Reassessment of the NH₄NO₃ thermal decomposition technique for calibration of the N₂O isotopic composition

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RATIONALE: In the last few years, the study of N2O site-specific nitrogen isotope composition has been established as a powerful technique to disentangle N2O emission pathways. This trend has been accelerated by significant analytical progress in the field of isotope–ratio mass–spectrometry (IRMS) and more recently quantum cascade laser absorption spectroscopy (QCLAS).

METHODS: The ammonium nitrate (NH4NO3) decomposition technique provides a strategy to scale the 15N site-specific (SP ≡ δ15Nα – δ15Nβ) and bulk (δ15Nbulk = (δ15Nα + δ15Nβ) / 2) isotopic composition of N2O against the international standard for the 15N/14N isotope ratio (AIR-N2).

Within the current project 15N fractionation effects during thermal decomposition of NH4NO3 on the N2O site preference were studied using static and dynamic decomposition techniques.

RESULTS: The validity of the NH4NO3 decomposition technique to link NH4+ and NO3- moiety-specific δ15N analysis by IRMS to site-specific nitrogen isotopic composition of N2O was confirmed. However, the accuracy of this approach for calibration of δ15Nα and δ15Nβ was found to be limited by non-quantitative NH4NO3 decomposition in combination with substantially different isotope enrichment factors for the conversion of the NO3- or NH4+ nitrogen atom into the α or β position of the N2O molecule.

CONCLUSIONS: The study reveals that the completeness and reproducibility of the NH4NO3 decomposition reaction currently confines the anchoring of N2O site specific isotopic composition to the international isotope ratio scale AIR-N2. The authors suggest to establish a set of N2O isotope reference materials with appropriate site-specific isotopic composition, as community standards, to improve inter-laboratory compatibility.
Important information on the transformation processes of the potent greenhouse gas and ozone depleting substance nitrous oxide (N₂O) is acquired by analysing its ¹⁵N site-specific and bulk isotopic composition[1, 2]. In the last two decades, research involving N₂O isotopic analysis was stimulated by continuing analytical progress in IRMS and more recently quantum cascade laser based absorption spectroscopy (QCLAS). The mass spectrometric analytical technique for the analysis of the intramolecular ¹⁵N distribution within the linear asymmetric N₂O molecule was accomplished first by Toyoda and Yoshida[3] and by Brenninkmeijer and Röckmann[4]. Since its first realization at Empa in 2008[5], QCLAS and cavity ring-down spectroscopy (CRDS) have been established as independent analytical techniques offering high selectivity for the N₂O isotopic species (¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁸O)[6] and the capability for real-time analysis[7-9]. Throughout the manuscript the terms “isotopomer”, for molecular species having the same number of each isotopic atom but differing in their positions (¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O) and “isotopologue”, for molecular species that differ in the isotopic composition (¹²N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁸O), are used. To specify the location of ¹⁵N substitution in the N₂O molecule, the central and terminal nitrogen atom are designated as α and β position, respectively[3]. The umbrella term "isotopocules" is applied to refer to both isotopomers and isotopologues[10]. Irrespective of the achieved analytical progress, however, the compatibility between laboratories for the N₂O isotopic composition is still limited to several δ -per mil units, due to the restricted availability of suitable reference materials[11].

The synthesis of N₂O by thermal decomposition of isotopically characterised ammonium nitrate (NH₄NO₃) has been suggested as an approach to link the position-dependent nitrogen isotopic composition of N₂O relative to the international standard for the ¹⁵N/¹⁴N isotope ratio, AIR-N₂[3]. The basic concept of this technique is that the nitrogen atom at the central (α) position of product N₂O originates from the NO₃⁻ ion, while the end (β) nitrogen comes from the NH₄⁺.
ion\(^{3, 12}\). The initial inconsistency with a second approach, the addition of small amounts of \(^{15}\)N\(_2\)O to a N\(_2\)O reference gas and tracking changes in the relative ion current species with mass 30, 31, 44, 45, and 46\(^{13}\), was resolved by Westley et al.\(^{14}\) and Griffith et al.\(^{15}\). They advocate inter-calibration of N\(_2\)O isotope measurement results with Tokyo Institute of Technology as the most efficient and reliable method for standardization and claim that isotope fractionation effects during NH\(_4\)NO\(_3\) decomposition are small and symmetrically distributed, which is an essential requirement for the validity of this approach.

In the presented study we reassessed the validity of the NH\(_4\)NO\(_3\) decomposition technique to scale the position-dependent nitrogen isotopic composition of N\(_2\)O to the international isotope ratio standard AIR-N\(_2\). In detail the following approach was applied: (1) NH\(_4\)NO\(_3\) salts with different isotopic composition were prepared and analysed by IRMS; (2) the same NH\(_4\)NO\(_3\) salts were decomposed and isotope fractionation effects for \(\delta^{15}\)N\(^{\alpha}\), \(\delta^{15}\)N\(^{\beta}\) and \(\delta^{18}\)O were studied in flow-through and static thermal decomposition experiments by QCLAS; (3) in addition, \(\delta^{15}\)N\(^{\text{bulk}}\) and \(\delta^{18}\)O of N\(_2\)O, produced by thermal decomposition, were analysed by IRMS relative to AIR-N\(_2\) and Vienna Standard Mean Ocean Water (VSMOW).

EXPERIMENTAL

Preparation of NH\(_4\)NO\(_3\) salts

Four NH\(_4\)NO\(_3\) salts (P1 – P4) with different isotopic composition were prepared by gravimetric mixing of NH\(_4\)NO\(_3\) (\(\geq 98\%\), Carl Roth GmbH, Karlsruhe, Germany) with isotopically pure (98 atom\% \(^{15}\)N) \(^{15}\)NH\(_4\)NO\(_3\) (Sigma-Aldrich Chemie GmbH, Buchs, Switzerland) and (\(\geq 98\%\), 99.9 atom\% \(^{14}\)N) \(^{14}\)NH\(_4\)^{14}NO\(_3\) (Cambridge Isotope Laboratories Inc., Tewksbury, USA). The prepared NH\(_4\)NO\(_3\) mixtures were recrystallized in 20 mL deionized water and dried overnight at 393 K. The isotopic homogeneity of the recrystallized salts was assessed by triplicate thermal decomposition and subsequent QCLAS analysis. The isotopic composition of N\(_2\)O (\(\delta^{15}\)N\(^{\alpha}\),
δ¹⁵Nβ and δ¹⁸O) from individual decomposition experiments coincided within the analytical precision of 0.1 - 0.2 ‰.

Isotopic analysis of NH₄NO₃ by IRMS

The four NH₄NO₃ salts were analysed by four different IRMS laboratories (Laboratory 1A and 1B, 2 and 3) for δ¹⁵N-NO₃⁻ and δ¹⁵N-NH₄NO₃ using their in-house analytical techniques. δ¹⁵N-NH₄⁺ was calculated from δ¹⁵N-NH₄NO₃ and δ¹⁵N-NO₃⁻.

Laboratory 1A: δ¹⁵N and δ¹⁸O in the NO₃⁻ moieties were determined after conversion of NO₃⁻ to N₂O by the bacterial denitrifier assay[16, 17]. For each of the four NH₄NO₃ salts (P1 - P4), four replicate samples were prepared for the denitrifier method, along with the nitrate calibration standards USGS32 (KNO₃, δ¹⁵Nbulk = 180 ± 1 ‰, δ¹⁸O = 25.7 ± 0.4 ‰), USGS34 (KNO₃, δ¹⁵Nbulk = -1.8 ± 0.2 ‰, δ¹⁸O = -27.9 ± 0.6 ‰) and USGS35 (NaNO₃, δ¹⁵Nbulk = 2.7 ± 0.2 ‰, δ¹⁸O = 57.5 ± 0.6 ‰), supplied by NIST (National Institute of Standards and Technology, Gaithersburg, MD). Additional standards were included in the batch to monitor and correct for instrumental drift and linearity. Isotope ratios of ¹⁵N/¹⁴N and ¹⁸O/¹⁶O in N₂O were measured using a ThermoFinnigan GasBench + PreCon trace gas concentration system interfaced to a ThermoScientific Delta V Plus isotope-ratio mass spectrometer (Bremen, Germany). Gas samples were purged from vials through a double-needle sampler into a helium carrier stream (25 mL min⁻¹). CO₂ is removed from the sample by passing through an Ascarite scrubber. N₂O is trapped and concentrated in two cryo-traps at 77 K (liquid N₂) operated in series. It is released from the traps in the helium carrier gas by warming and subsequently passed to the mass spectrometer via an Agilent GS-Q capillary column (30 m x 0.32 mm, 313 K, 1.0 mL min⁻¹, Agilent Technologies Inc., Santa Clara, USA). A reference N₂O peak is used to calculate provisional isotope ratios of the sample N₂O peak. Final corrected isotope values are calculated based on the provisional isotope ratios and the known isotope ratios of the nitrate calibration...
standards. The in-house limit of quantitation was determined to be 2 μM NO₃⁻ in water, the
repeatability for δ¹⁵N and δ¹⁸O of N₂O from NO₃⁻ by bacterial denitrification was 0.4 ‰ for
δ¹⁵N and 0.5 ‰ for δ¹⁸O, respectively.

Laboratory 1B: The measurement of δ¹⁵N-NH₄NO₃ values of P1 – P4 was performed using a
Flash EA 1112 Series elemental analyzer (Thermo Italy, former CE Instruments, Rhodano,
Italy) coupled to a Finnigan MAT Delta+XP isotope–ratio mass–spectrometer (Finnigan
MAT, Bremen, Germany) via a 6-port valve[18] and a ConFlo III (Finnigan MAT, Bremen,
Germany)[19]. The positioning of samples, blanks and (laboratory) standards in a measurement
sequence followed the Identical Treatment principle described by Werner and Brand[20]. Post-
run off-line calculations like blank-, offset- and possibly drift-corrections and a normalization
for assigning the final δ¹⁵N-values on the AIR-N₂ scale were performed according to Werner
and Brand[20]. Calibration of laboratory standards was periodically done by comparison of the
laboratory standards (acetanilide, caffeine, tyrosine) to the corresponding international
reference materials (IAEA-N-1: ((NH₄)₂SO₄, δ¹⁵Nbulk = 0.4 ± 0.2 ‰, IAEA-N-2: (NH₄)₂SO₄,
δ¹⁵Nbulk = 20.3 ± 0.2 ‰, IAEA-NO-3: KNO₃, δ¹⁵Nbulk = 4.7 ± 0.2 ‰) provided by the IAEA
(Vienna, Austria). The repeatability (several years) of our quality control standard (tyrosine)
was 0.15 ‰ or better for δ¹⁵N.

Laboratory 2: Analyses of the δ¹⁵N-NH₄NO₃ of salts P1 – P4 were performed by elemental
analyser–isotope–ratio mass–spectrometry (EA-IRMS) using an INTEGRA 2 instrument
(Sercon Ltd., Crewe, UK). Each salt has been measured in five replicates. In view of the
ammonium and nitrate moieties, which chemically constitute the four salts, and the expected
span in δ¹⁵N the following five isotopic reference materials have been measured in replicates
at the beginning, in the middle, and at the end of the analytical sequence: IAEA-N-1
((NH₄)₂SO₄, δ¹⁵Nbulk = 0.4 ± 0.2 ‰) and USGS26 ((NH₄)₂SO₄, δ¹⁵Nbulk = 53.7 ± 0.4 ‰), IAEA-
NO-3 (KNO₃, δ¹⁵N_{bulk} = 4.7 ± 0.2 ‰) and USGS32 (KNO₃, δ¹⁵N_{bulk} = 180 ± 1 ‰), and RSIL-N7373 (Reston Stable Isotope Laboratory, U.S. Geological Survey, Reston, USA, NaNO₂, δ¹⁵N_{bulk} = -79.6 ‰) [18]. These reference materials were used to check and correct for instrumental drift and for normalization to the AIR-N₂ scale. In order to avoid potential amount linearity effects, the analyzed quantities of the reference materials and salt samples were adjusted to contain (virtually) equal amounts of nitrogen. The repeatability for reference materials IAEA-N-1, USGS26, IAEA-NO-3, and USGS32 was ≤ 0.3 ‰ (1σ, n = 10). Reference material RSIL-N7373, which was specifically included in the analyses due to its very low δ¹⁵N value of -79.6 ‰, exhibited a repeatability of 0.4 ‰ (1σ, n = 10).

For analyses of the δ¹⁵N of the nitrate-moiety (δ¹⁵N-NO₃⁻) of P1 – P4, the salts as well as blanks and four international isotopic reference materials (IAEA-NO-3, USGS32, RSIL-N23 [21]: Reston Stable Isotope Laboratory, NaNO₂, δ¹⁵N_{bulk} = 3.7 ‰, RSIL-N7373) were prepared in replicates (P1 - P4: n = 5, reference materials: n = 4, respectively) using the “denitrifier method” [16, 17], modified according to McIlvin and Casciotti (2011) [22]. This method employs the denitrifying bacterium *Pseudomonas aureofaciens* (ATTC no. 13985), which lacks the N₂O reductase enzyme and quantitatively converts sample-derived NO₃⁻ to N₂O. The four reference materials were chosen with regard to the principle of identical treatment [20] and covering a wide-enough range in δ¹⁵N for isotopic calibration (RSIL-N7373: -79.6 ‰; USGS32: 180 ± 1 ‰).

Isotope analysis of the obtained N₂O was performed on an instrument consisting of an N₂O purification and purge-and-trap system designed after McIlvin and Casciotti (2010) [23], which is coupled to a Delta V Plus isotope–ratio mass–spectrometer (Thermo Fisher Scientific, Bremen, Germany). The four reference materials were used to check for potential instrumental drift and normalization to the AIR-N₂ scale. The repeatability (1σ) of δ¹⁵N-NO₃⁻ for the replicates of the reference materials (n = 4) and salts (n = 5) was ≤ 0.2 ‰.
Laboratory 3: $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NH}_4\text{NO}_3$ analysis of individual salts P1 – P4 was performed in triplicate or quadruplicate as described by P. Schleppi et al.\cite{Schleppi2011}. The applied technique also has the potential to determined $\delta^{15}\text{N}-\text{NH}_4^+$ values, which were not used for data interpretation, due to variable fractionation effects. Rather, $\delta^{15}\text{N}-\text{NH}_4^+$ was calculated from $\delta^{15}\text{N}-\text{NH}_4\text{NO}_3$ and $\delta^{15}\text{N}-\text{NO}_3^-$. For $\delta^{15}\text{N}-\text{NO}_3^-$ analysis, around 180 µL of a 32 µmol L$^{-1}$ aqueous NH$_4$NO$_3$ solution were supplemented with 40 mL of 0.7 mol L$^{-1}$ KCl solution (p.a., Sigma-Aldrich Chemie GmbH, Switzerland) in a 100 mL polyethylene flasks. NH$_4^+$ was removed by addition of 1.5 g L$^{-1}$ MgO (Sigma-Aldrich Chemie GmbH, Switzerland) over 5 days on a mechanical shaker. Thereafter, a 12 x 5 mm calcinated glass filter cut from round filters GF/F; (Whatman plc, Little Chalfont, UK), drenched with 30 µL of 2 mol L$^{-1}$ citric acid (Sigma-Aldrich Chemie GmbH, Switzerland) and sealed with a PTFE band by forming an envelope (Angst + Pfister, Zurich, Switzerland) was added. 0.4 g Devarda’s alloy (Sigma-Aldrich Chemie GmbH, Switzerland) were added to initiate NO$_3^-$ reduction to NH$_4^+$ and the solution was stirred for one week on a horizontal shaker. Thereafter, the filter was dried in a desiccator for 45 minutes, the PTFE membrane removed and the glass filter packed in a tin (Sn) capsule for subsequent IRMS analysis. For $\delta^{15}\text{N}$-NH$_4\text{NO}_3$ analysis, 30 µL of aqueous 0.2 mol L$^{-1}$ NH$_4$NO$_3$ solution were pipetted directly onto glass filters, sealed with a PTFE band and dried for 45 minutes in a desiccator. Then, the PTFE band was removed and the glass filters packed in Sn capsules for IRMS analysis. Blank values for $\delta^{15}\text{N}$-NH$_4$NO$_3$ and $\delta^{15}\text{N}$-NO$_3^-$ analysis were determined with 0.7 mol L$^{-1}$ KCl solution without NH$_4$NO$_3$ addition. After conversion to N$_2$ with an elemental analyser (Euro EA3000, Eurovector Srl, Milano, Italy), $^{15}\text{N}/^{14}\text{N}$ isotope ratios were determined by IRMS (DeltaV Advantage, Thermo Fisher Scientific Inc., Germany). Relative differences of isotope ratios ($\delta^{15}\text{N}$) to the international isotope ratio scale AIR-N$_2$, were determined by analysis of NIST Standard 1547 (peach leaves 996) ($\delta^{15}\text{N}_{\text{bulk}} = 1.969 \%$). All results were corrected for the nitrogen content and $\delta^{15}\text{N}$ values observed for the corresponding blanks.
Thermal decomposition of NH₄NO₃ – static method

For this method 1.3 g (16.2 mmol) of NH₄NO₃ (P1 – P4) were weighed into quartz-glass round-bottom flasks with break-seal (150 mL, Duran glass, Glasbläserei Willi Möller AG, Zürich, Switzerland), evacuated (< 10⁻¹ mbar) and flame-sealed. In addition for P1 smaller quartz glass ampoules with break-seal (4.4 mL, Duran glass, Glasbläserei Willi Möller AG, Zürich, Switzerland) were used for the initial isotope fractionation experiments filled with 60 – 80 mg (0.7 – 1.0 mmol) of NH₄NO₃. The sealed flasks or ampoules were placed in a circulating air oven (SalvisLab, Rotkreuz, Switzerland) and heated by 1.0 K min⁻¹ up to 543 K. For the isotope fractionation experiments (P1) the hold time at 543 K was set to vary between 1 and 24 hours in order to vary the yield of the thermal decomposition reaction. For the reassessment of the NH₄NO₃ decomposition reaction (P1-P4), a hold time of 24 hours was used to achieve maximum reaction yield. After the defined hold time quartz glass containers were removed from the oven and allowed to cool to room temperature. This is slightly different from the procedure applied by Toyoda, where the flasks remain in the oven after decomposition and are allowed to cool down more slowly (Sakae Toyoda, personal communications). Afterwards, the N₂O product gas was purified on a vacuum manifold by multiple cryogenic distillations. Reaction by-products and side-products (e.g. H₂O, HNO₃, NH₃) were trapped at 195 K (dry ice / ethanol bath) and N₂O at 77 K (liquid N₂), while N₂ and O₂ were removed by evacuation with an oil sealed rotary vane pump (RV3, Edwards Ltd., Crawley, UK). The N₂O yield of the decomposition reaction was calculated based on the mass of the NH₄NO₃ substrate and the volume of the product gas N₂O calculated from the inner volume of the gas line normalized for pressure (LEO3 Manometer, Keller AG, Winterthur, Switzerland) and temperature (GMH 3750 and GTF601, GHM-Greisinger, Regenstauf, Germany). The uncertainty of the yield was estimated using the laws of error propagation.
The yield of N$_2$ and O$_2$ was estimated from the pressure decrease after evacuation of the condensable gases at 77 K (liquid N$_2$). The purified N$_2$O product gas was filled in 50 mL stainless steel cylinders (SS-4CS-TW-50, Swagelok AG, Niederrohrdorf, Switzerland) and analysed by IRMS at Max-Planck-Institute for Biogeochemistry (MPI-BGC) as described in the following. For site-specific N$_2$O isotopic analysis by QCLAS the N$_2$O product gas was diluted in a two-step procedure with high–purity synthetic air (99.999 %, 20.5 % O$_2$ in N$_2$) to a target N$_2$O mole fraction of 90 ppm ($10^{-6}$ moles per mole of dry air). First a static dilution was performed in triplicate, where 3 mL of pure N$_2$O at 3000 to 5000 hPa were purged with synthetic air into a 6 L stainless steel cylinder (S6L Aerosphere, Labcommerce Inc., San Jose, USA) via a ten-port 2-position valve (EH2C10WEPH equipped with 3 mL sample loop, Valco Instruments Inc., Schenkon, Switzerland) to a final pressure of 2800 hPa. Secondly, a dynamic dilution was performed (mass flow controller, Vögtlin Instruments AG, Aesch, Switzerland) with synthetic air prior to analysis by QCLAS.

**Thermal decomposition of NH$_4$NO$_3$ – dynamic method**

Around 70 mg (0.9 mmol) of ammonium nitrate (P1) were placed into a quartz glass tube (12 mm outer diameter (OD), length 20 cm, Duran glass, Willi Möller AG, Zürich, Switzerland), which was purged with 10 mL min$^{-1}$ high purity nitrogen gas (99.999 %, Messer Schweiz AG, Lenzburg, Switzerland). The temperature of the tube was increased by 1.5 K min$^{-1}$ to a final temperature of 543 K. Downstream of the heated glass tube the reaction gas was diluted with 250 mL min$^{-1}$ high purity synthetic air (99.999 %, 20.5 % O$_2$ in N$_2$) and transferred through a heated PTFE line (453 K, Winkler GmbH, Heidelberg, Germany) to an FTIR spectrometer (CX-4000, Gasmet Technologies Oy, Helsinki, Finland). N$_2$O mixing ratios and reaction by-products (H$_2$O, NH$_3$, NO, NO$_2$, HNO$_3$) were quantified in real-time by Fourier Transform Infrared Spectroscopy (FTIR)$^{[25, 26]}$. Downstream of the FTIR spectrometer the process gas was dynamically diluted to a constant N$_2$O mole fraction of 90 ppm. The dilution ratio was
calculated on-line based on FTIR results and used to automatically (LabVIEW, National Instruments Switzerland Corp., Ennetbaden, Switzerland) set the dilution flow of synthetic air (mass flow controller, Vögtlin Instruments AG, Aesch, Switzerland)\(^{27}\). Thereafter, the N\(_2\)O isotopic composition was analysed by QCLAS (Aerodyne Research Inc., Billerica, USA), as described below\(^{5}\).

**Analysis of N\(_2\)O site-specific isotopic composition by QCLAS (Empa)**

Isotopic analysis of N\(_2\)O produced by static or dynamic thermal NH\(_4\)NO\(_3\) decomposition was performed by QCLAS. The employed laser spectrometer (Aerodyne Research Inc., Billerica, USA) was previously described by our laboratory in a number of studies\(^{6, 8, 28, 29}\). It includes a continuous wave quantum cascade laser source emitting at 2203 cm\(^{-1}\) (Alpes Lasers, St Blaise, Switzerland), which enables the simultaneous quantification of the four most abundant N\(_2\)O isotopic species (\(^{14}\)N\(^{14}\)N\(^{16}\)O, \(^{15}\)N\(^{14}\)N\(^{16}\)O, \(^{14}\)N\(^{15}\)N\(^{16}\)O, and \(^{14}\)N\(^{14}\)N\(^{18}\)O). The spectrometer was operated in a flow-through mode (50 mL min\(^{-1}\)) with a gas cell pressure and temperature of 25 hPa and 293 K, respectively. Ratios of N\(_2\)O isotopologues (\(^{15}\)N\(^{14}\)N\(^{16}\)O/\(^{14}\)N\(^{14}\)N\(^{16}\)O, \(^{14}\)N\(^{15}\)N\(^{16}\)O/\(^{14}\)N\(^{14}\)N\(^{16}\)O, \(^{14}\)N\(^{14}\)N\(^{18}\)O/\(^{14}\)N\(^{14}\)N\(^{16}\)O) were analysed at 1 Hz temporal resolution with a precision of < 0.6 ‰; with 450 s spectral averaging the spectrometer enables high precision analysis (<0.05 ‰, Allan precision\(^{30}\)) of isotope ratios. The spectroscopically determined isotope ratios were related to the international isotope ratio scales (AIR-N\(_2\) for \(^{15}\)N/\(^{14}\)N, VSMOW for \(^{18}\)O/\(^{16}\)O) through analysis of calibration gases CG1 (CG1-1: \(\delta^{15}\)N\(^{\alpha}\) = 2.06 ± 0.05 ‰, \(\delta^{15}\)N\(^{\beta}\) = 1.98 ± 0.20 ‰, \(\delta^{18}\)O = 36.12 ± 0.3 ‰; CG1-2: \(\delta^{15}\)N\(^{\alpha}\) = -0.13 ± 0.28 ‰, \(\delta^{15}\)N\(^{\beta}\) = 1.35 ± 0.29 ‰, \(\delta^{18}\)O = 38.46 ± 0.15 ‰) and CG2 (\(\delta^{15}\)N\(^{\alpha}\) = -82.14 ± 0.49 ‰, \(\delta^{15}\)N\(^{\beta}\) = -78.02 ± 0.52 ‰, \(\delta^{18}\)O = 21.64 ± 0.12 ‰) before and after every experiment. The isotopic composition of the calibration gases has been previously analysed by Tokyo Institute of Technology using their analytical technique as a link to the international scales.
The uncertainty in delta values, $\delta^{15}N^\alpha$, $\delta^{15}N^\beta$, $\delta^{18}O$, $\delta^{15}N_{\text{bulk}}$ and SP, of N$_2$O analysed by QCLAS was calculated from the standard deviation for repeated measurements by QCLAS and the standard deviation of calibration gases provided by Tokyo Institute of Technology using the laws of error propagation.

Analysis of $\delta^{15}N_{\text{bulk}}$ by IRMS (MPI-BGC)

Pure N$_2$O was introduced with a six port 2-position valve (Valco Instruments Inc., Schenkon, Switzerland) equipped with a 250 µl loop at 3000 – 4000 hPa. The valve was inserted into the transfer line between the oxidation and the reduction reactor of an EA 1110 CHN combustion analyser (CE Instruments Ltd, Wigan, UK). Isotopic analysis was made by coupling the EA effluent via a ConFlo III interface (Finnigan MAT, Bremen, Germany) to a Delta plus isotope–ratio mass–spectrometer (Thermo-Fisher, Bremen, Germany). Complete conversion of N$_2$O to N$_2$ in the reduction reactor was checked by monitoring the mass-to-charge ratio ($m/z$) 44 after N$_2$O injection. No appreciable signal was found, except small amounts of NO$_2$ on $m/z$ 46, indicating formation of this gas on the filament when N$_2$ enters the ion source, which does not interfere with the measurement. IAEA-N1 (ammonium sulphate) with an assigned value of 0.43‰ on the AIR-N$_2$ scale was used as the scale anchor. Additionally, an in-house working reference material “Ali-J3”, an acetanilide sample calibrated with IAEA-N1 was used. We refer to these substances as ‘combustible reference materials’. CO$_2$ and humidity from reference material combustion was removed using an Ascarite trap (NaOH on pumice) and Mg(ClO$_4$)$_2$ mounted in front of the EA-GC$^{[18]}$. The measurements were made by injecting the combustible reference, followed by a number of N$_2$O injections, and converting the measured isotopic distance to the AIR-N$_2$ scale.

Analysis of $\delta^{18}O$ by IRMS (MPI-BGC)
Plain air and pure N\textsubscript{2}O were injected via a 1 mL loop into the TC/EA high temperature conversion elemental analyser (CE Instruments Ltd, Wigan, UK) to produce CO from both. The reaction gases (N\textsubscript{2} and CO) were fully baseline-separated on the gas chromatograph and analysed on-line via a ConFlo III interface and Delta\textsuperscript{plus}XL isotope–ratio mass–spectrometer (Thermo-Fisher, Bremen, Germany). Compressed clean-sector, ultra-dry Jena air with $\delta^{18}$O (VSMOW) = 23.88 ‰ was used as scale anchor$^{[31]}$. 

RESULTS AND DISCUSSION

Isotope fractionation effects during thermal decomposition of NH\textsubscript{4}NO\textsubscript{3} – static method

Figure 1 presents the site-specific isotopic composition of the accumulated product N\textsubscript{2}O generated by thermal decomposition of NH\textsubscript{4}NO\textsubscript{3} salt P1. $\delta^{15}$N\textsubscript{α}, $\delta^{15}$N\textsubscript{β} and $\delta^{18}$O offer a distinct dependence on the reaction yield, which increases with increasing hold time at constant decomposition temperature (543 K), and reaches 91.2 ± 2.3 to 93.5 ± 2.4 % after 24 hours. A further increase in hold time to 68 hours did not significantly affect N\textsubscript{2}O production (90.5 ± 2.5 %). Plotting relative differences of isotope ratios of the accumulated product N\textsubscript{2}O versus -f ln f / (1-f) displays a linear relationship (Figure 1), with f being the fraction of the remaining substrate. The regression line is defined as (Eqn. (1))$^{[32]}$: 

$$\delta_{N_2O} = \delta_{NH_4NO_3} - \varepsilon \times \frac{f \times \ln f}{(1-f)}$$

where the slope $\varepsilon$ is the isotope enrichment factor of the reaction, assuming validity of the Rayleigh isotope fractionation model (e.g. unidirectionality, single-step reaction and constant $\varepsilon$). In particular the assumption of single-step reaction and isotope mass balance, which implies the absence of side reactions (or the isotopic characterisation of side-products) is only a first approximation, as discussed below and in the following sections.
The observed isotope enrichment factors indicate a pronounced fractionation for the conversion of the NH$_4^+$ nitrogen atom to the end (β) position of the N$_2$O molecule ($\varepsilon_{\text{NH}_4^{15}\text{N}_\beta} = -18.88 \pm 0.94$ ‰), while isotope fractionation effects are considerably less pronounced for the transformation of the NO$_3^-$ nitrogen atom to the middle (α) position of the N$_2$O molecule ($\varepsilon_{\text{NO}_3^{15}\text{N}_\alpha} = -4.23 \pm 0.55$ ‰) and for the O atom ($\varepsilon_{\text{NO}_3^{18}\text{O}} = 1.77 \pm 0.43$ ‰).

**Figure 1.** Site-specific isotopic composition ($\delta^{15}\text{N}_\alpha$, $\delta^{15}\text{N}_\beta$, $\delta^{18}\text{O}$) of the accumulated product gas N$_2$O obtained by thermal decomposition of NH$_4$NO$_3$ (P1) with different hold times (1 to 24 hours) and yields as analysed by QCLAS. Filled / open symbols represent N$_2$O produced by thermal decomposition in quartz glass 150 mL round bottom flasks / 6 mL ampoules, respectively. In accordance with the Rayleigh fractionation model, $\delta^{15}\text{N}_\alpha$, $\delta^{15}\text{N}_\beta$, $\delta^{18}\text{O}$ display a linear relationship versus $-f \ln f / (1-f)$, with $f$ being the fraction of unreacted substrate and the isotope enrichment factor ($\varepsilon$) the slope of the regression line. Data points with a N$_2$O yield below 5% were not included in the fit as they show a deviation from the linear relationship, and delta values are outside the 2σ confidence interval of the linear regression line for $\delta^{18}\text{O}$. The displayed error bars represent the (1σ) uncertainties in yield of the NH$_4$NO$_3$ decomposition reaction (X axis) and the delta values as analysed by QCLAS (Y axis).
$^{15}\text{N}$ and $^{18}\text{O}$ isotope effects during $\text{NH}_4\text{NO}_3$ thermal decomposition was experimentally determined by Friedman and Bigeleisen$^{[12]}$. They observed an increase in the $m/z$ 45 / 44 isotope ratio of the accumulated $\text{N}_2\text{O}$ product gas, i.e. $(^{14}\text{N}^{15}\text{N}^{16}\text{O} + ^{15}\text{N}^{14}\text{N}^{16}\text{O})/^{14}\text{N}^{14}\text{N}^{16}\text{O}$, by 7.5 ± 1 ‰ for extended decomposition periods, where they assumed complete reaction, in comparison to one percent decomposition. For low reaction yields, i.e. high $f$ values, $-f \ln f / (1-f)$ tends towards 1 and thus Eqn. (1) can be approximated by Eqn. (2)$^{[32]}$:

$$\delta_{\text{N}_2\text{O}} = \delta_{\text{NH}_4\text{NO}_3} + \varepsilon$$

The difference between the isotope enrichment factor determined by Friedman and Bigeleisen$^{[12]}$ of -7.5 ± 1 ‰ and our results (-11.6 ± 0.7 ‰, calculated as the mean of $\varepsilon_{\text{NH}_4-^{15}\text{N}}$ and $\varepsilon_{\text{NO}_3-^{15}\text{N}}$), might be partly explained by incomplete reaction, which is not considered in the applied approximations. Zielinski et al.$^{[33]}$ interpreted results from Friedman and Bigeleisen implying that the nitrogen – oxygen bond rupture in nitrate (or nitric acid) is the reaction rate and isotope fractionation determining step. Consequently, they hypothesized that $^{15}\text{N}$ fractionation (-15 ± 1 ‰) is confined to the conversion of the $\text{NO}_3^-$ nitrogen atom to the $\alpha$ position of the $\text{N}_2\text{O}$ molecule. This assumption is in contrast to our experimental observations, where $^{15}\text{N}$ fractionation was found to be substantially more pronounced for the conversion of the $\text{NH}_4^+$ nitrogen atom to the $\beta$ position of the $\text{N}_2\text{O}$ molecule. The disparity of the two nitrogen atoms can be interpreted with respect to the multi-step ionic reaction mechanism proposed for the $\text{NH}_4\text{NO}_3$ thermal decomposition at temperatures below 563 K (see Brower et al.$^{[34]}$ and references therein). The exact reasoning behind the observed isotope fractionation effects, however, is beyond the scope of the current manuscript. In principle, $^{15}\text{N}$ fractionation for the conversion of the ammonia nitrogen atom to the $\beta$ position of the $\text{N}_2\text{O}$ molecule might occur during the initial reaction step, $\text{NH}_4\text{NO}_3$ dissociation into ammonia ($\text{NH}_3$) and nitric acid ($\text{HNO}_3$)$^{[35]}$, as studied by Urey et al.$^{[36, 37]}$, or the oxidation of $\text{NH}_3$ by a nitronium ion ($\text{NO}_2^+$),
which yields N₂O and H₂O. NO₂⁺ is generated in an intermediate reaction step by protonation of HNO₃ to H₂NO₃⁺ and H₂O cleavage[38].

Regarding the ¹⁸O content in N₂O Friedman and Bigeleisen[12] observed two effects, a five per mil decrease in the $^{14}$N$^{14}$N$^{18}$O/$^{14}$N$^{14}$N$^{16}$O ratio of N₂O with one percent yield for the NH₄NO₃ decomposition reaction compared to extended reaction times, and a 23 ± 3 ‰ difference between the ($^{14}$N$^{14}$N$^{18}$O/$^{14}$N$^{14}$N$^{16}$O) and the (H₂$^{18}$O/H₂$^{16}$O) ratio. The second is equivalent to a 15 ‰ higher ¹⁸O content in N₂O compared to the NH₄NO₃ starting material. Both observations, a slight decrease in the ¹⁸O content with increasing N₂O yield (Figure 1) and an around 15 ‰ increase in the ¹⁸O content of N₂O compared to NH₄NO₃ starting material (Table 1), are in accordance with our results.

Isotope fractionation effects during thermal decomposition of NH₄NO₃ – dynamic method

Figure 2 (left) displays instantaneous site-specific isotopic composition ($δ^{15}$N₁α, $δ^{15}$N₁β, $δ^{18}$O) and accumulated N₂O production observed during thermal decomposition of NH₄NO₃ (P1) in a progressively heated quartz glass tube (1.5 K min⁻¹) under a constant flow of high-purity nitrogen gas. Real-time analysis of trace gas mixing ratios by FTIR spectroscopy indicated N₂O generation at temperatures above 463 K and maximum production at peak temperatures (543 K). In addition, release of stoichiometric amounts of the reaction by-product water vapour (H₂O), and trace amounts (≤ 1 % of N₂O) of the dissociation products NH₃ and HNO₃, as well as the side-product nitrogen dioxide (NO₂) were detected (data not shown). The integrated overall yield of the dynamic decomposition experiment in N₂O (0.17 mmol) was only 19 % of the starting material (0.9 mmol), as vaporised NH₄NO₃ reactant and dissociation product (NH₃, HNO₃) were flushed out of the heated glass tube and adsorbed (or re-crystallized) at “cold spots” downstream of the heated tube. This is in contrast to the static decomposition experiments, where reaction yields of 91 to 93 % were achieved at maximum decomposition time.
Plotting the delta values of the accumulated N$_2$O product as a function of $-f \ln f / (1-f)$ according to Eqn. (1) (Figure 2 (right)) indicates similar isotope enrichment factors for the dynamic decomposition experiment as compared to the static decomposition discussed in the previous section (Figure 1). This agreement is despite the fact, that a substantial fraction of the unreacted NH$_4$NO$_3$ substrate as well as the dissociation products (NH$_3$, HNO$_3$) evaded thermal decomposition by evaporation. Deviations in delta values between static and dynamic decomposition experiments might be due to fractionation effects attributed to evaporation.

Figure 2. Thermal decomposition of NH$_4$NO$_3$ to N$_2$O, under a constant flow of high-purity nitrogen gas, in a progressively heated quartz glass tube (1.5 K min$^{-1}$). (left) Temperature of the quartz glass tube and accumulated N$_2$O production based on FTIR results. The fraction of unreacted substrate ($f$) is approximated in relation to the total N$_2$O yield (19 %). Changes in the site-specific isotopic composition of the N$_2$O product gas indicate strong isotope fractionation effects. (right) solid lines: Isotopic composition of the accumulated product N$_2$O derived from the dynamic decomposition experiment plotted versus $-f \ln f / (1-f)$; dotted lines: Isotopic composition of the accumulated product N$_2$O versus $-f \ln f / (1-f)$ as derived from the static decomposition experiments (Figure 1).
Reassessment of the NH$_4$NO$_3$ decomposition reaction

Within this section the validity of the NH$_4$NO$_3$ decomposition reaction to scale the N$_2$O site-specific isotopic composition relative to the international isotope ratio standard AIR-N$_2$ is assessed. This is accomplished by comparison of site-specific isotopic composition of the thermal decomposition product N$_2$O, at maximum reaction yield (90.6 ± 2.3 % to 94.4 ± 2.4 %) of the static decomposition experiments, with moiety-specific isotope analysis in the reactant NH$_4$NO$_3$ (P1 – P4, Table 1). Results in Table 1 indicate a substantial $^{15}$N depletion in N$_2$O ($\delta^{15}$N$^{\text{bulk}}$) both analysed by QCLAS (Empa) as well as IRMS (MPI-BGC) as compared to the NH$_4$NO$_3$ substrate ($\delta^{15}$N-NH$_4$NO$_3$, IRMS, Lab 1 – 3) by 0.67 ± 0.43 ‰ or 1.14 ± 0.37 ‰, respectively. This might be either caused by the generation of reaction side-products (e.g. N$_2$) with higher $^{15}$N content, $^{15}$N fractionation during thermal NH$_4$NO$_3$ decomposition as described in the previous sections, or a combination of both. The yield of volatile reaction side-products, noncondensable at liquid nitrogen temperatures and hypothesised to be mainly N$_2$, in our static decomposition experiments was around 4 %. To compensate for N$_2$ production Toyoda et al.[3] analysed $\delta^{15}$N-N$_2$ and used differences between $\delta^{15}$N-NH$_4$NO$_3$ and $\delta^{15}$N-N$_2$ to correct $\delta^{15}$N$^{\text{bulk}}$ (N$_2$O) by -0.1 to -0.9 ‰, thus in a similar range than observed in this study. In contrast, Westley et al.[14] used a constant offset correction by -0.79 ‰ irrespective of the observed $\delta^{15}$N-N$_2$ values and the reaction yield. Differences in $\delta^{15}$N$^{\text{bulk}}$ (N$_2$O) between IRMS (MPI-BGC) and QCLAS (Empa) by 0.46 ± 0.13 ‰, were probably caused by differences in the anchoring of the analytical results. This observation also confirms earlier findings by Mohn et al. (0.39 ‰)[7] and Toyoda et al (0.3 ‰)[3], where discrepancies in $\delta^{15}$N$^{\text{bulk}}$ of N$_2$O were attributed to isotope fractionation during incomplete NH$_4$NO$_3$ decomposition.
Differences between the $N_2O$ site-specific isotopic composition and the moiety-specific isotopic composition of the $NH_4NO_3$ salts, thus between $\delta^{15}N^\alpha$ versus $\delta^{15}N-NO_3^-$ and $\delta^{15}N^\beta$ versus $\delta^{15}N-NH_4^+$, display a similar magnitude $-0.72 \pm 0.21$ ‰ and $-0.61 \pm 0.80$ ‰, respectively (Table 1). Consequently, the $N_2O$ site-preference, defined as the difference between $\delta^{15}N^\alpha$ and $\delta^{15}N^\beta$, measured by QCLAS, and the difference in $\delta^{15}N-NO_3^-$ - $\delta^{15}N-NH_4^+$, as analysed by IRMS, agreed within $0.10 \pm 0.80$ ‰ (-0.9 to 1.1 ‰). Therefore, in summary, it can be concluded that the results of the $NH_4NO_3$ thermal decomposition technique, developed by Toyoda and Yoshida$^{[3]}$ to calibrate $N_2O$ site preference, can be reproduced. This was already confirmed by Marian Westley et al.$^{[14]}$, but the explanatory power of their experiments was limited, due to a much lower reaction yield of only 55 to 74 %, which may have affected the isotopic composition of the decomposition product $N_2O$. The accuracy of the $NH_4NO_3$ thermal decomposition reaction to link the $N_2O$ SP to the international isotope ratio scales, however, is restricted by significant formation of side-products (e.g. $N_2$) in combination with the observed site-specific isotope fractionation effects. The formation of side-products also prevents the use of the Rayleigh model to correct fractionation effects by incomplete reaction.

The validity of the $NH_4NO_3$ decomposition reaction to link the $^{15}N$ site preference of $N_2O$ to the international isotope ratio scale AIR-$N_2$ could be enhanced by a further increase in the reaction yield. The yield of the $NH_4NO_3$ decomposition reaction and the product distribution, however, depends on various factors such as sample size and purity, presence of other chemicals (catalysts) as well as the reaction conditions, e.g. pressure, temperature and heating rate$^{[39]}$. Sulfuric and hydrochloric acid were both shown to catalyse the $NH_4NO_3$ decomposition reaction$^{[40]}$, the mechanism for both acids, however, is different. Sulfuric acid replaces the nitrate ion in the $NH_4NO_3$ molecule, promoting the build-up of $HNO_3$, while hydrochloric acid increases the generation of the intermediate product $NH_3NO_2^+$.$^{[41]}$ But, the addition of chlorides may lead to enhanced production of the side-product $N_2$ by decomposition of the reaction.
intermediate NH₂Cl⁴¹. Similarly, addition of Cr³⁺ catalyses NH₄NO₃ thermal decomposition favouring the exothermic formation of N₂⁴², which prevents using this technique for standardisation of ¹⁵N site preference in N₂O. A promising technique might be the decomposition of NH₄NO₃ in a NH₄HSO₄ – (NH₄)₂SO₄ melt was shown to yield 99 – 99.5 % N₂O and only 1.0 – 0.5 % N₂⁴³ offering the potential to link the ¹⁵N isotopic composition of the central (α) N atom of the N₂O molecule via analysis of ¹⁵N-NO₃⁻ to the international isotope ratio scales.

Although it is not in the main focus of the presented study it is worth mentioning the observed differences in δ¹⁸O analysed by QCLAS (Empa) and IRMS (MPI-BGC) (Table 1). Differences were only 0.31 ‰ for P4 but 1.40 ± 0.25 ‰ (1.19 to 1.74 ‰) for the samples P1 – P3 and might be rationalized by differences in the referencing to the international isotope ratio scale, in particular an expanded uncertainty of QCLAS measurements for δ¹⁸O induced by the implemented calibration strategy (Table 1). The high uncertainty in δ¹⁸O values analysed by QCLAS was provoked by the limited range in δ¹⁸O values covered by the standards (CG1-1, CG1-2 versus CG2) relative to the measured delta values especially for P1 – P3.
Table 1. Isotopic composition of NH$_4$NO$_3$ reactant P1 – P4 (IRMS Lab 1 – 3) and the thermal decomposition product N$_2$O by IRMS for $\delta^{15}$N$_{\text{bulk}}$ and $\delta^{18}$O values and QCLAS for $\delta^{15}$N$_{\alpha}$, $\delta^{15}$N$_{\beta}$ and $\delta^{18}$O values, given in $\delta$-units. IRMS and QCLAS analysis was performed versus the international isotope ratio scales AIR-N$_2$ ($^{15}$N/$^{14}$N) and VSMOW ($^{18}$O/$^{16}$O). QCLAS analysis is based on calibration gases analysed at Tokyo Institute of Technology, using their analytical technique as a link to the international scales. The indicated uncertainty for IRMS and QCLAS results was calculated as described in the experimental section.

<table>
<thead>
<tr>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
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<tbody>
<tr>
<td><strong>Lab 1</strong></td>
<td>NH$_4$NO$_3$</td>
<td>$\delta^{15}$N-NO$_3^-$</td>
<td>-0.7 ± 0.1</td>
<td>17.4 ± 0.02</td>
</tr>
<tr>
<td><strong>Lab 2</strong></td>
<td>NH$_4$NO$_3$</td>
<td>$\delta^{15}$N-NO$_3^-$</td>
<td>-0.7 ± 0.1</td>
<td>17.0 ± 0.2</td>
</tr>
<tr>
<td><strong>Lab 3</strong></td>
<td>NH$_4$NO$_3$</td>
<td>$\delta^{15}$N-NO$_3^-$</td>
<td>-1.1 ± 0.1</td>
<td>16.9 ± 0.2</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>NH$_4$NO$_3$</td>
<td>$\delta^{15}$N-NO$_3^-$</td>
<td>-0.8 ± 0.2</td>
<td>17.1 ± 0.2</td>
</tr>
<tr>
<td><strong>QCLAS</strong></td>
<td>N$_2$O</td>
<td>$\delta^{15}$N$^{\alpha}$</td>
<td>-1.8 ± 0.2</td>
<td>16.3 ± 0.2</td>
</tr>
<tr>
<td><strong>IRMS</strong></td>
<td>-</td>
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| **Lab 1** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ | -4.1 ± 0.1 | -5.7 ± 0.1 | 62.4 ± 0.3 | 51.9 ± 0.3 | a |
| **Lab 2** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ | -3.7 ± 0.2 | -4.8 ± 0.2 | 63.0 ± 0.2 | 51.5 ± 0.2 | a |
| **Lab 3** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ | -2.8 ± 0.2 | -2.3 ± 0.2 | 64.0 ± 0.3 | 50.2 ± 0.2 | a |
| **Average** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ | -3.5 ± 0.6 | -4.3 ± 1.4 | 63.1 ± 0.7 | 51.2 ± 0.7 | 3 |
| **QCLAS** | N$_2$O | $\delta^{15}$N$^{\beta}$ | -3.8 ± 0.4 | -5.2 ± 0.4 | 63.5 ± 1.0 | 52.9 ± 0.6 | 3 |
| **IRMS** | - | - | - | - |

| **Lab 1** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ - $\delta^{15}$N-NH$_4^+$ | 3.3 ± 0.1 | 23.1 ± 0.1 | -25.7 ± 0.3 | 16.4 ± 0.4 | b |
| **Lab 2** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ - $\delta^{15}$N-NH$_4^+$ | 3.0 ± 0.2 | 21.8 ± 0.4 | -26.9 ± 0.3 | 16.2 ± 0.2 | b |
| **Lab 3** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ - $\delta^{15}$N-NH$_4^+$ | 1.7 ± 0.5 | 19.2 ± 0.3 | -27.9 ± 0.5 | 14.5 ± 0.3 | b |
| **Average** | NH$_4$NO$_3$ | $\delta^{15}$N-NH$_4^+$ - $\delta^{15}$N-NH$_4^+$ | 2.7 ± 0.7 | 21.4 ± 1.6 | -26.8 ± 0.9 | 15.7 ± 0.8 | 3 |
| **QCLAS** | N$_2$O | SP | 1.9 ± 0.4 | 21.4 ± 0.4 | -27.7 ± 1.0 | 16.8 ± 0.8 | 3 |
| **IRMS** | - | - | - | - |

| **Lab 1** | NH$_4$NO$_3$ | $\delta^{15}$N | -2.4 ± 0.1 | 5.8 ± 0.1 | 49.5 ± 0.3 | -43.7 ± 0.2 | 4 |
| **Lab 2** | NH$_4$NO$_3$ | $\delta^{15}$N | -2.2 ± 0.1 | 6.1 ± 0.1 | 49.5 ± 0.1 | -43.4 ± 0.1 | 5 |
| **Lab 3** | NH$_4$NO$_3$ | $\delta^{15}$N | -1.9 ± 0.2 | 7.3 ± 0.1 | 50.0 ± 0.1 | -43.0 ± 0.1 | 3-4 |
| **Average** | NH$_4$NO$_3$ | $\delta^{15}$N | -2.2 ± 0.2 | 6.4 ± 0.6 | 49.7 ± 0.2 | -43.4 ± 0.3 | 3 |
| **QCLAS** | N$_2$O | $\delta^{15}$N$^{\text{bulk}}$ | -2.8 ± 0.2 | 5.5 ± 0.2 | 49.7 ± 0.5 | -44.5 ± 0.4 | 3 |
| **IRMS** | -3.2 ± 0.01 | 5.2 ± 0.01 | 49.1 ± 0.01 | -45.0 ± 0.003 | 3 |

| **Lab 1** | NH$_4$NO$_3$ | $\delta^{18}$O | 28.0 ± 0.3 | 27.4 ± 0.3 | 27.5 ± 0.1 | 18.4 ± 0.3 | 4 |
| **Lab 2** | NH$_4$NO$_3$ | $\delta^{18}$O | - | - | - | - | c |
| **Lab 3** | NH$_4$NO$_3$ | $\delta^{18}$O | - | - | - | - | c |
| **Average** | NH$_4$NO$_3$ | $\delta^{18}$O | 28.0 | 27.4 | 27.5 | 18.4 | 3 |
| **QCLAS** | N$_2$O | $\delta^{18}$O | 41.6 ± 0.8 | 41.8 ± 0.8 | 42.2 ± 0.8 | 33.6 ± 0.5 | 3 |
| **IRMS** | 42.8 ± 0.01 | 43.0 ± 0.003 | 43.9 ± 0.03 | 33.9 ± 0.02 | 3 |

461 a calculated from: $\delta^{15}$N-NH$_4^+ = 2 \times \delta^{15}$N-NH$_4$NO$_3$ - $\delta^{15}$N-NO$_3^-$
462 b calculated from: $\delta^{15}$N-NH$_4^+ - \delta^{15}$N-NO$_3^-$
463 c not analysed
CONCLUSION

The study investigates the validity of the NH$_4$NO$_3$ decomposition technique to link NH$_4^+$ and NO$_3^-$ moiety-specific $\delta^{15}$N analysis by IRMS to N$_2$O site-specific nitrogen isotopic composition. It confirms that the moiety-specific nitrogen isotopic composition is transferred from the NH$_4$NO$_3$ starting material to the N$_2$O product gas. The accuracy of this approach for calibration of $\delta^{15}$N$^\alpha$ and $\delta^{15}$N$^\beta$, however, was found to be limited by non-quantitative NH$_4$NO$_3$ decomposition in combination with substantially different isotope enrichment factors for the conversion of the NO$_3^-$ or NH$_4^+$ nitrogen atom to the $\alpha$ or $\beta$ position of the N$_2$O molecule and generation of side-product (e.g. N$_2$). Thereby, the study reveals that the accuracy of the NH$_4$NO$_3$ decomposition reaction currently confines the anchoring of N$_2$O site specific isotopic composition to the international isotope ratio scale AIR-N$_2$. To improve inter-laboratory compatibility for N$_2$O isotopomers analysis, the authors suggest to establish a set of N$_2$O isotope reference materials with appropriate site-specific isotopic composition in the form of community standards.

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