Response to RC1

We thank the referee for a generous review and thoughtful suggestions that will improve this manuscript further. We address specific comments as follows, with additions to the manuscript text denoted in red.

> My only significant recommendation is that the authors should do a better job of assessing their progress toward the ultimate goal of having a sufficiently accurate reference frame. That is to say, is equilibrium achieved with sufficient accuracy to match the measurement uncertainty? It seems, at least in some cases, that this is not the case (See Fig 4 and Table 1) since at line 180, the authors state that the measurement uncertainty "ranged from 0.09 ‰ to 0.18 ‰ for all isotopologues". If complete equilibration is not achieved, then the authors should say why not and how significant is any remaining systematic variation and what they propose to do about it in future work. If, on the other hand, they believe that they have achieved complete randomization within the experimental error, they should state that more clearly and quantitatively.

It is indeed the case that the uncertainty we estimate for individual measurements is better than that determined for repeated equilibration experiments (Table 1). We can identify several possible sources for this divergence: the temperature variability of the catalyst in the equilibration system, the overprinting of a kinetic isotope effect associated with thermal decomposition during equilibration,or uncharacterized variability associated with sample introduction or spectroscopic measurement for repeat analyses. From the temperature uncertainty of 2 K in our equilibration system (Line 146), we can account for about ± 0.15 ‰ of variability in SP and ± 0.08 ‰ in $\Delta^{14}N^{15}N^{18}O$ and $\Delta^{15}N^{14}N^{18}O$. Although we rule out kinetic isotope effects from thermal decomposition as the dominant control of the observed variability in SP, $\Delta^{*14}N^{15}N^{18}O$, and $\Delta^{*15}N^{14}N^{18}O$ (Sect. 3.4), we cannot exclude that they contribute to the unexplained variability.

To evaluate possible contributions from decomposition to observed variability, we consider a worst-case scenario in which a sample fully reaches equilibrium, and then decomposes with the kinetic isotope effects observed in this study. In the case of 30 % decomposition, this leads to changes in SP, $\Delta^{*14}N^{15}N^{18}O$, and $\Delta^{*15}N^{14}N^{18}O$ of -0.36 ‰, -1.59 ‰, and 1.42 ‰, respectively. Compounded with the uncertainty in temperature and in the measurement itself, we estimate 0.40 ‰, 1.60 ‰, and 1.43 ‰ for this 'worst-case scenario,' which matches (for SP) or substantially exceeds (for $\Delta^{*14}N^{15}N^{18}O$, and $\Delta^{*15}N^{14}N^{18}O$) the standard deviation observed in our repeated experiments (Table 1). We now provide the calculations associated with this estimate with our revised manuscript (Supplementary Table 1). We expanded on the sentence (Line 339), "Nevertheless, we cannot exclude the possibility that some of the variation seen in repeated measurements at 200 °C comes from variable expression of kinetic isotope effects," using the outcome of these scenarios:

Indeed, a decomposition fraction of 30 % could drive changes in SP, $\Delta^{*14}N^{15}N^{18}O$, and $\Delta^{*15}N^{14}N^{18}O$ of -0.36 ‰, -1.59 ‰, and 1.42 ‰, respectively, and so could contribute to

the variability seen in repeated equilibrium experiments (Sect. 3.6 and 3.7, Supplementary Table 1).

Establishing a broadly acceptable reference frame for clumped isotopologues and especially for SP on the basis of these equilibration experiments requires further quantification and minimization of the role of any thermal decomposition reactions. The discussion in Sect 3.7 (Line 396) was already intended to point towards this work. We added text to make these connections explicit:

Thereby we can determine if the uncertainty in the results reported here is tied to the equilibration experiments themselves, including perhaps the imprint of a kinetic isotope effect from thermal decomposition. This work can be coupled to further repeat measurements of equilibrated reference materials to evaluate any room for improvement in measurement or gas handling procedures.

> At line 165, unspecified decomposition products were separated from N2O. How was this accomplished and what were the likely products?

The decomposition products are predominantly gases with low boiling points, likely N_2 (bp -196 °C) and O_2 (bp -183 °C), and possibly NO (bp -152 °C). Added at Line 167:

After reaction durations of 15 to 64 minutes, residual N_2O was extracted cryogenically and decomposition products, likely N_2, O_2, and NO (Lewis and Hinshelwood, 1938), were removed under vacuum.

> At line 88, the authors begin a description of their fast dual-inlet system for trapped gases and cite two references. They should also cite Wang et al. (Anal. Chem. 2020, 92, 2, 2034–2042), which first described this innovation.

We added this reference accordingly (Line 90).

Response to RC2

We thank the referee for a sympathetic and careful reading of our manuscript, and for detailed comments that will improve its quality. We address specific comments as follows, with additions to the manuscript text denoted in red. All line numbers in our responses refer to the updated version of the manuscript.

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> Before publication the quality of the figures needs to be improved, both in resolution and in presentation.

We have changed the file format for images inserted into the manuscript file to ensure better quality. In addition, we will provide the editorial office with the original figure files during the final submission process.

> Also, applicability of the research would benefit if the authors relate the results in the research better to the precision and accuracy requirements of the applications in environmental research. This will pave the way for future work on this subject and enhance applicability of the research done.

> Line 174: There is stated that this precision is adequate to resolve differences among natural materials, but no reference or indication is given about the required precision for measurement of natural materials. Please add this information to the introduction.

We are guided, as in past clumped isotopic applications for other molecules, by the range seen for thermodynamic equilibrium and theoretical predictions. Yet we do not consider thermometry likely to be a significant application for N_2O. For now, the best set of comparisons is the small existing set of publications and datasets reporting natural isotopic variations. We added specific references to these and the phrase "observed to date" to the statement at Line 178. That said, as we start to explore natural systems, we seek the highest precision and accuracy practicable to maximize the possible observable signals.

This precision is adequate to resolve differences observed to date among natural or experimental materials (Kantnerová et al., 2020b, 2022; Magyar, 2017; Magyar et al., 2016) or predicted in literature (Schmidt and Johnson, 2015; Wang et al., 2004; Yeung, 2016), [...]

> Line 152: From the text so far, it is not clear why the duration has to be between 6 and 162 hours, please add some context to clarify.

In fact, this range of 6 -162 h should refer to the durations of the experiments to establish the equilibrium nature and evaluate the kinetics of the reactions among N_2O isotopologues, described in the succeeding paragraph. The experiments where N_2O was heated to establish the activation of the catalyst at different temperatures were all

performed for ≥ 20 h, with no further exploration of timescale. The text has been updated accordingly, at Line 156 and Line 159.

After a duration of at least 20 h, [...]

After the temperature threshold for catalyst activation was established, further experiments, with incubation periods between 6 and 162 h, were conducted to establish the equilibrium nature and evaluate the kinetics of the reactions of N_2O isotopologues over γ-Al_2O_3.

> Line 179: As the experiments covered in this research are as long as a week, please add information on stability of the instrument over longer time periods than 15 minutes.

Experiments were conducted and samples measured over the course of ~1 year, so while the experimental duration of up to a week is not specifically relevant, we agree that further explanation of the relevant considerations for measurements over timescales longer than ~20 minutes could make the discussion clearer. We accordingly added the following text (Line 182):

Since all samples are measured against the same internal working reference gas, results can be compared for samples measured in different analytical sessions. In addition, we find that the magnitude and even sign of concentration dependence correction associated each isotopologue can vary over time. Such variation has been observed in another recent study measuring ^{17}O in CO_2 by laser spectroscopy (Ellis et al., 2025) and supports our approach of determining a specific concentration correction factor for each sample.

> Line 181: Figure S2 shows that the first expansion is clearly less stable than the subsequent expansions. Is there an explanation for this? Is this also observed when doing sample measurements, and should the first expansion be excluded from the data analysis to improve precision?

In this case the deviations are likely due to the establishment of the spectral fit at the start of the first measurement block, and we do exclude them from the reported statistics, as we now make clear in the caption for Supplementary Fig. 2. Such variability is rarely seen in the measurements of samples.

The reported summary statistics exclude the first measurement block, where initial variability is evident.

> Figure 4: From the zoom frame of the upper figure, it is expected that the outlier is also included in the zoom, which it is not. Please correct this.

We adjusted the size of the inset box in Fig. 4 to better reflect the area covered by the zoom plot.

Line 220: Here there is stated that 3 starting materials were used while only two starting materials are shown in figure 4?

For graphical clarity in demonstrating convergence we include just the $\Delta^{*14}N^{15}N^{18}O$ and $\Delta^{*15}N^{14}N^{18}O$-spiked gases in Fig. 4, but in estimating the average value that is converged upon, we include the full suite of three starting gases. This value of 10.32 ± 0.60 ‰ for $\Delta^{*14}N^{15}N^{18}O$ is indistinguishable from the value of 10.44 ± 0.43 ‰ for just the $\Delta^{*14}N^{15}N^{18}O$ and $\Delta^{*15}N^{14}N^{18}O$-spiked gases.

Line 253: Please make clear in the text that results from experiments that were previously done at 200 degree C are also included in the results in figure 6.

We added a statement (Line 266) to make clear that the 200 °C dataset already discussed is also included in this temperature-dependence analysis:

We compare the results to the experiments conducted for > 24 h at 200 °C discussed in the preceding sections.

Figure 6: Can you add the information on the amount of N2O in the figure to make sure readers do not miss this information?

We added the following note to the caption for Fig. 6 to clarify the amount of N_2O in each experiment:

Experiments at 218 °C were performed with 300 µmol N_2O, as was one experiment at 200 °C (see Sect. 3.3). All other experiments were performed with 1200 µmol N_2O.

Line 287: Is this the temporal isotopic evolution, not clear from the text or from figure 7.

In the current text, we have "continuous" in Line 302 to refer to the temporal nature of this evolution. We adjusted a sentence at Line 305 to make this even more clear. In addition, we corrected the text regarding the duration of the timepoints associated with 80 % destruction; the data were plotted correctly in the figure.

In both experiments, nearly half of the supplied N_2O was destroyed after 15 min, reaching about 80 % after one hour.

Table 1: please use consistent terminology in your table, caption and text. Now it is confusing to read “theoretical prediction” in the text and caption but “Equilibrium” as the header of the column.

This is a good point, as both predicted and measured values are interpreted as corresponding to equilibrium. The header in Table 1 has been adjusted accordingly.

Please add “Measured” before “SP values are reported using the value assigned by comparison with Science Tokyo …” in the caption of table 1.

Adjusted accordingly.

Line 27 add right punctuation: “The clumped isotopologues of N2O: $^{14}N^{15}N^{18}O$, $^{15}N^{14}N^{18}O$, and $^{15}N^{15}N^{16}O$, show…”

We rephrase as "The clumped isotopologues $^{14}N^{15}N^{18}O$, $^{15}N^{14}N^{18}O$, and $^{15}N^{15}N^{16}O$", which is both grammatically correct, and hopefully smoother for the reader to encounter.

Line 34: add space between “of” and “ ≥8”

A space was already present after "of," but we added a space between "≥" and "8" to ensure compatibility with AMT formatting regulations.

Line 61: Add dot at end of sentence

Done

Line 92: “to be delivered to the intermediate gas volume..”

Added

Line 141 add dot at end of sentence

Done