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).