δ(Ar/N_2) residual analysis

To test the hypothesis that large artifacts or biases in δ(Ar/N_2) were introduced during flask sample collection, we look for the presence of a pressure dependency of δ(Ar/N_2) after removing what we have shown is the natural gravitational signal. Pressure serves as a proxy for sampling conditions and aircraft velocity simultaneously here because aircraft velocity also increases systematically with altitude or pressure altitude. A vertical profile of δ(Ar/N_2) (Fig. S1A) reveals no strong dependency on pressure in the troposphere below about 300 mb. Above ~300 mb, some samples represent stratospheric conditions and therefore have an age of air (AoA) greater than zero and more negative δ(Ar/N_2). For further analysis, we correct δ(Ar/N_2) for the natural gravitational signal ($\delta(Ar/N_2)_{grav}$) using observed AoA from each sample and a quadratic fit of the AoA-δ(Ar/N_2) relationship simulated in TOMCAT ($\delta(Ar/N_2)_{grav} = -8.124\, AoA^2 - 22.73\, AoA + 0.9529$). The result is shown in Figure S1B. Although there is scatter in the corrected data, in particular for HIPPO1–5, no systematic relationship between pressure and gravitationally-corrected δ(Ar/N_2) is evident, supporting the interpretation that aircraft sampling did not create large biases in δ(Ar/N_2). While there is some evidence of a pressure dependence in the ORCAS data from the Southern Hemisphere (SH), this could also be the result of an incomplete correction for gravitational fractionation if there are differences in the true AoA-δ(Ar/N_2) relationship for the SH not captured by TOMCAT. However, stratospheric samples from ORCAS were almost exclusively taken at the same pressure, so our analysis of the δ(Ar/N_2)-AoA relationship should be robust regardless.

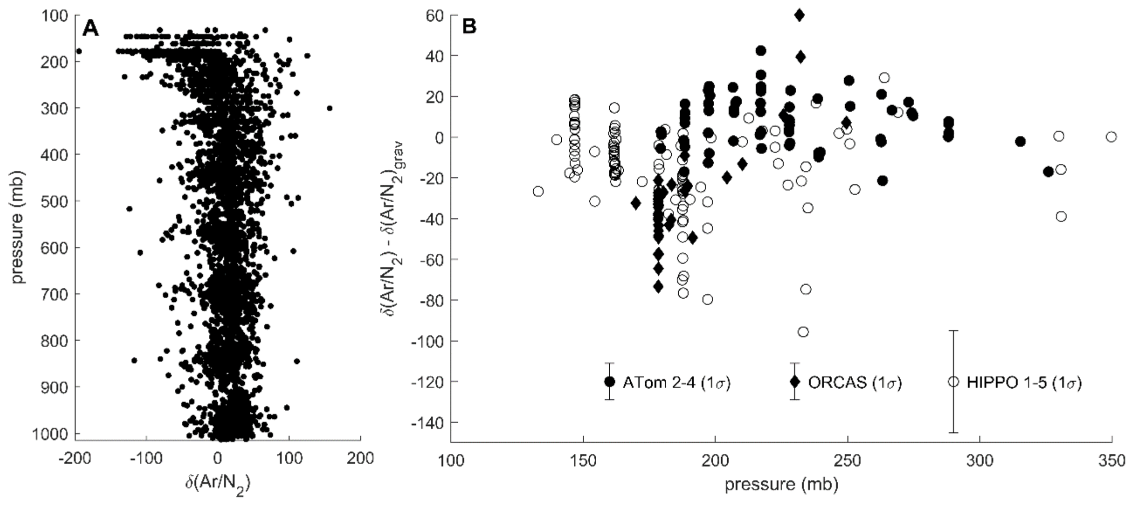

Figure S1. Pressure relationship of Medusa flask δ(Ar/N_2) (A) and residual δ(Ar/N_2) (B), i.e., δ(Ar/N_2) corrected for the influence of gravity in the stratosphere (see text). Data from HIPPO (open circles) and ATom (solid circles), and ORCAS (solid diamonds) are shown separately in (B) with their respective error bars.

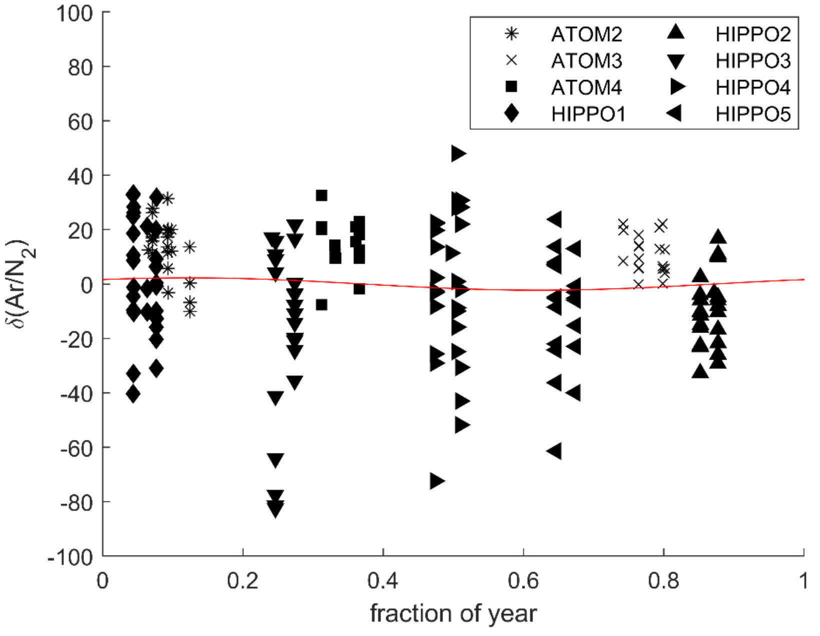

Figure S2. Seasonal cycle of δ(Ar/N_2) in the topical free troposphere (20°>lat>-20° & altitude 3-8 km).

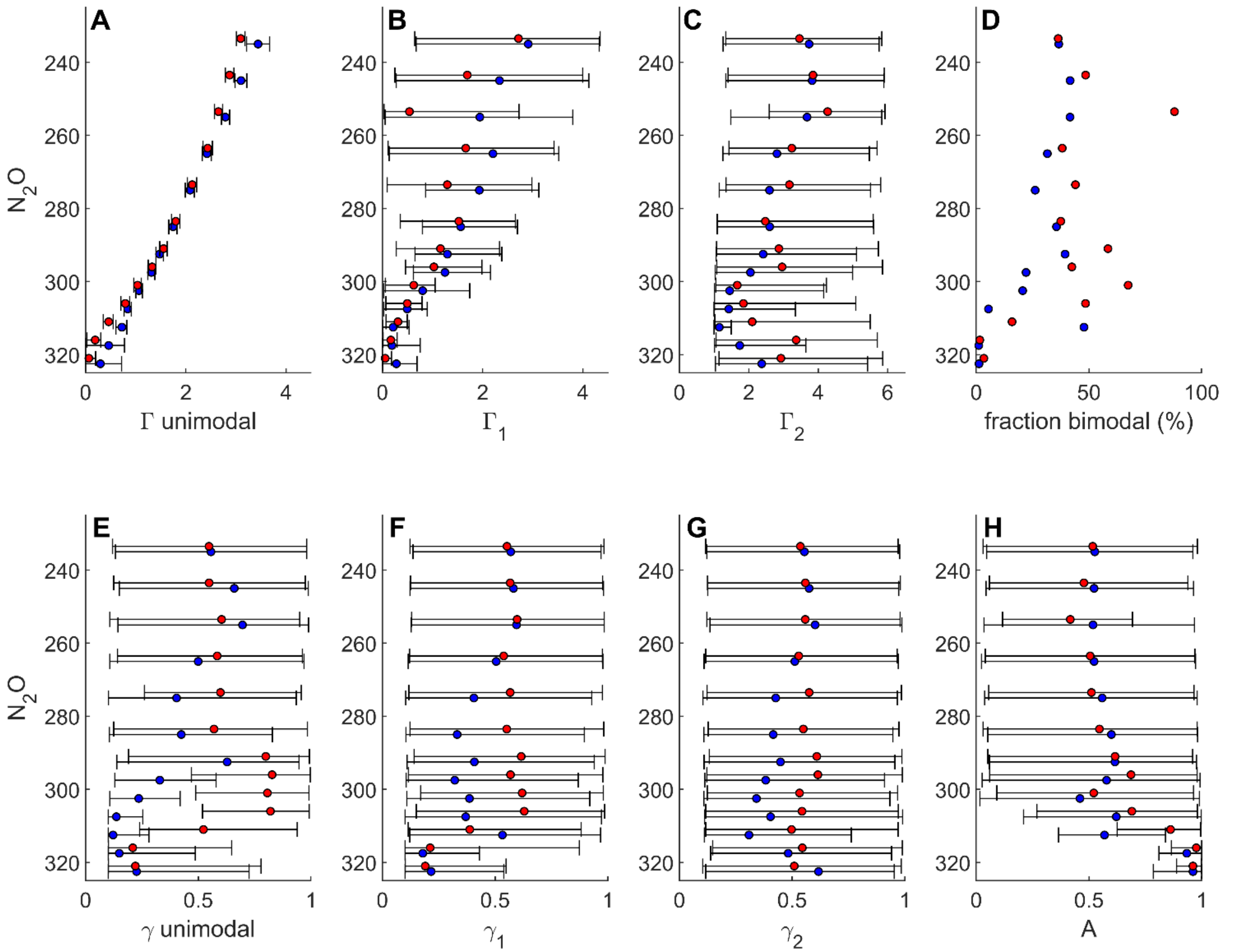

Figure S3. Age spectrum parameter values selected by the Markov chain Monte Carlo algorithm in each N_2O bin for the Southern (blue) and Northern (red) Hemispheres with error bars showing 95% confidence interval. NH N_2O bin values were adjusted by -1.5 ppb here for visual clarity only. The mean AoA is well constrained but the algorithm fails to clearly distinguish between unimodal and bimodal age spectra and places poor constraints on the width of unimodal and bimodal age spectra.

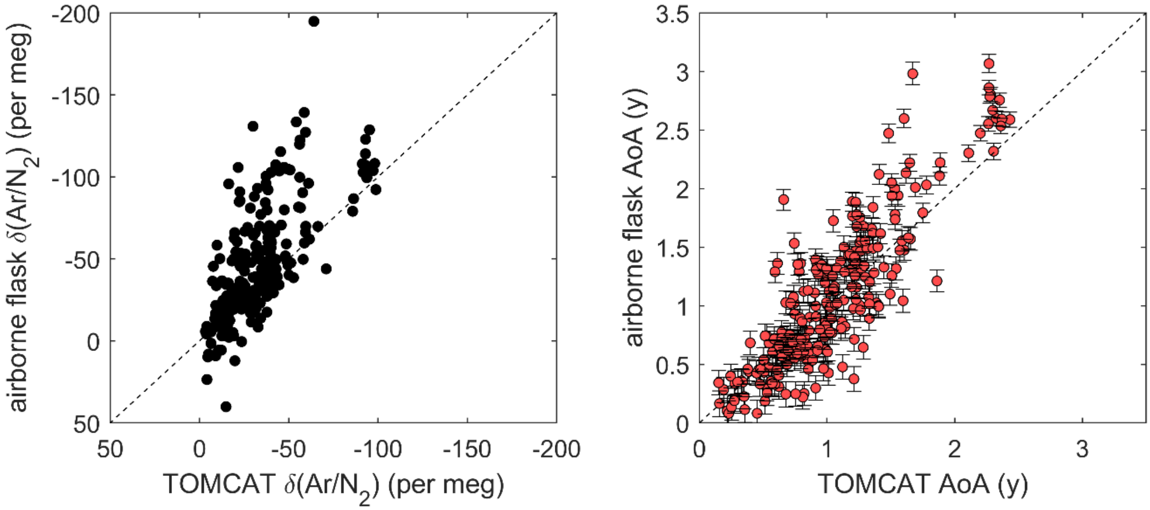

Figure S4. Comparison of δ(Ar/N₂) (left) and AoA (right) between stratospheric HIPPO, AToM and ORCAS observations and TOMCAT in the lowermost stratosphere. TOMCAT grid cells are chosen to be closest in space and time to the observations, but unresolved mixing processes can allow more fractionated/older air to be present in the observations than can be reproduced by TOMCAT. These deviations from the 1:1-line are correlated between δ(Ar/N₂) and AoA, and therefore will partially cancel in the AoA-δ(Ar/N₂) relationship (see Fig. 5 in main paper).

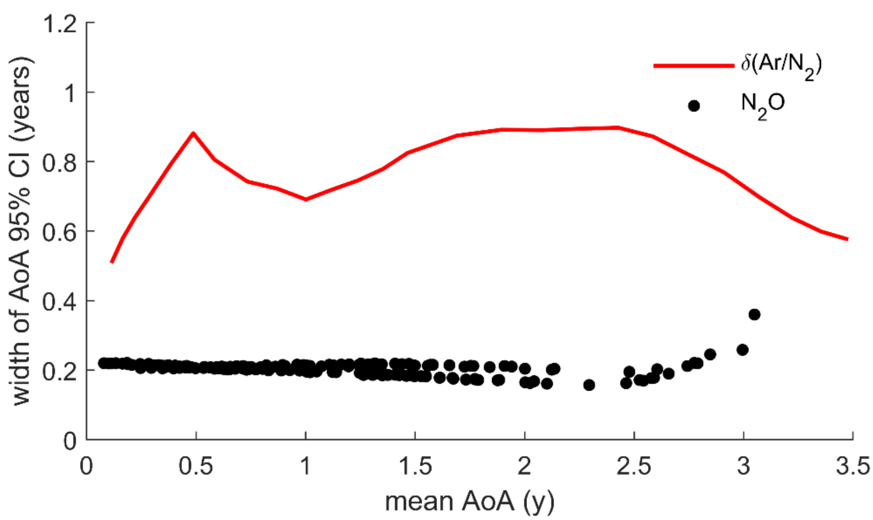

Figure S5. Width of the 95% confidence interval for AoA estimates from N_2O based on the Markov chain Monte Carlo algorithm (points) and from $\delta(Ar/N_2)$ using the AoA-$\delta(Ar/N_2)$ relationship in TOMCAT (red line).