Recommendations on offline combustion-based nitrogen isotopic analysis of silicate minerals and rocks

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Abstract

RATIONALE: Due to isotope fractionations during partial nitrogen release from minerals and rocks, a complete extraction of nitrogen for analysis is crucial to ensure high-quality nitrogen isotopic data. However, the appropriate nitrogen extraction conditions (e.g., temperature, duration) have not been established for most of silicate minerals and rocks.

METHODS: Nitrogen in a number of common minerals and rocks was extracted by the most robust sealed-tube offline combustion techniques, purified and quantified in a custom-made manifold, and carried by helium gas to an isotope-ratio mass spectrometer for isotopic measurement at nanomolar N_2 level. Each mineral or rock was combusted in a variety of temperatures and durations to compare the nitrogen yields and isotopic compositions.

RESULTS: Nitrogen yields and isotopic compositions of minerals and rocks are strongly affected by combustion temperature and duration. The optimal combustion temperature is lowest for cyclosilicate minerals, followed by phyllosilicate, tectosilicate and inosilicate minerals. Preheating of samples can induce significant nitrogen loss and $\delta^{15}N$ shift. Overheating of samples higher than their optimal temperatures may cause nitrogen re-assimilation by the residual mineral or rock.

CONCLUSIONS: Each mineral or rock has a characteristic optimal temperature and duration for complete nitrogen release. Preheating, under-heating, or over-heating can cause nitrogen loss and isotopic shift. Therefore, we recommend to use the offline combustion techniques and the optimal combustion conditions obtained in this study for nitrogen quantification and isotopic analysis of minerals and rocks.

Key Words: Nitrogen isotopes, offline combustion, combustion temperature, minerals, rocks.

1 | INTRODUCTION

Nitrogen in silicate minerals mainly occurs as NH_4^+ substituting K^+ or Na^+ in crystal lattice (e.g., biotite, muscovite, K-feldspar, plagioclase)[1], N_2 in fluid inclusions, or diverse species (e.g., N_2, NH_4^+) in cyclosilicate minerals (e.g., cordierite, beryl)[2-3]. While N_2 in fluid inclusion is more difficult to work with because of its extremely low content and complicated history (e.g., coexistence of multiple generations), the lattice-site and C-channel nitrogen species have been explored to characterize geological and biological nitrogen cycles over Earth's history based on their isotopic compositions.

Due to the relatively small magnitudes of equilibrium nitrogen isotope fractionations between minerals[3-6], the application of nitrogen isotopes to field studies requires high-precision and high-accuracy isotopic analysis. In this regard, a complete nitrogen extraction from the study target is crucial to avoid any isotopic shift during nitrogen extraction.

Compared with other commonly used nitrogen extraction techniques, e.g., Kjeldahl digestion (which may volatize significant amounts of nitrogen during chemical processing) and short-time combustion in elemental analyzer (which combusts samples for only a few seconds at relatively low temperatures of 900-1000 ºC), the sealed-tube combustion method surpasses for its capability of combustion at higher temperatures (up to 1200 ºC) and longer time (for hours) while retaining all released nitrogen intact inside a tube[7-11].

Depending on the binding strength of the nitrogen species in a mineral, the required combustion temperature and duration may vary among different minerals. For example, previous studies found that combustion at about 950 ºC overnight can efficiently release the nitrogen in muscovite[4, 12], as well as altered oceanic basalts[13], whereas an extra step of combustion at 1200 ºC for 30 min is needed to completely release the nitrogen in biotite[4, 12]. Using step-heating extraction with 30-45 minutes at each step, some studies[14-15] found that notable amounts of nitrogen could be still yielded at >1200 ºC for feldspar and granite. Bebout and Sadofsky[12] also observed slightly higher nitrogen yields from buddingtonite when combustion temperature increased from 910 ºC to 1100 ºC. Therefore, combustion temperature and duration are crucial parameters for nitrogen analysis, but have not been well constrained for most of the minerals and rocks.

In addition, some inconsistent sample pretreatment methods exist among different laboratories. For example, Busigny et al.[7] employed a step of preheating at 450 ºC for 12 hours with 1 hour under an O_2 environment to remove possible organic contamination and absorbed air in samples, whereas other laboratories employed a lower temperature (e.g., 150 ºC)[10,16] or no preheating at all[8]. The effect of preheating on nitrogen yields and isotopic compositions has not been assessed, which makes the inter-laboratory data comparison difficult.

In this contribution, we carried out extensive tests on natural samples aiming to standardize the protocols for combustion extraction of nitrogen in silicate minerals and rocks, with the focus on recommending (1) the optimal combustion temperature and duration, and (2) whether to apply a pretreatment on samples for nitrogen isotopic analysis.

2 | MATERIALS AND METHODS

The analytical line (Figure 1) used at University of Alberta includes a Thermo MAT 253 isotope-ratio mass spectrometer, a GasBench II interface, and a custom-made ultrahigh-vacuum metal line. The setup is similar to the ones at Lehigh University[8] and Chinese Academy of Sciences[16], but improved in two aspects: (1) the tube breaker was expanded from 1 to a set of 6, which allow to run 6 samples in a batch without breaking the system vacuum to air by reloading samples; (2) 6 extra ports were added for cryogenic sample collection, which allow to collect CO_2 gas from the same sample (if there is any) for additional carbon isotopic analysis.

The protocols for nitrogen extraction and isotopic analysis in our laboratory are briefly described below:

(1) All involved materials including a one-end sealed quartz tube and quartz wool were combusted at 1200 ºC for 2 hours in a muffle furnace to remove possible contamination.

(2) Fine powders (< 200 mesh) of a sample, precleaned quartz wool, and Cu_xO_x reagent prepared following the procedure of Bebout et al.[8] were sequentially loaded into the precleaned quartz tube, which was evacuate overnight in a custom-made metal manifold and subsequently sealed under high vacuum (2.5×10^{-7} mbar).

(3) For any sample that requires combustion at >1000 ºC, under which the Cu_xO_x reagent would react relatively easily with quartz tube and cause tube cracking, the combustion was carried out in an open-end tube furnace, with the sample being placed at the peak-temperature center and Cu_xO_x being separated by quartz wool to the low-temperature part of the furnace. This step can be omitted for samples that do not require extra combustion over 1100 ºC.

(4) The entire quartz tube was put into a programmable muffle furnace to combust at 900 ºC (700, 800 or 1000 ºC in some tests; see Table 1) for 8 hours, and then cooled down to 600ºC and stayed for 2 hours, before it was naturally cooled down to room temperature. The step of 600 ºC is to convert all the NO_x from high-temperature combustion to N_2, which is the working gas for nitrogen isotopic measurement in isotope-ratio mass spectrometer.

(5) The combusted tube was loaded into a tube cracker attached on the metal manifold (Figure 1) and pumped overnight to reach high vacuum (1.5×10^{-7} mbar).

(6) The tube was cracked to release N_2, which was then cryogenically purified (Cold trap #1 in Figure 1), and concentrated to a molecular sieve-filled volume (U trap #2 in Figure 1) for quantification by a capacitance manometer.

(7) After quantification, the N_2 was collected into a molecular sieve-filled U trap (#3 in Figure 1) with a 4-way Valco valve, which allows the N_2 to be carried by an ultrahigh pure helium gas flow to another molecular sieve-filled U trap (#4 in Figure 1) for concentration. This step is to achieve a better peak shape for nitrogen isotopic analysis.

(8) Finally, the N_2 was sent through a GasBench II interface to the isotope-ratio mass spectrometer for nitrogen isotopic measurement.

The total background N_2 is about 15 nmol in our system, in which 70% is contributed by the Cu_xO_x reagent, 20% is from quartz wool and tube, and 10% is from the metal manifold. Because H_2O and CO_2 can be efficiently removed by the cold traps in the metal manifold, the water traps in the GasBench II system, and the helium carrier gas, we do not include CaO in the reagent, which would otherwise give much higher blank[7]. The $\delta^{15}N$ value of total background N_2 vary from $-5.4^{\pm1.2}$‰ to $-2.8^{\pm1.2}$‰ (2σ) among different batches of Cu_xO_x and quartz wool. Repeated analyses of a high- and a low-organic content sediment standard yielded analytical uncertainties of <0.2‰ (2σ) for $\delta^{15}N$ value in our system. Duplicate or triplicate sample analyses at individual combustion conditions yielded consistent uncertainties (Table S1).

Following the analytical protocol above, two batches of experiments were carried out. The first batch aims to determine the optimal combustion conditions for a number of minerals and rocks by comparing the yields and isotopic compositions of nitrogen released under a variety of temperatures and durations. The second batch aims to assess the preheating effect on nitrogen yield and isotopic composition, exemplified by three submarine basalts and an ultrahigh-pressure metamorphic phengite. The preheating was carried out on the metal manifold overnight at a variety of temperatures from 100ºC to 400 ºC before the sample was sealed into quartz tube for combustion. Following the procedure of Busigny et al.[7], the sample was exposed to a pure O_2 atmosphere (generated from heated Cu_xO_x) for an hour to remove any organic contamination and pumped for the rest of time during the course of this preheating step.

All the samples used in this study are described in detail in the Supplementary Information. For rock samples, fresh pieces of hand specimens were pulverized into fine powders (<200 mesh). For mineral samples, except the clay sample which was an isotope reference material (IAEA-B-8) for boron isotope analysis from the International Atomic Energy Agency (IAEA, Vienna, Austria), all other minerals were separated from fresh rock samples and purified by hand-picking. The mineral separates were then pulverized into fine powders (<200 mesh) by agate pestle and mortar to ensure content and isotopic homogeneity.

3 | RESULTS AND DISCUSSION

3.1 | Controlling factors on nitrogen release from silicate minerals and rocks

The results of the first batch of experiments on combustion condition are given in Supplementary Table S1 and plotted in Figure 2.

Figure 2 illustrates that temperature has a strong control on nitrogen release from all the investigated minerals and rocks. All minerals and rocks show increasing nitrogen yields from their lowest testing temperatures toward higher testing temperatures. The $\delta^{15}N$ values of all samples except clay and serpentinite (see more discussion below) also show correlated increase. This demonstrates that partial nitrogen release from minerals and rocks is associated with isotope fractionations.

Each individual sample reaches its maximal nitrogen yield at a specific temperature. Combustion at higher temperatures either gives equivalent nitrogen yields with similar $\delta^{15}N$ values (e.g., cordierite, clay, muscovite, biotite, phlogopite, plagioclase, altered basalt, clay; Figure 2) or lower nitrogen yields with either elevated $\delta^{15}N$ values (e.g., K-feldspar; fresh basalts, gabbro, granite) or lowered $\delta^{15}N$ values (e.g., clinopyroxene, blueschist, eclogite). The decrease in nitrogen yield at higher temperatures suggests that overheating can sometimes drive part of the released nitrogen back into the solid phase in the tube, although the isotopic behavior during this process is more complicated than a single isotope fractionating reaction. The exact nitrogen sink in the solid phases is not clear yet. Nevertheless, this phenomenon indicates that higher temperature is not always better for nitrogen extraction.

Among the examined minerals, cyclosilicate minerals (e.g., cordierite and tourmaline) can completely release their nitrogen at 900 ºC. Although more nitrogen is yielded from the tourmaline sample at 1000 ºC, it has a much lower $\delta^{15}N$ value relative to the nearly constant $\delta^{15}N$ values at 700-900 ºC (Figure 2). This suggests that the extra nitrogen released by the 1000 ºC combustion is from a different source, likely some micro-inclusions of mica and/or feldspar in the sample. Therefore, we recommend to use 900 ºC overnight combustion for cyclosilicate minerals.

Combustion at higher temperatures may have higher chance to introduce nitrogen contamination from micro-mineral inclusions, particularly giving that mica and feldspars are common minerals coexisting with natural cyclosilicate minerals.

Compared with cyclosilicate minerals, phyllosilicate, tectosilicate and inosilicate minerals appear to require higher temperatures to completely release their nitrogen (Figure 2). This may be attributed to the relative binding energy – the nitrogen in cyclosilicate minerals is mainly as N_2 in C-channels and thus weakly bonded, whereas the nitrogen in the other silicate minerals is as ammonium in the lattice and thus more strongly bonded.

Among the phyllosilicate minerals, the two low-temperature minerals, clay and serpentine (which dominates the serpentinite samples), show strikingly different isotopic patterns to the other high-temperature minerals. They display steadily decreasing $\delta^{15}N$ values with increasing nitrogen yields (Figure 2). This pattern implies that clay and serpentine probably contain nitrogen in at least two different sites, with depleted ^{15}N in the more strongly bonded nitrogen. The nitrogen yields and isotopic compositions of the clay sample and one of the serpentinite sample do not show much difference from 900 ºC to1000 ºC. However, the other tested serpentinite sample yielded extra nitrogen at 1200 ºC, which is speculated to source from some more refractory minerals, such as residual pyroxene that potentially remains in the sample.

The high-temperature phyllosilicate minerals, such as muscovite, biotite and phlogopite, require higher temperatures for complete nitrogen release (Figure 2). Previous studies[4, 12] have found that white micas (including muscovite, toebite, fucsite) could efficiently release nitrogen at 910 – 950 °C for white micas and 1050-1200 ºC for biotite. However, the nitrogen yields and isotopic compositions in these recommended temperature ranges, particularly for white micas, show relatively large variability[4, 12]. Based on a detailed look into the data in [4, 12] and our independent tests on biotite and phlogopite, we recommend to use an extra step of 30 min combustion at 1100 ºC for white mica and at 1200 ºC for biotite and phlogopite (Table 1).

The nitrogen release becomes more and more difficult from phyllosilicate, tectosilicate, to inosilicate. This may be attributed to the increasing binding strength of ammonium in these mineral structures[6].

Besides the binding effect, crystallinity may also affect the nitrogen release temperature. This can be inferred from the observation that gabbro and eclogite samples require much higher temperature (1200 ºC) than that of (900ºC) basalt and blueschist samples.

Water content has been speculated to promote nitrogen release during combustion and thus may decrease the combustion temperature. However, our tests indicate that the altered basalt sample (with a water content of ~ 2.5 wt.%) requires the same combustion condition to the fresh basalt sample (from Hawaii, with a volatile content <0.1% based on loss on ignition analysis). This comparison indicates that water content may not play an important role in nitrogen release during combustion.

3.2 | Optimal combustion conditions for nitrogen extraction

The optimal combustion temperature and duration for each of the tested minerals and rocks are selected based on the following criteria. If a plateau is achieved for nitrogen yield and $\delta^{15}N$ value (e.g., cordierite, phyllosilicates, plagioclase), the combustion condition corresponding to the start of the plateau is used; if a plateau is not achieved, the combustion condition giving the highest nitrogen yield is used (e.g., K-feldspar, clinopyroxene, basalts, gabbro, blueschist, eclogite, granite). The tourmaline and one of the serpentinite samples are slightly more complicated because extra nitrogen from other minerals were likely involved at higher temperatures. The optimal combustion conditions for the tested minerals and rocks are listed in Table 1.

3.3 | Preheating or not?

Preheating test results are listed in Supplementary Table S2 and plotted in Figure 3.

The preheating tests clearly show that overnight degassing of samples at a temperature as high as 400ºC can result in significant (50-80%) nitrogen loss from submarine basalts (Figure 3; Table S2). Mass-balance calculations show that the lost nitrogen from the basalt samples is characterized by diverse $\delta^{15}N$ values from -3.0‰ to +9.9‰, which do not point to either air contamination or organic contamination. Instead, the content and isotopic signatures of the lost nitrogen are similar to those of ammonium added into the basalts through seawater-basalt interaction[13, 17]. Therefore, these experimental results suggest that secondary nitrogen in submarine basalts can be significantly degassed by 400 ºC heating. This is not surprising because the secondarily added nitrogen is mostly hosted by low-temperature secondary minerals (e.g., clay) [13, 17]. Accordingly, we recommend not to use preheating treatment for samples, particularly for these aiming to address relatively low-temperature processes, such as microbe-rock interaction, hydrothermal alteration, weathering.

We further tested the impact of preheating on the nitrogen yield and isotopic composition of high-temperature minerals, using phengite in an ultrahigh-pressure eclogites sample from the Sulu belt in eastern China[9]. The results of overnight heating at 100 ºC and 200 ºC show that only minor amounts of nitrogen are lost (Figure 3; Table S2). This suggests that air and organic contamination of nitrogen on samples is very minor. A blank control going through the same procedure of the phengite sample also indicates that air and organic contaminations are negligible. However, when heated overnight at 400 ºC, phengite can lose about 40% of its nitrogen. This fraction is much larger than those from the step-heating method by Boyd et al.[14], who showed that only a small fraction of nitrogen could be released below 500 ºC. It is not clear yet whether this difference is caused by the heating duration difference between our tests (overnight) and the step-heating method (30-45 min). Nevertheless, we recommend to avoid using preheating treatment as much as possible during nitrogen isotopic analysis, even for high-temperature minerals. If preheating has to be used in case-specific circumstances, we recommend to heat at temperatures < 200 ºC.

3.4 | Isotopic effect during nitrogen devolatilization from minerals and rocks

Among some of the combustion experiments, the minerals and rocks only partially released their nitrogen, even at temperatures as high as 700-1200 ºC (Figure 2). This provides an opportunity to look into the nitrogen release from silicate minerals and rocks and associated isotopic effect in high-temperature oxic environment, which mimics the devolatilization process during metamorphism.

Incomplete nitrogen release from all the minerals and rocks except clay and serpentinite gave ^{15}N-depleted N_2 (Figure 2; Table S1), indicating that nitrogen devolatilization from minerals and rocks favors ^{14}N. Assuming that the average nitrogen yields and $\delta^{15}N$ values obtained at the optimal combustion conditions represent the true contents and isotopic compositions of the minerals and rocks, we did a ballpark estimate on the nitrogen isotope fractionation factors during high-temperature nitrogen devolatilization using both Rayleigh kinetic model[18] and batch equilibration model[19] (Figure 4).

The isotopic shifts associated with partial nitrogen devolatilization spread over a large range. The data can be modeled by either Rayleigh fractionations with isotope fractionation factors ranging from 0.9996 to 0.9964 or batch fractionations with isotope fractionation factors ranging from 0.9995 to 0.9940 (Figure 4). A fractionation factor of 0.9940 defined by the clinopyroxene data is much lower than the predicted equilibrium fractionation factors (0.9960 to 0.9975 at 900-1200 ºC) between clinopyroxene and N_2 derived from Li et al.[6, 20], suggesting equilibrium isotopic effect did not dominate the nitrogen devolatilization process. However, no clear data relationship show that a kinetic isotopic effect dominated the nitrogen devolatilization process either. The data do suggest that cyclosilicate minerals show the least isotope fractionation, whereas tectosilicate (e.g., plagioclase) and inosilicate (e.g., clinopyroxene) show the largest isotope fractionations during nitrogen devolatilization. The small isotope fractionations for cyclosilicate minerals (cordierite and tourmaline) could be attributed to their dominant nitrogen species is N_2 rather than NH_4^+.

4 | CONCLUSION

The release of nitrogen from silicate minerals and rocks is strongly controlled by temperature. Incomplete nitrogen release can induce significant isotopic shifts even at high temperatures of >1000 ºC. Cyclosilicate minerals have the least nitrogen isotope fractionations during nitrogen release and overnight combustion at 900 ºC is enough to completely release their nitrogen. Phyllosilicate, tectosilicate and ionsilicate minerals show progressive nitrogen retention capability and require higher combustion temperature and longer duration for complete nitrogen release. We recommend to use the optimal combustion condition of individual mineral or rock obtained in this study to for accurate nitrogen quantification and isotopic analysis. Either insufficient combustion or overheating can cause nitrogen loss and isotopic shift. Preheating samples at temperature higher than 200 ºC is not recommended, even for high-temperature minerals.

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Figure Captions:

Figure 1. Schematic manifold for nitrogen extraction from combusted quartz tube for quantification and isotopic analysis.

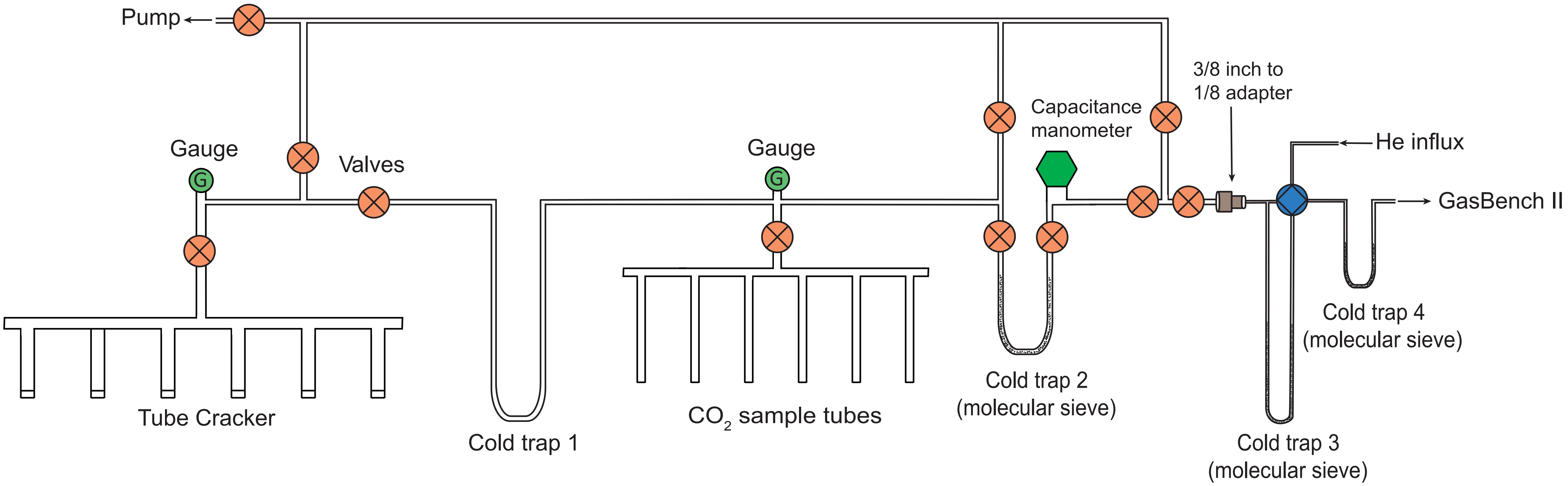
Figure 2. Nitrogen yields and δ^{15}N values of silicate minerals and rocks combusted at a variety of temperatures and durations. 1 = 700 ºC for 8 hours; 2 = 800 ºC for 8 hours; 3 = 900 ºC for 8 hours; 4 = 1000 ºC for 8 hours; 5 = 1100 ºC for 30 minutes + 900 ºC for 8 hours; 6 = 1200 ºC for 30 minutes + 900 ºC for 8 hours; 7 = 1200 ºC for 60 minutes + 900 ºC for 8 hours; 8 = 1200 ºC for 90 minutes + 900 ºC for 8 hours. Optimal combustion condition of each mineral or rock is highlighted by a grey bar. Note that more than one sample (denoted by different symbols) were tested for muscovite and serpentinite. See Table S1 for data. The error bars are smaller or close to the symbols, and thus not shown.

Figure 3. Nitrogen yields and δ^{15}N values of three basalt sample and one phengite sample with no preheating (squares) and 400 ºC preheating (magenta circles). The phengite sample was also tested for 100 ºC (yellow circle) and 200 ºC (orange circle) preheating.

Figure 4. Isotope modeling of the partially released nitrogen for minerals and rocks using Rayleigh kinetic (curves) and batch equilibration (linear lines) models. f denotes the fraction of remaining nitrogen in a sample after combustion. The initial nitrogen content and δ^{15}N value of a mineral or rock are represented by the average values from combustions at the optimal condition. The isotope fractionation factors for the two Rayleigh fractionation curves are 0.9996 (upper curve) and 0.9964 (lower curve), respectively. The isotope fractionation factors used for the batch fractionation modeling are 0.9995 (upper line) and 0.9940 (lower line), respectively. Data source: this study and Ref 4, 12.

Table 1. Recommended temperature and duration for combustion extraction of nitrogen from minerals and rocks for isotopic analysis.

Minerals/rocks	**Recommended T and t**
Cordierite	900 ºC (8 h)
Tourmaline	900 ºC (8 h)
Clay	900 ºC (8 h)
White mica	1100 ºC (30 min) + 900 ºC (8 h)
Biotite	1200 ºC (30 min) + 900 ºC (8 h)
Phlogopite	1200 ºC (30 min) + 900 ºC (8 h)
K-feldspar	1200 ºC (30 min) + 900 ºC (8 h)
Plagioclase	1200 ºC (60 min) + 900 ºC (8 h)
Clinopyroxene	1200 ºC (60 min) + 900 ºC (8 h)
Serpentinite	1000 ºC (8 h)
Basalt	1000 ºC (8 h)
Blueschist	1000 ºC (8 h)
Gabbro	1200 ºC (30 min) + 900 ºC (8 h)
Eclogite	1200 ºC (60 min) + 900 ºC (8 h)
Granite	1200 ºC (60 min) + 900 ºC (8 h)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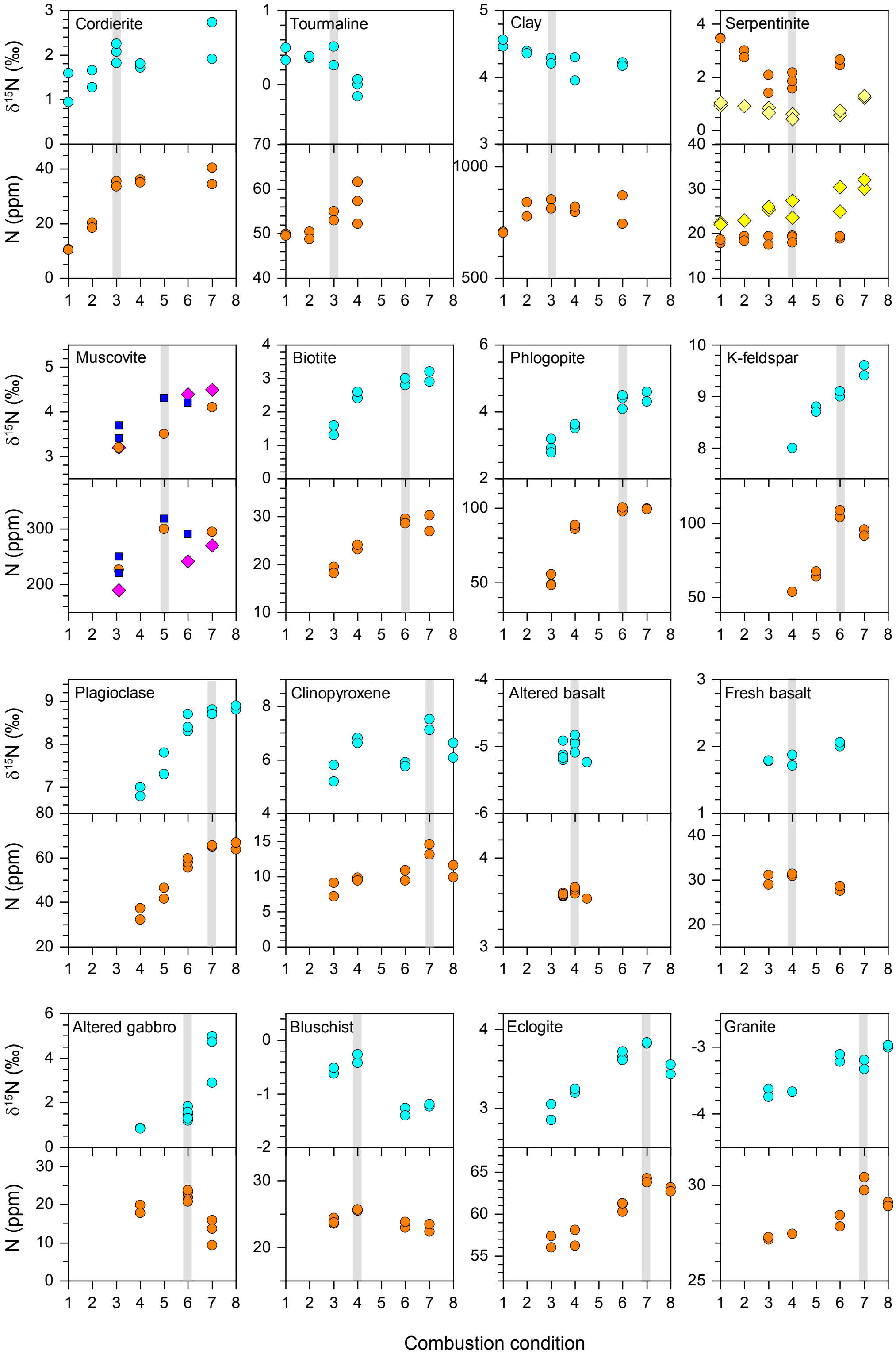
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Biotite
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K-feldspar
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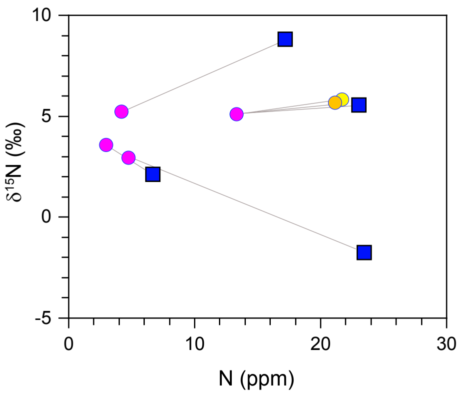
Combustion condition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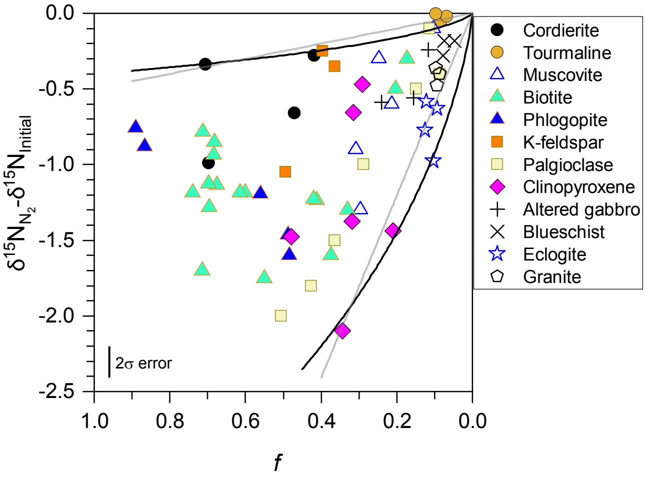
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Cordierite
Tourmaline
Muscovite
Biotite
Phlogopite
K-feldspar
Palgioclase
Clinopyroxene
Altered gabbro
Blueschist
Eclogite
Granite

Recommendations on offline combustion-based nitrogen isotopic analysis of silicate minerals and rocks

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Supporting Information

Contents:

Description of samples:

The samples used in this study were from three sources:

1. Commercial samples: the clay sample was purchased from the International Atomic Energy Agency (IAEA; Vienna, Austria). It is the international reference material (IAEA-B-8) for boron isotope analysis.
2. ODP/IODP samples:
   These include the altered gabbro and two serpentinite samples used for the optimal combustion tests and three altered basalt samples for the pre-heating tests.
   All these samples are fresh cuts from the ODP/IODP cores. While secondary minerals are common as a result of seawater alteration at various degrees, no obvious organic matter is observed in these samples, although organic components at sub-micron scale by microbial alteration cannot be excluded.
3. Natural samples
   All the natural samples used in this study were collected from outcrops around the world. All mineral samples were separated from large fresh samples and purified by handpicking under microscope. All bulk-rock samples were prepared by crushing and grinding fresh hand specimens after removing any weathered surface. The information on each sample is given below:
   (1) Cordierite: this sample was separated from a pegmatite sample from western China, and it also contains muscovite, biotite and plagioclase. The cordierite crystal is clear and in subhedral to euhedral shape. No obvious mineral inclusions are observed under a microscope.
   (2) Tourmaline: this sample was a megacryst (~3×4×6 cm^3) from the Mineralogy and Petrology Collection of the Department of Earth and Atmospheric Sciences of University of Alberta. No obvious mineral inclusion was observed.
   (3) Biotite: this sample was separated from a cretaceous granite sample from eastern China, which has an arc affinity related to the westward subduction of the Pacific Plate.
   (4) K-feldspar and plagioclase: both samples were separated from metapelite samples from Mica Creek (British Columbia, Canada), which belongs to the Omineca Belt of the Canadian Cordillera. The K-feldspar has a composition of An80Ab19Or1. The plagioclase has a composition of An0.1Ab10Or90.
   (5) Phlogopite and clinopyroxene: both minerals were separated from mantle xenolith samples in kimberlite from South Africa.
   (6) Fresh basalt: this sample is a subaerial basalt from Hawaii. The sample is fresh and contain very low volatile components (loss on ignition: <0.1%).
   (7) Blueschist: this sample was collected from the Heilongjiang high-pressure metamorphic belt in Northeast China, which was formed by the westward subduction of the Paleo-Pacific Plate in the Jurassic. This sample is composed of glaucophane, albite, chlorite, epidote, phengite, with accessory phases of titanite, aragonite, rutile, zircon, apatite and ilmenite.
   (8) Eclogite and phengite: the eclogite sample was collected from the Sulu belt in eastern China, which is an ultrahigh-pressure metamorphic belt formed by the southward subduction of the North China Craton beneath the Yangtze Craton in the Triassic. The sample is mainly constituted of garnet, omphacite, phengite, kynite, quartz with minor accessory minerals such as zoisite, rutile, zircon. The phengite sample was separated from another eclogite sample collected from the same locality.
   (9) Granite: this is a Neoproterozoic granite collected from eastern China. It was formed in an extensional setting during the breakup of the Rodinia supercontinent. The sample is composed of quartz, K-feldspar, plagioclase, biotite, and muscovite with minor accessory minerals such as magnetite and zircon.

Table S1: Yield (expressed as ppm content) and isotopic composition of nitrogen released from minerals and rocks by combustion at various temperatures and durations.

Sample	**Combustion step 1**		**Combustion step 1**		**N yield (ppm)**	**δ^{15}N (‰)**
	T (ºC)	**Duration (min)**	**T (ºC)**	**Duration (h)**		
Cordierite			700	8	10.6	0.9
			700	8	10.3	1.6
			800	8	20.4	1.7
			800	8	18.6	1.3
			900	8	35.5	1.8
			900	8	35.6	2.1
			900	8	33.5	2.3
			1000	8	36.1	1.7
			1000	8	35.0	1.8
	1200	60	900	8	34.5	1.9
	1200	60	900	8	40.4	2.7
Tourmaline			700	8	50.0	0.5
			700	8	49.5	0.3
			800	8	50.4	0.4
			800	8	48.8	0.4
			900	8	55.0	0.3
			900	8	53.0	0.5
			900	8	57.3	0.0
			1000	8	61.7	-0.2
			1000	8	52.3	0.1
Clay			700	8	707.5	4.5
			700	8	702.2	4.6
			800	8	841.3	4.4
			800	8	778.2	4.4
			900	8	854.4	4.3
			900	8	758.4	4.1
			900	8	812.2	4.2
			1000	8	798.0	4.0
			1000	8	821.3	4.3
	1200	30	900	8	743.6	4.2
	1200	30	900	8	870.8	4.2
Muscovite (data from Ref 4, 12)			910		190.0	3.2
			1200		242.0	4.4
			1250		270.0	4.5
			910		226.0	3.2
			1100		300.0	3.5
			1250		294.0	4.1
			910		220.0	3.4
			910		250.0	3.7
			1100		318.0	4.3
			1200		290.0	4.2

Sample	Combustion step 1		Combustion step 1		N yield (ppm)	δ^{15}N (‰)
	T (ºC)	Duration (min)	T (ºC)	Duration (h)		
Biotite			900	8	19.5	1.6
			900	8	18.2	1.3
			1000	8	23.2	2.4
			1000	8	24.1	2.6
	1200	30	900	8	29.6	2.8
	1200	30	900	8	28.6	3.0
	1200	60	900	8	27.0	3.2
	1200	60	900	8	30.3	2.9
Phlogopite			900	8	48.6	2.9
			900	8	55.7	3.2
			900	8	48.2	2.8
			1000	8	86.2	3.5
			1000	8	88.5	3.6
	1200	30	900	8	100.0	4.1
	1200	30	900	8	97.8	4.4
	1200	30	900	8	100.6	4.5
	1200	60	900	8	99.8	4.6
	1200	60	900	8	99.5	4.3
K-feldspar			1000	8	53.8	8.0
	1100	30	900	8	64.1	8.8
	1100	30	900	8	67.6	8.7
	1200	30	900	8	104.0	9.0
	1200	30	900	8	108.5	9.1
	1200	60	900	8	95.7	9.6
	1200	60	900	8	91.6	9.4
Plagioclase			1000	8	37.4	7.0
			1000	8	32.3	6.8
	1100	30	900	8	41.5	7.3
	1100	30	900	8	46.5	7.8
	1200	30	900	8	55.6	8.3
	1200	30	900	8	57.9	8.7
	1200	60	900	8	59.6	8.4
	1200	60	900	8	65.0	8.8
	1200	90	900	8	65.6	8.7
	1200	90	900	8	63.7	8.8
Clinopyroxene			900	8	7.2	5.8
			900	8	9.1	5.2
			1000	8	9.8	6.8
			1000	8	9.4	6.6
		30	900	8	9.4	5.9
		30	900	8	10.9	5.8
		60	900	8	13.1	7.5
		60	900	8	14.6	7.1
		90	900	8	9.9	6.1
		90	900	8	11.6	6.6

Sample	**Combustion step 1**		**Combustion step 1**		**N yield (ppm)**	**δ^{15}N (‰)**
	T (ºC)	**Duration (min)**	**T (ºC)**	**Duration (h)**		
Altered basalt (data from ref 13)			950	8	3.6	-5.2
			950	8	3.6	-5.1
			950	8	3.6	-5.1
			950	8	3.6	-4.9
			950	8	3.6	-5.2
			1000	8	3.6	-4.9
			1000	8	3.6	-5.0
			1000	8	3.6	-5.1
			1000	8	3.7	-4.8
			1050	8	3.5	-5.2
Fresh basalt			900	8	28.9	1.8
			900	8	31.2	1.8
			1000	8	30.9	1.9
			1000	8	31.4	1.7
	1200	30	900	8	27.6	2.0
	1200	30	900	8	28.6	2.1
Altered gabbro			1000	8	19.8	0.9
			1000	8	17.8	0.8
	1200	30	900	8	21.9	1.5
	1200	30	900	8	21.9	1.8
	1200	30	900	8	20.7	1.2
	1200	30	900	8	23.1	1.6
	1200	60	900	8	23.8	1.3
	1200	60	900	8	15.9	2.9
	1200	90	900	8	13.7	5.0
	1200	90	900	8	9.4	4.7
Blueschist			900	8	24.4	-0.5
			900	8	23.6	-0.6
			900	8	23.7	-0.5
			1000	8	25.5	-0.4
			1000	8	25.7	-0.3
	1200	30	900	8	23.0	-1.3
	1200	30	900	8	23.8	-1.4
	1200	60	900	8	22.4	-1.2
	1200	60	900	8	23.5	-1.2
Eclogite			900	8	56.0	3.1
			900	8	57.3	2.8
			1000	8	58.1	3.2
			1000	8	56.2	3.2
	1200	30	900	8	60.3	3.7
	1200	30	900	8	61.2	3.6
	1200	30	900	8	61.3	3.7
	1200	60	900	8	64.3	3.8
	1200	60	900	8	63.8	3.8
	1200	90	900	8	63.2	3.6
	1200	90	900	8	62.7	3.4

Sample	**Combustion step 1**		**Combustion step 1**		**N yield (ppm)**	**$\delta^{15}N$ (‰)**
	T (ºC)	**Duration (min)**	**T (ºC)**	**Duration (h)**		
Granite			900	8	27.2	-3.6
			900	8	27.3	-3.7
			1000	8	27.5	-3.7
	1200	30	900	8	27.8	-3.2
	1200	30	900	8	28.5	-3.1
	1200	60	900	8	30.4	-3.2
	1200	60	900	8	29.7	-3.3
	1200	90	900	8	29.1	-3.0
	1200	90	900	8	28.9	-3.0
Serpentinite						
Sample 1			700	8	17.9	3.5
			700	8	18.6	3.4
			800	8	19.5	3.0
			800	8	18.3	2.7
			900	8	19.5	1.4
			900	8	17.6	2.1
			1000	8	19.5	1.6
			1000	8	19.3	1.8
			1000	8	18.0	2.2
	1200	30	900	8	18.9	2.4
	1200	30	900	8	19.4	2.6
Sample 2			700	8	22.7	1.2
			700	8	22.4	0.9
			800	8	22.1	1.0
			900	8	23.0	0.9
			900	8	25.4	0.9
			1000	8	26.0	0.7
			1000	8	23.6	0.6
	1200	30	900	8	27.4	0.4
	1200	30	900	8	25.0	0.6
	1200	60	900	8	30.5	0.8
	1200	60	900	8	30.1	1.2
	1200	60	900	8	32.1	1.3

Table S2: Comparison of yield (expressed as ppm content) and isotopic composition of nitrogen released from minerals and rocks without pre-heating (at room T) and pre-heating at 100-400 ºC overnight. The fraction and $\delta^{15}N$ value of the lost N are calculated by mass balance between the results of heated and non-heated samples.

Sample	Pretreatment	N yield (ppm)	$\delta^{15}N$ (‰)
Basalt 1	Room T	23.5	-1.8
	400 ºC heating	4.8	2.9
	Lost N	80%	-3.0
Basalt 2	Room T	6.7	2.1
	400 ºC heating	3.0	3.6
	Lost N	55%	0.9
Basalt 3	Room T	17.2	8.8
	400 ºC heating	4.2	5.2
	Lost N	52%	9.9
Phengite	Room T	24.1	5.4
	Room T	22.0	5.7
	Average	23.1	5.5
	100 ºC pre-heating	21.4	5.4
	100 ºC pre-heating	22.1	5.8
	Average	21.8	5.8
	Lost N	6%	0.9
	200 ºC pre-heating	21.1	5.6
	200 ºC pre-heating	21.2	5.7
	Average	21.2	5.7
	Lost N	8%	4.3
	400 ºC pre-heating	14.2	5.0
	400 ºC pre-heating	13.9	5.2
	400 ºC pre-heating	12.0	5.0
	Average	13.4	5.1
	Lost N	42%	6.2