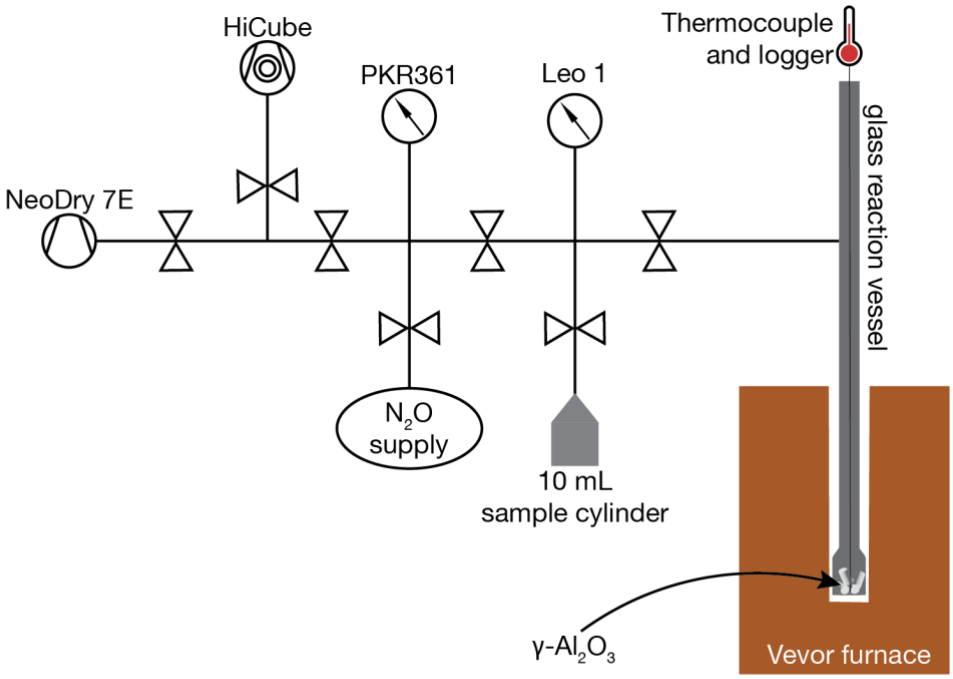
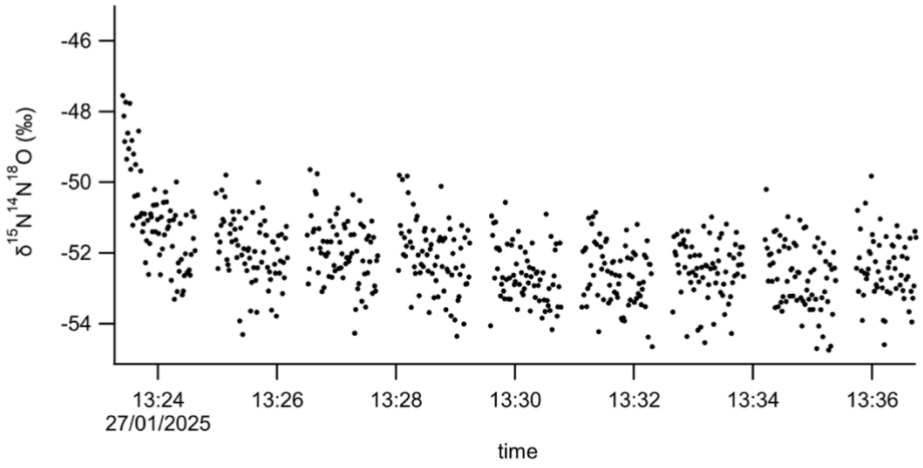
Supporting Information



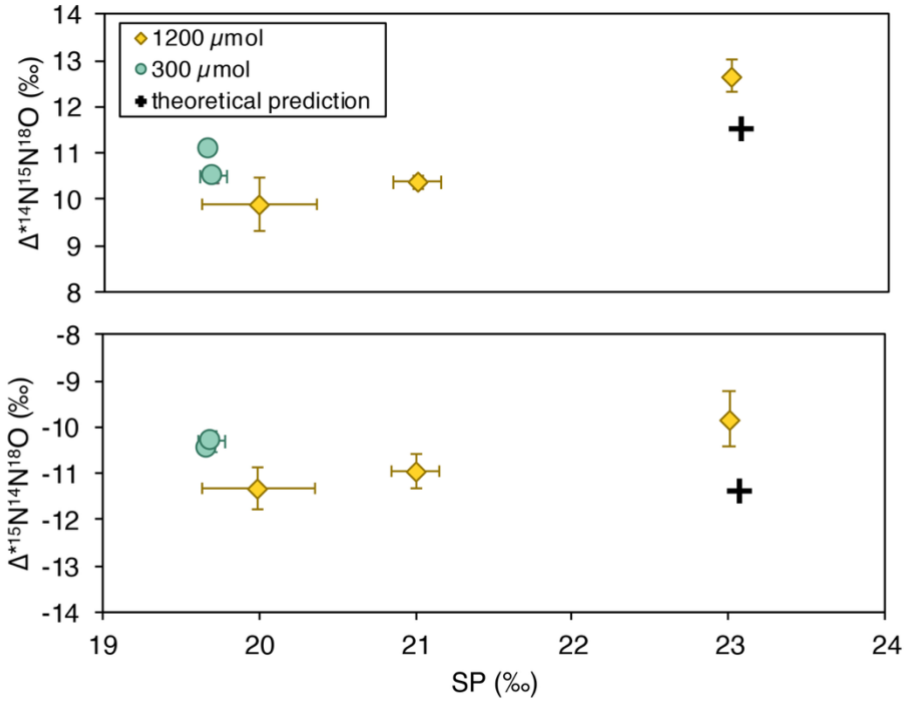
: Swagelok diaphragm-sealed valves

Figure S1. Vevor furnace and vacuum line used for equilibration of N_2O over γ-Al_2O_3 and sample loading and recovery. The glass reaction vessel is a 12 mm quartz glass tube, widening at the base to 22 mm. Within the furnace it is packed in sand and then placed within a stainless-steel thermal mass to maximize the uniformity of temperature. The thermocouple is placed in a 3 mm glass tube passing through an UltraTorr connection (Swagelok, USA) at the top of the glass reaction vessel.

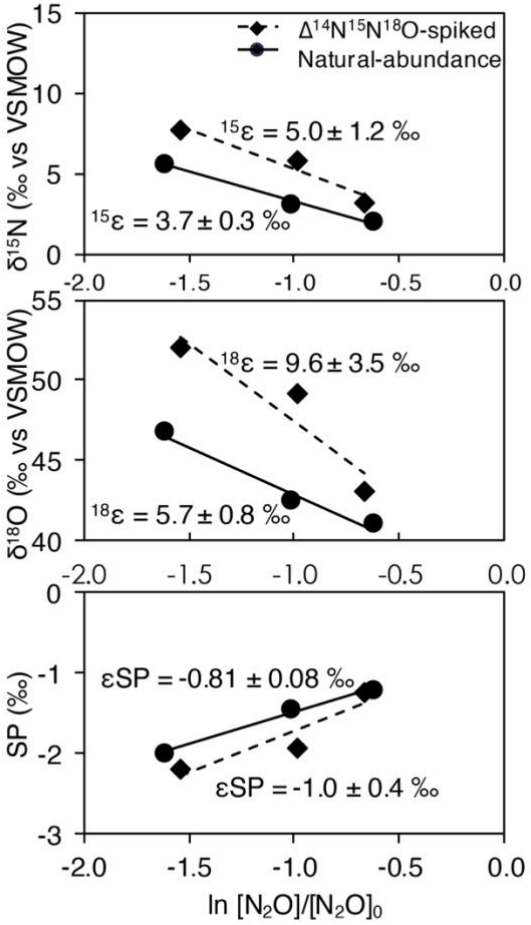


‰	$\delta^{14}N^{15}N^{16}O$	$\delta^{15}N^{14}N^{16}O$	$\delta^{14}N^{14}N^{17}O$	$\delta^{14}N^{14}N^{18}O$	$\delta^{15}N^{15}N^{16}O$	$\delta^{14}N^{15}N^{18}O$	$\delta^{15}N^{14}N^{18}O$
value	0.022	0.006	-0.017	-0.010	-0.046	-0.127	-0.039
1 s. e.	0.085	0.091	0.115	0.182	0.143	0.108	0.118

Supplementary Figure 2. Representative repeatability of working gas measurements, shown for $\delta^{15}N^{14}N^{18}O$ and summarized for all isotopologues. The values here are reported directly as calculated from isotopologue concentrations reported by TDLWintel, before any corrections are applied.



Supplementary Figure 3. Clumped isotopic composition of N_2O heated over γ-Al_2O_3 at 218 °C. Variable outcomes for 1200 µmol N_2O and convergence on a single composition for 300 µmol samples are observed, as discussed in Sect. 3.4. The offset between this converged-upon value and the theoretical prediction matches those seen at other temperatures, as discussed in in the main text.



Supplementary Figure 4. Rayleigh fractionation plots used to determine the isotope effects e associated with the thermal decomposition of N_2O. The reaction progress is from right to left.