Measurement of nitrous oxide isotopologues and isotopomers by the MAT 253 Ultra

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The global budget of nitrous oxide is dominated by terrestrial and marine biological sources and atmospheric sinks. Details of the budget remain unclear, including the cause of increasing atmospheric N_2O concentrations. Marine sources of N_2O include denitrification and nitrification. Our understanding of the major microbial players in the nitrogen cycle has changed in recent years (for example, the nitrifying Archaea), and the overall contributions of these organisms to N_2O production and their isotopic signatures are poorly constrained [1].

Here we examine the suitability of the MAT 253 Ultra, a new high resolution gas source mass spectrometer [2], for measurements of rare, previously unanalyzed isotopologues and isotopomers of N_2O, including 'clumped' species and high-precision direct analysis of ^{17}O-substituted species. Such measurements could provide additional constraints to the global cycle of N_2O, and in particular offer a fresh opportunity for distinguishing among biosynthetic N_2O sources. Preliminary experiments include examining N_2O produced by pure cultures of denitrifying bacteria.

In the instrument's 'medium resolution' setting (16 μm entrance slit; resolving power ~16-18,000, M/ΔM), [$^{14}N^{15}N^{18}O + {}^{15}N^{14}N^{18}O$] is well resolved from $^{13}C^{18}O^{16}O$ and the $^{15}N^{18}O$ fragment from $^{17}O^{18}O$. In zero-enrichment measurements, precision of 0.2‰ was achieved for mass 47 species and 0.4‰ for $^{15}N^{18}O$; both equaled counting statistics limits for the integration times used (11 and 17 minutes, respectively) and should be improved by increasing the source pressure, reducing resolution (e.g., using a 20 μm entrance slit) or increasing counting time. At mass 45, $^{14}N_2{}^{17}O$ is well resolved from [$^{14}N^{15}N^{16}O + {}^{15}N^{14}N^{16}O$], with external precision of 0.03‰ achieved after 11 minutes of integration (again, counting statistics limited and potentially improvable).

By measuring both these species (as well as unsubstituted and singly substituted isotopologues), the position-specific clumping (i.e., clumping of ^{15}N with ^{18}O, and its dependence on site preference of ^{15}N) can be examined. Such measurements will complement the information already available from N_2O site preference measurements alone. Calculations suggest that site preference of ^{15}N in thermodynamically equilibrated N_2O will differ by ~1‰ between ^{16}O and ^{18}O isotopologues [3]. A larger range of signals could arise from photochemical and biological fractionations. Precise measurement of ^{17}O will enable detection of even subtle contributions of atmospheric mass-independent fractionation, or study of variations in mass laws of biological and other fractionations.

[1] Santoro *et al.* (2011) *Science* **333**, 1282-1285. [2] Eiler *et al.* The MAT 253 Ultra — a novel high-resolution, multi-collector gas source mass spectrometer. Goldschmidt 2012. [3] Wang *et al.* (2004) *Geochim. Cosmochim. Acta* **68,** 4779-4797.

Oxygen isotopes from Chinese caves: records not of monsoon rainfall but circulation regime

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Current interpretation of cave $\delta^{18}O$ records

Oxygen isotope variations in Chinese stalagmites have been widely interpreted as a record of the amount of East Asian summer monsoonal rainfall. This interpretation infers decreasing monsoonal rainfall from the mid-Holocene and large, dipolar rainfall oscillations within glaciations. However, the cave $\delta^{18}O$ variations conflict with independent palaeoclimate proxies (cave $\delta^{13}C$, loess/palaeosol magnetic properties, n-alkanes), which indicate no systematic decline in rainfall from the mid-Holocene, and no glacial rainfall maxima.

Mass balance calculations show moisture source is key control

Using mass balance calculations, we demonstrate that the cave $\delta^{18}O$ variations cannot be accounted for by summer rainfall changes, nor rainfall seasonality nor winter cooling, but instead reflect changes in moisture source. A possible driver of the $\delta^{18}O$ variations in Chinese stalagmites is precessional forcing of inter-hemispheric temperature gradients, in a mechanism similar to that of the modern day Indian Ocean dipole. Through such forcing, Indian monsoon-sourced $\delta^{18}O$ may have dominated at times of high boreal summer insolation, local Pacific-sourced moisture at low insolation. Suppression of summer monsoonal rainfall during glacial stages may reflect diminished sea and land surface temperatures and the radiative impacts of increased regional dust fluxes.