An extreme enrichment in atmospheric $^{15}N^{15}N$: Biotic and abiotic contributions

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Molecular nitrogen (N_2) is a major component of many planetary atmospheres. On Earth, and probably also other planets, its first appearance and long-term evolution are associated with astrochemical and geologic processes [1]. However, Earth's N_2 budget today is dominated by biological cycles. The paucity of abiotic N_2 sources—and the abundance of abiotic sinks—has lead some to suggest that the persistence of N_2 in a mature planetary atmosphere could be a biosignature [2]. Inspired by this suggestion, we report the first study of $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ (i.e., the "clumped" isotope distribution in N_2) in Earth's atmosphere.

Our clumped-isotope approach to a planetary N_2 budget removes one of the reservoir effects associated with N_2 biogeochemistry by tracking N-N bonds. Unlike for bulk nitrogen, N-N bonding is reset on timescales of global N_2 cycling. Moreover, bonding patterns are insensitive to the bulk $^{15}N/^{14}N$ ratio of a planet. This approach can be applied to determine mechanisms of N_2 cycling on a planetary scale.

We observe a 19‰ enrichment in atmospheric $^{15}N^{15}N$ relative to a random distribution of ^{15}N and ^{14}N isotopes within N_2 (i.e., Δ_{30} = 19‰). This enrichment is in excess of that predicted for thermodynamic equilibrium anywhere on Earth. Clumped-isotope signatures from microbial and geologic N_2 sources are $\Delta_{30} \leq$ 1‰. Electrolysis experiments simulating ion chemistry of the upper atmosphere cause large and variable $^{15}N^{15}N$ enrichments. Estimated timescales of upper-atmospheric N_2 cycling suggest atmospheric $^{15}N^{15}N$ excesses reflect a balance of biological and ionospheric N_2 cycling integrated over 10^7-yr timescales.

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[2] Capone, D. G. et al. *Science* **312**, 708 (2006).