the CuO_x reagent for 3 h under vacuum at 475 °C, as well as re-use of reagent from previous blank runs heated to 950 °C, yielded no significant reduction in this blank. In earlier testing, we determined that the Cu metal in our original reagent mixture was contributing significantly to the blank, and we no longer use Cu in these experiments. It appears that the CuO_x produced in our lab contains some unoxidized Cu metal, ensuring the proper oxygen buffering capacity of the reagent. Transfer of tank He through trap (6), held at liquid nitrogen temperature, with no exposure to the other sections of the metal extraction line, followed by analysis of the trapped N_2 by the GBII system, resulted in a "tank gas" blank of ~0.2 nmol. We suggest that the low $\delta^{15}N$ of the total blank (presently near $-7‰$) partly reflects the preferential diffusion of light N_2, from the atmosphere, through various small leaks into the system (through valve stems, connections of gauges, valves, and the air aliquoter).

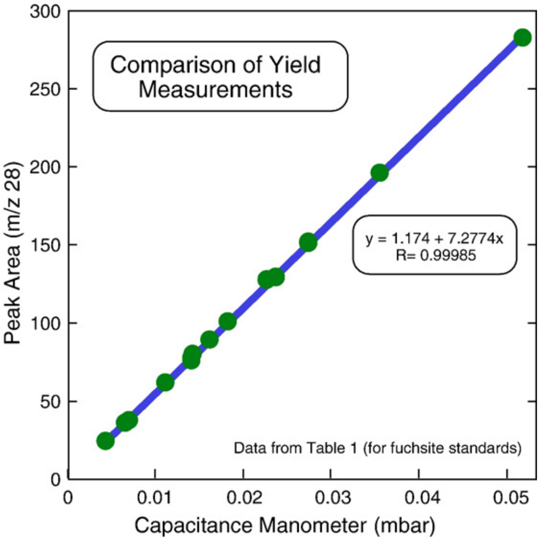

Fig. 3. Demonstration of linear relationship between yield measurements using the capacitance manometer and the area of the *m*/*z* 28 peak. Data are for the two fuchsite standards for which data are provided in Table 1 and plotted (raw and blank corrected δ^{15}N vs. sample size) in Fig. 4.

Busigny et al. (2005) similarly concluded that most of their blank came from reagents (CuO_x+Cu+CaO in their case); with 50% of the blank contributed by CaO. Those authors claimed CaO was necessary to remove H_2O and CO_2 in order to prevent production of CO and hydrocarbons. In our methods, we separate any CO and hydrocarbons from the N_2 by use of the GC, and our previous work has demonstrated that the heating (and slow cooling) routine we employ, using only CuO_x, results in extremely efficient speciation of C, N, and H as CO_2, N_2 and H_2O, respectively (see Bebout and Fogel, 1992; also see Macko, 1981).

As discussed above, our attempts to lower the blank by reducing the quantity of reagent used in the sealed sample tubes led to poor blank reproducibility and imprecise corrected results for unknowns. We have not yet addressed any other potential means of blank reduction, but an obvious area to explore is the preparation of the CuO_x reagent used in the experiments. At present, we prepare CuO_x by heating to 550 °C in a furnace exposed to atmosphere, potentially occluding some N_2, and it is possible that production of the reagent in a more controlled fashion would reduce the blank somewhat (see the methods employed by Busigny et al., 2005). A part of our current blank could be produced by outgassing of the metal extraction line and its various traps, in addition to the component due to leakage of atmospheric N_2 into the system (through valves and various connections). The line was baked at ~200 °C during its initial pumpdown, but we do not routinely bake it after loading samples, since this would greatly reduce sample throughput given the current configuration of the line. It is our impression that the blank could probably be reduced to ~2 nmol (approximately one-half of its present size) through improvements in reagent preparation and reconfiguration of the extraction line to expose a smaller volume of the line to air during sample changes. It is worth noting that Boyd and Pillinger (1990) developed a sealed-tube method for reliable analyses of silicate N isotopic compositions with a static mass spectrometer that involved no Cu metal or CuO_x reagent.

Thus far, our current blank of ~4 nmol has not proved limiting in our analyses of 15–300 nmol of N_2 by our methods (see Li et al., in press, and discussion below). Blank corrections must be made to most measured N abundances and isotope ratios, particularly for small samples, but the consistency of the blank over periods of days to weeks has allowed us to make these corrections

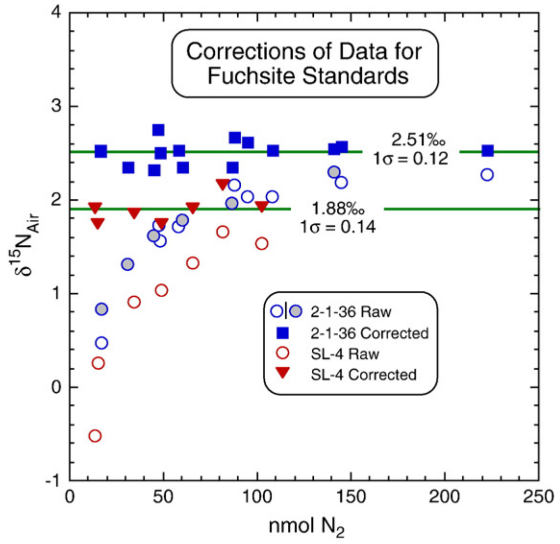

Fig. 4. Raw and blank corrected results for silicate standards 2-1-36 and SL-4, both fuchsite-rich ultramafic samples calibrated isotopically by dual-inlet methods of Bebout and Sadofsky (2004; also see Bebout, 1997). The precision of these data rivals that of dual-inlet methods (1σ of 0.12 and 0.14‰ for 2-1-36 and SL-4, respectively; ≥8 analyses, over an N_2 sample size range of 12 to 225 nmol). The total experimental blank for these analyses was near 12 nmol (with δ^{15}N near −2.0‰), except for the analyses of 2-1-36 indicated by the patterned circles (for these latter analyses, the blank was ~4 nmol with δ^{15}N near −8.0‰, corresponding to the use of 1 g of CuO_x as the reagent, with no Cu metal). This dataset demonstrates the robustness of the blank corrections possible through careful daily monitoring of the system blank. The nmol of N_2 yielded in these experiments were calculated using the N concentrations for these fuchsite samples reported by Bebout (1997) and Bebout and Sadofsky (2004).

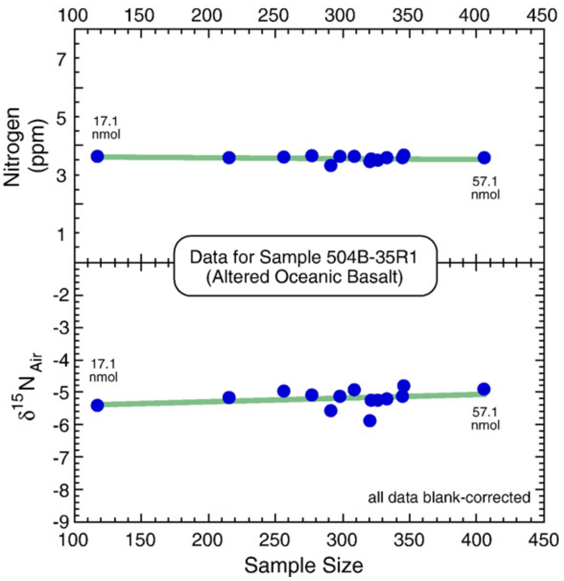

Fig. 5. Tests of N yield (top) and isotopic composition (bottom) of N_2 for samples of seafloor basalt sample 504B-35R, using the sealed-tube-based methods described in this manuscript, over a sample size range corresponding to 17.1 to 57.1 nmol of extracted N_2. All analyses of the altered oceanic basalts were conducted with a total experimental blank near 3.8 nmol N_2, with $\delta^{15}N$ near −7.8‰ (with only minor day to day variation).

with reasonably good precision. Because the blank is presumably dependent upon many factors, including the purity of the He carrier gas and the cleanliness of the extraction line, it needs to be monitored carefully during a series of analyses of unknowns.

3.3. Testing on silicate standards (2-1-36, SL-4) and mid-ocean ridge basalts

We have conducted extensive tests of the new methods for analyses of the N isotope composition of small amounts of N bound in silicate minerals and whole-rock samples.

3.3.1. Analyses of silicate standards

Figs. 3 and 4 present the results of replicate analyses, at varying sample sizes, and with daily monitoring of the total experimental blank, of two silicate standards used in our laboratory (data in Table 1), both fuchsite-rich ultramafic schists previously calibrated isotopically and for N concentration by Bebout (1997). Fig. 3 demonstrates the validity of our use of the capacitance manometer and/or *m*/*z* 28 peak areas as means of calculating N_2 sample size and thus calculating concentrations of unknowns. Our blank corrected isotopic compositions for these standards rival those obtained by the dual-inlet method, as described in Bebout and Sadofsky (2004; see data for these two samples in Bebout, 1997). For seven analyses of fuchsite-rich sample SL-4 (1850 ppm N) ranging in sizes from 12–250 nmol, we obtained a mean blank-corrected $\delta^{15}N$ of +1.88‰ ($1\sigma = 0.14$‰), and fifteen analyses of

Table 1
Representative replicate analyses of fuchsite standards

nmol N_2	CM pressure (mbar)*	Area m/z 28	Raw $\delta^{15}N$	Corrected $\delta^{15}N$
Fuchsite SL-4 (1850 ppm)				
13.88	0.004	24.18	−0.52	1.90
15.55	0.007	37.80	0.25	1.73
34.82	0.011	61.75	0.91	1.84
49.35	0.014	79.94	1.03	1.73
65.97	0.018	101.18	1.32	1.90
81.85	0.023	127.43	1.66	2.15
102.62	0.027	151.78	1.53	1.92
			Mean	1.88
			1σ	0.14
Fuchsite 2-1-36 (790 ppm)				
58.33	0.016	89.69	1.71	2.53
48.79	0.014	77.76	1.55	2.49
145.35	0.036	196.00	2.19	2.57
108.40	0.027	150.77	2.04	2.52
223.09	0.052	282.57	2.27	2.53
17.10	0.007	35.91	0.47	2.52
47.57	0.014	76.21	1.73	2.75
95.22	0.024	129.31	2.02	2.60
			Mean	2.56
			1σ	0.08

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[a] Measured using the capacitance manometer (see Fig. 1).

fuchsite-rich sample 2-1-36 (790 ppm N) yielded a mean $\delta^{15}N$ of +2.51‰ ($1\sigma=0.12$; see Fig. 4). For the same samples, Bebout (1997) reported $\delta^{15}N$ of +1.9‰ and +2.5‰ obtained by dual-inlet analyses of N_2 samples in the size range of 5–50 μmol. With a blank of ~4 nmol ($\delta^{15}N$ near −8‰), we obtained a mean $\delta^{15}N$ of +2.40‰ ($1\sigma=0.10$‰) for another fuchsite-rich sample, which compares favorably with the $\delta^{15}N$ value of +2.4‰ obtained previously by the dual-inlet method. In general, the precision of the dual-inlet method employing sealed-tube extractions approaches 0.1‰ (1σ) for $n \geq 2$ analyses (see detailed discussion and representative data in Bebout and Sadofsky, 2004). Therefore, despite the need for careful blank characterization and correction, the sealed tube-carrier-gas method appears to introduce no appreciable loss of precision (or accuracy) relative to the dual-inlet method, while reducing the minimum sample size by a factor of ~400.

3.3.2. Testing of extractions of small amounts of N from mid-ocean ridge basalts

Repeat analyses of two altered oceanic basalt samples over a range of temperatures and sample sizes demonstrate complete release of the N from these samples and the dependability of our method for analyses of samples with extremely low N concentrations (see Fig. 5; Li et al., in press). Analysis of basalt 504B-35R1 (3.6 ppm N) from ODP Site 504B using combustions temperatures of 950, 1000, and 1050 °C yielded indistinguishable N concentrations and isotopic compositions of 3.60±0.04 ppm and −5.06±0.13‰, respectively, with no apparent relationship between these parameters and temperature. Likewise, variably sized aliquots of this sample and another altered oceanic basalt (396B-15R3-83-89; 12.1 ppm) produced extremely uniform N yields and isotopic values over a large range of sample sizes. Fourteen analyses of sample 504B-35R1, with sample sizes ranging from 110 to 405 mg and including samples heated to 1000° and 1050 °C, yielded a mean N concentration of 3.55 ppm ($1\sigma=0.10$ ppm, or 3%), and mean $\delta^{15}N$ of −5.10‰ ($1\sigma=0.28$‰). Five samples of 396B-15R3-83-89, with a range of sample sizes of 60–400 mg, yielded a mean N concentration of 11.8 ppm ($1\sigma=0.66$ ppm, or 5.5%) and mean $\delta^{15}N$ of +4.59‰ ($1\sigma=0.30$‰). The significant differences in $\delta^{15}N$ for these and other oceanic basalt samples (also see Busigny et al., 2005) are believed to reflect varying seafloor alteration histories (see Li et al., in press).

3.3.3. Reheating of experimental runs

To test for full extraction of N from the various samples we have analyzed, we conducted a series of re-heating experiments on the run products from previous analyses. The samples and the original CuO_x reagent, which was partially fused to the samples, were loaded into new quartz tubes with 0.5 g of new CuO_x reagent, then treated in the same manner as in the initial experiments. Of a total of 10 samples that were re-analyzed by this method, nine produced re-extracted N abundances that deviated by no more than 25% from the ~3.8 nmol experimental blank (i.e., they released less than 1 nmol of additional gas), and the re-extracted components represented <5% of the N obtained during the initial analysis of these samples. These re-heated samples might reasonably be expected to produce N_2 yields somewhat higher than blank levels, since new CuO^x reagent (a significant source of blank, see above) is added prior to the re-heating, and heating associated with the initial extraction may not have removed all of the blank N from the original reagent charge.

4. Comparison with other methods for analyzing small N_2 samples from silicates

The methods we describe here complement those recently developed in laboratories employing static mass spectrometry for silicate N analysis. The application of the GC in the GBII affords separation of N_2 from other gases potentially producing isobaric interferences during analyses (most notably CO). The methods of Humbert et al. (2000) have a “hot” analytical blank of only 2.2 pmol, probably due largely to the use of CO_2 laser heating, and produce only a minor compromise in analytical precision relative to our methods. Methods recently developed by Busigny et al. (2005), employing static mass spectrometry and sealed-tube extractions with heating to 950–1100 °C (also see Boyd and Pillinger, 1990), yield impressive data for samples in the 10–300 nmol range, but require non-standard static mass spectrometry. This technique is presently limited by the size of the blank from the reagents (0.65± 0.30 nmol [2σ]; Busigny et al., 2005), as the static mass spectrometers can easily analyze the isotopic compositions of N_2 into the picomole size range. In contrast, our methods will ultimately be limited by the sensitivity of the mass spectrometer, as signals are already relatively low for measurements of blanks at the 3.8 nmol level. As in our study, Busigny et al. (2005) concluded that complete N extraction in many geological materials (e.g., whole-rock samples, micas, basalts, and ultramafic rocks) is achieved at 950 °C (for extended periods of heating, in our case, 3 h at the peak temperatures). At present, the methods we describe here, involving sealed-tube heating for 3 h at peak temperatures of 950–

1050 °C, appear to yield results more reliable than those using the EA methods. The latter appear to suffer from kinetic problems in the heating that must be alleviated by using fluxes, which in turn can contribute significantly to the analytical blank (see Jia et al., 2003; discussion by Brauer and Hahne, 2005).

5. Conclusions

The methods we describe here for the extraction and analysis of N from relatively low-N materials, merge current carrier-gas technology and our experience with sealed-tube extractions, the latter of which circumvent the kinetic fractionation problems inherent with shorter-duration heating experiments on silicate materials (see discussion of this latter effect by Brauer and Hahne, 2005). The relatively uniform size and isotopic composition of the small N_2 blank in our experiments has allowed us to obtain precise and accurate N abundances and isotopic compositions for N2 samples as small as 10–15 nmol (see Fig. 4). Further work needs to be focused on reduction of the total analytical blank; however, the minimum N_2 sample size will ultimately be dictated by the sensitivity of the mass spectrometer, With current technology, the practical lower limit for sample N_2 abundance that can be handled using sealed tube-carrier-gas methods is probably on the order of 1 nmol.

Our experimentation, and the resulting analytical methodology, complement recent work on the analysis of small samples of silicate N using combinations of sealed-tubes and laser heating with static mass spectrometry (Humbert et al., 2000; Papineau et al., 2005; Busigny et al., 2005). Unlike these methods, those we describe can be implemented relatively easily in laboratories that currently employ dynamic vacuum mass spectrometry for stable isotopic analysis, requiring only the addition of a commercially produced carrier-gas interface (in this case, the Finnigan Gas Bench II), and the fabrication of a relatively simple metal extraction line from readily available components.

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References

Beaumont, V., Robert, F., 1999. Nitrogen isotope ratios of kerogens in Precambrian cherts: a record of the evolution of atmosphere chemistry? Precambrian Res. 96, 63–82.

Bebout, G.E., 1997. Nitrogen isotope tracers of high-temperature fluid–rock interactions: case study of the Catalina Schist, California. Earth Planet. Sci. Lett. 151, 77–91.

Bebout, G.E., Fogel, M.L., 1992. Nitrogen-isotope compositions on metasedimentary rocks in the Catalina Schist, California: implications for metamorphic devolatilization history. Geochim. Cosmochim. Acta 56, 2139–2149.

Bebout, G.E., Sadofsky, S.J., 2004. δ^{15}N analyses of ammonium-rich silicates by sealed-tube extractions and dual inlet, viscous-flow mass spectrometry. In: de Groot, P. (Ed.), Handbook Stable Isotope Techniques. Elsevier, pp. 348–360.

Bebout, G., Idleman, B., Li, L., Hilkert, A., 2004. High-precision isotopic analysis of nanomole quantities of silicate nitrogen (extended abstract). In: Wanty, R.B., Seal III, R.R. (Eds.), Water–Rock Interaction, vol. 1. A.A. Balkema, Brookfield, Vt.

Boyd, S.R., 2001. Nitrogen in future biosphere studies. Chem. Geol. 176, 1–30.

Boyd, S.R., Pillinger, C.T., 1990. Determination of the abundance and isotope composition of nitrogen within organic compounds: a sealed tube technique for use in static vacuum mass spectrometers. Meas. Sci. Technol. 1, 1176–1183.

Brand, W., 1996. High precision isotope ratio monitoring techniques in mass spectrometry. J. Mass Spectrom. 31, 225–235.

Brauer, K., Hahne, K., 2005. Methodical aspects of the ^{15}N-analysis of Precambrian and Palaeozoic sediments rich in organic matter. Chem. Geol. 218, 361–368.

Busigny, V., Laverne, C., Bonifacie, M., 2005. Nitrogen content and isotopic composition of oceanic crust at a superfast spreading ridge: a profile in altered basalts from ODP Site 1256, Leg 206. Geochem. Geophys. Geosyst. 6. doi:10.1029/2005GC001020.

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

Hilton, D.R., Fischer, T.P., Marty, B., 2002. Noble gases and volatile recycling at subduction zones. In: Porcelli, D., et al. (Ed.), Noble Gases in Geochemistry and Cosmochemistry. Rev. Mineral. Geochem., vol. 47, pp. 319–370.

Humbert, F., Libourel, G., France-Lanord, C., Zimmermann, L., Marty, B., 2000. CO_2-laser extraction-static mass spectrometry analysis of ultra-low concentrations of nitrogen in silicates. Geostand. Lett. 24, 255–260.

Jia, Y., Kerrich, R., Gupta, A.K., Fyfe, W.S., 2003. ^{15}N-enriched Gondwana lamproites, eastern India: crustal N in the mantle source. Earth Planet. Sci. Lett. 215, 43–56.

Kyser, K., Klassen, K., Mitchell, R., 2000. Analysis of N isotopes in micas and amphiboles using EA-CF-IRMS: problems, solutions and implications for the origin of N in hydrous phases from the mantle. Proc. GeoCanada. Alberta, Calgary. May.

Li, L., Bebout, G. E., Idleman, B. D., in press. Nitrogen concentration and δ^{15}N of altered oceanic crust obtained on ODP Legs 129 and 185: Insights into alteration-related nitrogen enrichment and the nitrogen subduction budget. Geochem. Cosmochim. Acta. doi:10.1016/j.gca.2007.02.001.

Macko, S., 1981. Stable nitrogen isotope ratios as tracers of organic geochemical processes. Ph.D. dissertation, Univ. Texas.

Merritt, D.A., Hayes, J.M., 1994. Factors controlling precision and accuracy in isotope-ratio-monitoring mass spectrometry. Anal. Chem. 66, 2336–2347.

Ono, S., Wing, B., Rumble, D., Farquhar, J., 2006. High precision analysis of all four isotopes of sulfur (^{32}S, ^{33}S, ^{34}S and ^{36}S) at nanomole levels using a laser fluorination isotope-ratio- monitoring gas chromatography–mass spectrometry. Chem. Geol. 225, 30–39.

Papineau, D., Mojzsis, S.J., Karhu, J.A., Marty, B., 2005. Nitrogen isotopic composition of ammoniated phyllosilicates: case studies from Precambrian metamorphosed sedimentary rocks. Chem. Geol. 216, 37–58.

Sadofsky, S.J., Bebout, G.E., 2000. Ammonium partitioning and nitrogen isotope fractionation among coexisting micas during high temperature fluid–rock interactions: examples from Vermont and Maine, U.S.A. Geochim. Cosmochim. Acta 64, 2835–2849.

Snyder, G.R., Poreda, R., Fehn, U., Hunt, A., 2003. Sources of nitrogen and methane in Central American geothermal settings: noble gas and ^{129}I evidence for crustal and magmatic volatile components. Geochem. Geophys. Geosyst. doi:10.1029/2002GC000363.

Young, E.D., Fogel, M.L., Rumble III, D., Hoering, T.C., 1998. Isotope-ratio-monitoring of O_2 for microanalysis of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ in geological materials. Geochim. Cosmochim. Acta 62, 3087–3094.