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## ATMOSPHERIC SCIENCE

Extreme enrichment in atmospheric  $^{15}\text{N}^{15}\text{N}$ 

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Molecular nitrogen ( $\text{N}_2$ ) comprises three-quarters of Earth's atmosphere and significant portions of other planetary atmospheres. We report a 19 per mil (‰) excess of  $^{15}\text{N}^{15}\text{N}$  in air relative to a random distribution of nitrogen isotopes, an enrichment that is 10 times larger than what isotopic equilibration in the atmosphere allows. Biological experiments show that the main sources and sinks of  $\text{N}_2$  yield much smaller proportions of  $^{15}\text{N}^{15}\text{N}$  in  $\text{N}_2$ . Electrical discharge experiments, however, establish  $^{15}\text{N}^{15}\text{N}$  excesses of up to +23‰. We argue that  $^{15}\text{N}^{15}\text{N}$  accumulates in the atmosphere because of gas-phase chemistry in the thermosphere (>100 km altitude) on time scales comparable to those of biological cycling. The atmospheric  $^{15}\text{N}^{15}\text{N}$  excess therefore reflects a planetary-scale balance of biogeochemical and atmospheric nitrogen chemistry, one that may also exist on other planets.

## INTRODUCTION

Nitrogen is a major component of many planetary atmospheres. On Earth, it probably first appeared early, degassing from the mantle because of its low solubility in oxidized silicate melts (1, 2). Its present-day budget is dominated by biological cycling. Nitrogen fixation (natural + industrial) is the major sink of  $\text{N}_2$ , whereas denitrification (via nitrate or nitrite reduction and ammonia oxidation) is its major source. Global rates are typically estimated to be between 400 and 500 TgN year<sup>-1</sup> (3–5), with a total atmospheric inventory of  $3.92 \times 10^9$  TgN. Abiotic  $\text{N}_2$  cycling mechanisms are much slower and include  $\text{N}_2$  fixation by lightning (~5 TgN year<sup>-1</sup>) and geologic outgassing [0.1 TgN year<sup>-1</sup> (6)]. This vast difference in magnitude between biotic and abiotic fluxes suggests that  $\text{N}_2$ —particularly its isotopic composition—records biological nitrogen cycling at the planetary scale. A planetary-scale perspective on nitrogen cycling would offer new opportunities to evaluate Earth's enigmatic nitrogen budget.

We describe a new isotopic tracer that unlocks this signal by exploiting natural variations in  $^{15}\text{N}^{15}\text{N}$ , the  $\text{N}_2$  molecule containing two rare isotopes. The tracer characterizes the relative natural abundances of  $^{14}\text{N}^{14}\text{N}$ ,  $^{14}\text{N}^{15}\text{N}$ , and  $^{15}\text{N}^{15}\text{N}$  as a  $\Delta_{30}$  value, which quantifies the excess in  $^{15}\text{N}^{15}\text{N}$  relative to a random distribution of  $^{15}\text{N}$  and  $^{14}\text{N}$  atoms in  $\text{N}_2$  molecules. Mathematically, the  $\Delta_{30}$  tracer is defined by  $\Delta_{30} \equiv {}^{30}R / ({}^{15}R)^2 - 1$ , where  ${}^{30}R = {}^{15}\text{N}^{15}\text{N} / {}^{14}\text{N}^{14}\text{N}$  and  ${}^{15}R = {}^{15}\text{N} / {}^{14}\text{N}$ . Other isotopic notations used throughout include  $\delta^{15}\text{N}$ ,  $\delta^{29}\text{N}_2$ , and  $\delta^{30}\text{N}_2$ , defined similarly:  $\delta^{15}\text{N} = {}^{15}R / {}^{15}R_{\text{air}} - 1$ ,  $\delta^{29}\text{N}_2 = {}^{29}R / {}^{29}R_{\text{air}} - 1$ , and  $\delta^{30}\text{N}_2 = {}^{30}R / {}^{30}R_{\text{air}} - 1$ , where  ${}^{29}R = {}^{14}\text{N}^{15}\text{N} / {}^{14}\text{N}^{14}\text{N}$ . All  $\delta$  and  $\Delta_{30}$  values are reported in per mil (‰).

At isotopic equilibrium, a small  $^{15}\text{N}^{15}\text{N}$  excess is expected because of its higher thermodynamic stability compared to  $^{14}\text{N}^{14}\text{N}$  and  $^{14}\text{N}^{15}\text{N}$  molecules. Thermodynamic control of  $\Delta_{30}$  values would cause them to vary monotonically between 1.9 and 0.07‰ for temperatures between 200 and 1000 K, respectively (fig. S1) (7). When out of isotopic equilibrium, however, they may express a wider range of values that reflect biogeochemical processing (8–11). Crucially, the  $\Delta_{30}$  value is mainly sensitive to the chemistry that makes and breaks N–N bonds, allowing

it to evolve independently from the  $^{15}\text{N} / {}^{14}\text{N}$  ratio in  $\text{N}_2$  on time scales governed by the rates at which its bonds are broken and remade: The  $\Delta_{30}$  value traces N–N bond-forming chemistry by quantifying the number of naturally occurring  $^{15}\text{N}$ -atom pairs. We analyzed the  $\Delta_{30}$  composition of  $\text{N}_2$  from a variety of natural and laboratory samples to an estimated accuracy of  $\pm 0.3\%$ , free of isobaric interferences, using an ultrahigh-resolution isotope ratio mass spectrometer (12). The measurements were calibrated against  $\text{N}_2$  gas that was driven to isotopic equilibrium by reordering on a strontium nitride catalyst at 800°C.

## RESULTS

Air sampled from the University of California, Los Angeles (UCLA) and Rice University shows a 19‰ excess in  $^{15}\text{N}^{15}\text{N}$  relative to  $\text{N}_2$  containing a random distribution of  $^{14}\text{N}$  and  $^{15}\text{N}$  isotopes [that is,  $\Delta_{30} = 19.1 \pm 0.1\%$  (95% confidence interval); Fig. 1]. Stratospheric air sampled at 32 km in 2004 (13, 14) and dissolved air sampled from the surface ocean in 2017 are analytically indistinguishable from surface air (table S1;  $P > 0.4$ ). The atmosphere's high  $\Delta_{30}$  value is 10 times larger than that for thermodynamic equilibrium in its coldest regions (that is,  $\Delta_{30} \sim 2\%$  at 180 K), indicating that the atmospheric  $\Delta_{30}$  value is governed by kinetic processes. The stratospheric sample suggests that the  $\Delta_{30}$  value is homogeneous up to at least 32 km.

To determine the effects of biological cycling on the  $\Delta_{30}$  value of  $\text{N}_2$ , we analyzed (i)  $\text{N}_2$  produced by cultures of denitrifying bacteria and (ii)  $^{15}\text{N}^{15}\text{N}$  isotopic fractionation factors for nitrogen-fixing cyanobacteria. Axenic cultures of *Pseudomonas stutzeri* and *Paracoccus denitrificans* produced  $\text{N}_2$  with  $\Delta_{30}$  values ranging from 0.4 to 1.4‰, with a decreasing trend as the reaction progressed. The denitrification  $\Delta_{30}$  values for high nitrate conversion are lower than those for isotopic equilibrium at the culturing temperatures ( $\Delta_{30, \text{equil}} = 1.0\%$  at 303 K), indicating that kinetic and/or combinatorial isotope effects are expressed in biological denitrification (table S2). Isotopic fractionation resulted in either no change or a slight decrease in  $\Delta_{30}$  values for nitrogen fixation in batch cultures of *Anabaena variabilis* expressing the molybdenum-containing variant of nitrogenase (Fig. 1 and table S1). This observation implies that the  $^{15}\text{N}^{15}\text{N} / {}^{14}\text{N}^{14}\text{N}$  isotopic fractionation factor for  $\text{N}_2$  fixation is roughly equal to the square of that for  $^{15}\text{N} / {}^{14}\text{N}$  [that is,  ${}^{30}\alpha \approx ({}^{15}\alpha)^2$ ], resulting in little change to  $\Delta_{30}$  values in the residual  $\text{N}_2$  reservoir during  $\text{N}_2$  fixation.

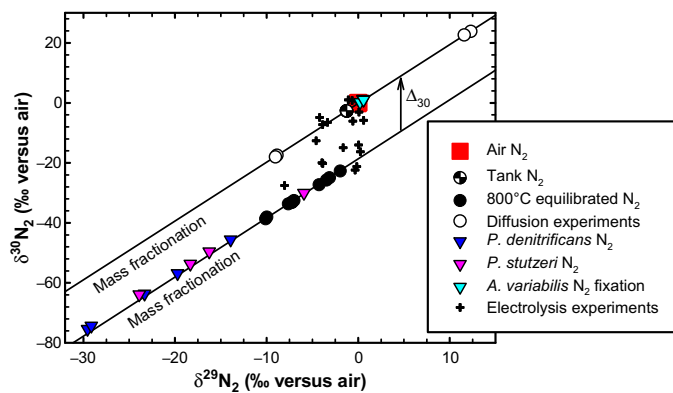
Neither bacterial denitrification nor  $\text{N}_2$  fixation can explain the atmospheric  $\Delta_{30}$  value. Moreover, the low  $\Delta_{30}$  values in  $\text{N}_2$  coming from bacterial denitrification must be offset by another process characterized by

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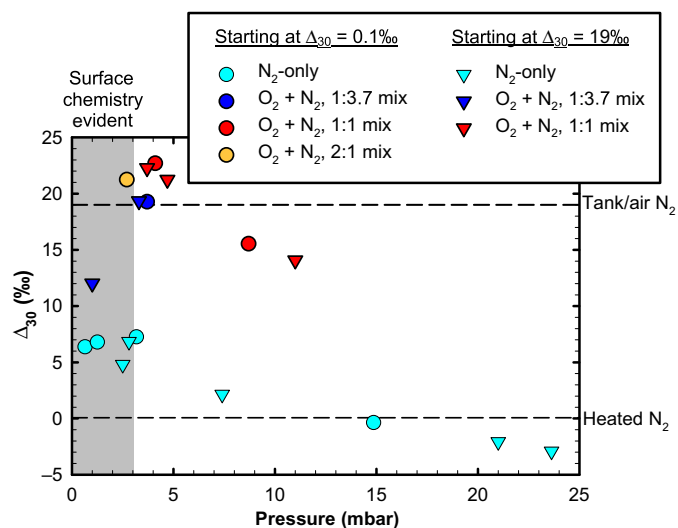
**Fig. 1. Isotopic composition of N<sub>2</sub> from natural samples and laboratory experiments.** The covariation of all three isotopic variants of N<sub>2</sub> is shown by plotting  $\delta^{30}\text{N}_2$  versus  $\delta^{29}\text{N}_2$ . Mass-dependent fractionation curves for air and high-temperature equilibrated N<sub>2</sub> are also shown. Error bars are smaller than the data points.

extremely high  $\Delta_{30}$  values ( $\gg 19\%$ ). Therefore, we evaluated whether other processes relevant to the atmospheric N<sub>2</sub> budget can elevate atmospheric  $\Delta_{30}$  values to such a degree. Fungal denitrification produces N–N bonds as N<sub>2</sub>O and expresses different isotope effects from those found in bacteria (15, 16), but it contributes on the order of 1% to the global N<sub>2</sub> budget (4). Its contribution to  $\Delta_{30}$  values is likely negligible on the basis of mass balance. Anaerobic ammonia oxidation (anammox) may have an important impact on atmospheric  $\Delta_{30}$  values; thus, we measured N<sub>2</sub> samples of opportunity from an anammox reactor at the University of Utah, which had been flushed with air-N<sub>2</sub> to render it anaerobic (17). These samples showed  $\Delta_{30}$  values lower than atmospheric values (table S2), indicating that the  $\Delta_{30}$  value of anammox-N<sub>2</sub> is less than that of the atmosphere. A large difference in  $^{15}\text{N}/^{14}\text{N}$  ratios and kinetic isotope effects for ammonium and nitrite in nature (18) suggests that end-member  $\Delta_{30}$  signatures for the anammox process are near or less than zero because of combinatorial effects and mass-dependent fractionation (9). Experiments with enriched cultures are needed to determine the range of  $\Delta_{30}$  values characteristic of anammox-N<sub>2</sub> and its contributions to the global budget, but the evidence presented here suggests that it cannot explain the high atmospheric  $\Delta_{30}$  value.

Mixing of N<sub>2</sub> reservoirs that have similar  $\Delta_{30}$  values but different  $^{15}\text{N}/^{14}\text{N}$  ratios can yield elevated  $\Delta_{30}$  values. However, the difference in the reservoir  $^{15}\text{N}/^{14}\text{N}$  ratios must be at least 300‰ different, larger than any thus far observed on Earth, to cause  $\Delta_{30} = 19\%$  upon mixing (see Materials and Methods). Other physical effects such as gravitational and thermal fractionation are mass-dependent, yielding changes in  $\Delta_{30}$  value that are much smaller in magnitude than that required to explain the atmospheric  $\Delta_{30}$  value (19–21).

The slow biological recycling time of N<sub>2</sub> in the atmosphere [ $\sim 10$  million years (My) based on the N<sub>2</sub> inventory and biological fluxes] suggests that atmospheric chemistry could affect its isotopic composition. Extreme  $\delta^{15}\text{N}$  enrichments ( $>500\%$  versus Earth's N<sub>2</sub>) have been observed in the atmospheres of Mars (22, 23) and Titan (24), possibly arising from unusual isotope effects in photochemistry near the N<sub>2</sub> dissociation threshold (80 to 100 nm; 12.4 to 15.5 eV) (25–27). These and other unconventional isotopic fractionation mechanisms may also be operating in the middle and upper atmosphere of Earth, influencing both the  $^{15}\text{N}/^{14}\text{N}$  ratios and the proportions of  $^{15}\text{N}^{15}\text{N}$  in atmospheric N<sub>2</sub>.

We tested this possibility by conducting high-voltage radio-frequency discharge experiments with an Oudin coil to simulate the chemistry of



**Fig. 2. Results of laboratory electrolysis experiments demonstrating clumped-isotope reordering.** Initial isotopologue compositions were either N<sub>2</sub> that had been equilibrated at 800°C (circles) or pure tank N<sub>2</sub> (triangles). Surface chemistry effects likely became dominant below  $\sim 3$  mbar. Error bars are smaller than the size of the data points.

N<sub>2</sub> in the upper atmosphere. Pure N<sub>2</sub> gas and O<sub>2</sub>/N<sub>2</sub> mixtures were introduced into a glass vacuum chamber that contained electrical feedthroughs made of tungsten. Experiments lasting 1 hour yielded N<sub>2</sub> with  $\Delta_{30}$  values ranging from  $-3$  to  $+23\%$ , with a marked dependence on initial pressure and O<sub>2</sub>/N<sub>2</sub> ratio (Fig. 2 and table S3). The  $\Delta_{30}$  values of electrolyzed N<sub>2</sub> show a step-like increase when O<sub>2</sub> is added, and they decrease with increasing pressure above  $\sim 3$  mbar. Partial isotope equilibration on tungsten surfaces may be important below this pressure (28). The pressure dependence of postelectrolysis  $\Delta_{30}$  values above 3 mbar is independent of the initial isotopic composition, suggesting that a laboratory steady state is approached under these conditions and that N<sub>2</sub> bonds are being broken and remade. Together, these experiments demonstrate that gas-phase chemistry of N<sub>2</sub> and its ions can potentially explain the extreme  $\Delta_{30}$  values observed in the atmosphere.

The marked increase in  $\Delta_{30}$  values with the addition of O<sub>2</sub> in the experiments points to an oxygen-containing species in the key  $^{15}\text{N}^{15}\text{N}$ -concentrating step(s). The decrease in steady-state  $\Delta_{30}$  values with increasing pressure suggests that this step becomes less important at higher pressures. At these higher pressures, the system is affected more by a step that disfavors  $^{15}\text{N}^{15}\text{N}$  bonds. This balance between two opposing reactions would qualitatively explain the laboratory steady state. Our kinetic model of the experiments (29) suggests that the most important N–N bond-breaking mechanisms are electron impact dissociation ( $\text{N}_2 + e^- \rightarrow \text{N}^+ + \text{N} + 2e^-$ ) and the ion-molecule reaction  $\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$ . Nitrogen-nitrogen bond-making occurs fastest via  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ . These reactions compete primarily with recombination on chamber surfaces and gas-phase recombination (that is,  $\text{N} + \text{N} + \text{M} \rightarrow \text{N}_2 + \text{M}$ , where M is a third body or wall). On the basis of the dramatic increase in  $\Delta_{30}$  values when O<sub>2</sub> is introduced, we hypothesize that the  $\text{N}_2^+ + \text{O}$  and/or  $\text{N} + \text{NO}$  reactions are key to concentrating  $^{15}\text{N}$  in  $^{15}\text{N}^{15}\text{N}$  molecules in the laboratory experiments: Both reactions require an oxygen source and they contribute a larger proportion to the total N–N bond recycling rate as pressure decreases. The other reactions involving oxidic species comprise minor channels, typically several orders of magnitude slower (fig. S4). We note that any

trace oxygen source in the  $N_2$ -only experiments (for example, from a surface; it need not be  $O_2$ ) could be responsible for the pressure dependence for  $\Delta_{30}$  values observed there. However, a  $\Delta_{30}$  pressure dependence for the  $N_2$ -only chemistry cannot be ruled out.

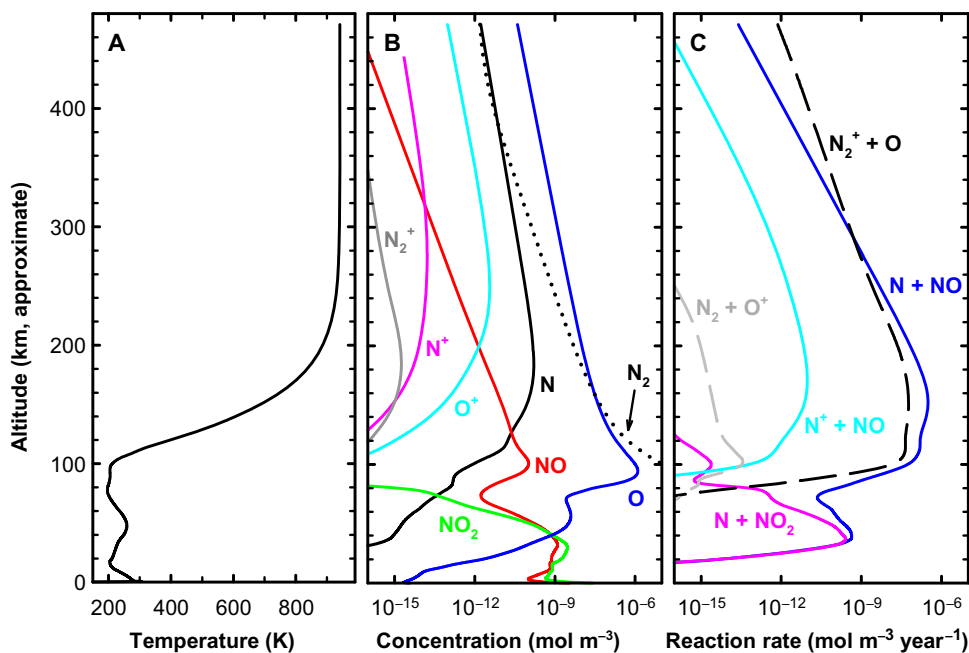
In the atmosphere,  $N_2^+$ , NO, N, and O are also key species, particularly in the thermosphere (100 to 500 km altitude). We estimated the time scale of photochemical  $N_2$  cycling in the atmosphere using species concentrations derived from the Whole Atmosphere Community Climate Model, eXtended version (WACCM-X) model, from the surface to  $\sim 500$  km (30), and temperature-dependent reaction rates. We find that in model year 2001, 302 TgN is recombined via  $N + NO$ , whereas 0.01 TgN is recombined by the  $N + NO_2$  and  $N^+ + NO$  channels combined (Fig. 3). The most important chemical channel of  $N_2$  destruction,  $N_2^+ + O$ , destroys about 74 TgN  $year^{-1}$ . Photolytic, electrolytic, and nonthermal  $N_2$  bond rupture cannot be explicitly calculated from the WACCM-X species concentrations; hence, we assume that the sum of all destruction mechanisms balances chemical recombination to maintain a steady state for  $N_2$  concentrations. In such a steady state, the thermosphere would recycle a mass of  $N_2$  equal to the atmospheric inventory ( $3.92 \times 10^9$  TgN) in 13 My. Locally nonthermal conditions in the thermosphere and variations in incident solar radiation can alter this estimate (see Supplementary Text). Nevertheless, the time scale of atmospheric  $N_2$  recycling is likely comparable to that for biological  $N_2$  cycling.

Furthermore, mass exchange between the upper and lower atmosphere is sufficient to mix high- $\Delta_{30}$  thermospheric  $N_2$  into the troposphere on these time scales. The anthropogenic  $CO_2$  rise has recently been detected in the lower thermosphere by satellites (31, 32), suggesting that gases emitted at the surface can enter the thermosphere within several hundred years and vice versa. The atmosphere's  $\Delta_{30}$  value therefore carries signatures of both gas-phase and biological processing of  $N_2$ .

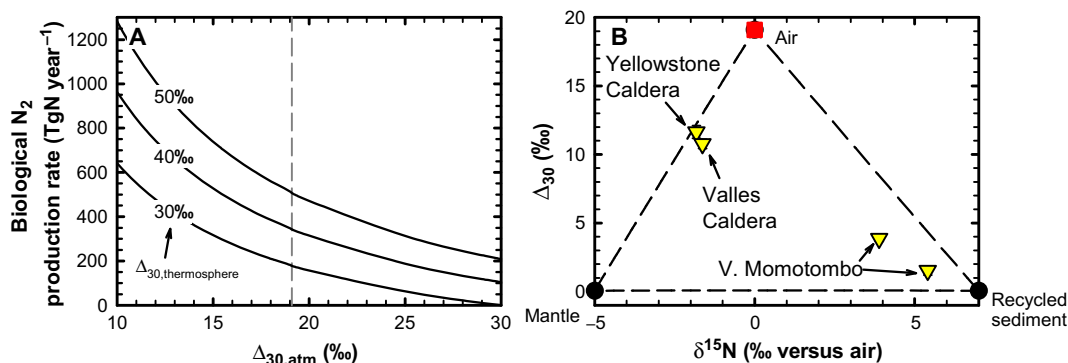
## DISCUSSION

We interpret the atmospheric  $\Delta_{30}$  value in  $N_2$  (hereafter  $\Delta_{30,atm}$ ) as the balance between two planetary-scale cycles that drive  $\Delta_{30}$  toward characteristic end-member values. Atmospheric chemistry, primarily in the thermosphere, drives  $\Delta_{30,atm}$  toward its end-member value,  $\Delta_{30,thermosphere}$ , at a rate represented by  $F_{thermosphere}$  (TgN  $year^{-1}$ ). Biological  $N_2$  cycling drives  $\Delta_{30,atm}$  toward its end-member value  $\Delta_{30,bio}$  at the rate  $F_{bio}$ . Our data suggest that  $N_2$  fixation does not alter atmospheric  $\Delta_{30}$  values significantly (that is, it does not discriminate strongly and fractionates mass-dependently); thus, the biological signature of  $\Delta_{30,bio}$  is primarily that associated with denitrification. The steady-state global  $\Delta_{30}$  mass balance is thus approximately described by  $F_{bio}(\Delta_{30,atm} - \Delta_{30,bio}) + F_{thermosphere}(\Delta_{30,atm} - \Delta_{30,thermosphere}) \approx 0$  (see Supplementary Text). Using  $\Delta_{30,bio} = 0.4\%$  and the WACCM-X-derived  $F_{thermosphere} = 302$  TgN  $year^{-1}$ , we find that  $\Delta_{30,thermosphere} = 40$  to 50‰ would be consistent with current bottom-up estimates of the global denitrification flux of  $N_2$  ( $F_{bio} \sim 400$  to 500 TgN  $year^{-1}$ ; Fig. 4A). A larger  $\Delta_{30,thermosphere}$  end-member value would imply a larger global biological  $N_2$  cycling rate and vice versa. Refining  $\Delta_{30,bio}$ ,  $\Delta_{30,thermosphere}$ , and  $F_{thermosphere}$  may thus allow one to constrain the average global rate of denitrification integrated over the past  $\sim 10$  My. In principle, this idea can also be applied to extraterrestrial atmospheres to determine rates of biogeochemical nitrogen cycling once the controls on  $\Delta_{30,thermosphere}$  and  $F_{thermosphere}$  (for example, those tied to solar flux and the presence of oxidic species) are understood. On smaller scales, the  $\Delta_{30}$  tracer should be an in situ measure of denitrification that does not rely on tracer injections and their associated uncertainties (33). It may be particularly useful for studying nitrogen cycling in oceanic oxygen minimum zones and subsurface terrestrial environments.

More broadly,  $\Delta_{30}$  measurements are of utility as an unambiguous measure of air content in geochemical mixtures. For example, gases



**Fig. 3. Calculated global, annual mean outputs from the WACCM-X model (year 2001).** (A) Temperatures, (B) species concentrations, and (C) gas-phase thermal reaction rates relevant to N–N bond rupture and formation are shown. Nonthermal effects are important in the upper atmosphere but are not included in these calculations. Photolysis reactions have been omitted from this plot.



**Fig. 4. Applications of the  $\Delta_{30}$  tracer.** Using atmospheric  $\Delta_{30}$  values to constrain the global denitrification rate (A) [the dashed line in (A) represents the current atmospheric  $\Delta_{30}$  value] and the nitrogen sources of geologic  $N_2$  outgassing (B). Error bars are smaller than the size of the data points.

that are mixtures of atmospheric  $N_2$  and geologically outgassed  $N_2$  can be partitioned into contributions from atmospheric  $N_2$ , mantle nitrogen, and crustal nitrogen using  $\Delta_{30}$  values,  $\delta^{15}N$  values, and isotopic mass balance in  $N_2$  (Fig. 4B). For high-temperature geologic nitrogen sources,  $\Delta_{30}$  signatures are expected to be low because of combinatorial effects or isotope exchange equilibrium (for example,  $\Delta_{30} = 0.07\text{‰}$  at 1000 K), whereas  $\delta^{15}N$  values will reflect the source material [for example,  $+7\text{‰}$  versus air for sedimentary sources and  $-5\text{‰}$  for mantle sources (6, 34), although mantle  $\delta^{15}N$  values may be lower (35)]. The residence time of gases in hydrothermal systems (weeks or less) is short relative to time scales of isotopic equilibration in those environments (that is,  $T < 400^\circ\text{C}$  without engineered catalysts; see heating experiments in Materials and Methods); air is expected to retain its high  $\Delta_{30}$  value under such conditions. The  $\Delta_{30}$  value of  $N_2$  from fumaroles should therefore allow one to quantify the proportion of air in the sample, whereas the  $\delta^{15}N$  value can be used to partition the remaining nitrogen between mantle and recycled-sediment sources.

Fumarole gases collected at the summit crater of the Momotombo volcano (36), in the Nicaraguan volcanic front, show low  $\Delta_{30}$  values of 1.5 and 3.9‰. Gases drawn from fumaroles in Valles Caldera (New Mexico, USA) and Yellowstone Caldera (Wyoming, USA) show higher  $\Delta_{30}$  values (10.8 and 11.6‰, respectively), indicating a higher proportion of background air contribution. We find that 82 and 91% of the volcanic nitrogen in the Momotombo samples come from subducted sediment sources. The caldera samples, representing mantle hot spots or continental rifts with little influence from subducted sediments, contain primarily mantle-derived  $N_2$ : 11 and 3% of the non-atmospheric  $N_2$  come from sedimentary  $N_2$  at Valles Caldera and Yellowstone Caldera, respectively. Although noble gas-based source apportionment yields similar subducted sediment fractions for the Momotombo samples (86 and 94%, respectively), they disagree for the Yellowstone Caldera sample (3% sedimentary from  $\Delta_{30}$  values versus 19% from  $N_2/\text{He}$  ratios; table S5). Signatures of mantle and crustal outgassing are variable, and postsampling gas loss will affect gas species ratios much more so than isotopic ratios; hence, the combined  $\Delta_{30}$ - $\delta^{15}N$  approach is likely more robust for these questions. Applying the  $\Delta_{30}$  tracer to volcanic  $N_2$  outgassing may constrain the  $^{15}N$  isotopic composition of the primordial mantle, which has implications for planetary accretion, differentiation, and the development of the early atmosphere (37).

## MATERIALS AND METHODS

### Analytical methods

Natural and laboratory-generated samples of  $N_2$  were analyzed on an ultrahigh-resolution gas source mass spectrometer that separates  $^{14}N^{14}N$ ,  $^{14}N^{15}N$ , and  $^{15}N^{15}N$  from their main isobaric interferences (12). Spike-dilution experiments suggest that residual isobaric effects on  $N_2$  are minor, comparable to other analytical uncertainties. Measurements were calibrated to a thermodynamically based reference frame by equilibrating  $N_2$  gases at  $800^\circ\text{C}$  with strontium nitride (fig. S1) (38). Methodological accuracy was verified using the pinhole-diffusion and  $N_2$  re-equilibration experiments described below.

$N_2$  gas was analyzed at mass/charge ratio ( $m/z$ ) = 28, 29, and 30 ( $^{14}N^{14}N^+$ ,  $^{14}N^{15}N^+$ , and  $^{15}N^{15}N^+$ , respectively) on the Nu Instruments Panorama mass spectrometer (UCLA).  $^{14}N^{14}N^+$  and  $^{14}N^{15}N^+$  ions were collected on Faraday cups with intensities ranging from 15 to 480 pA for  $^{14}N^{14}N^+$ , with all natural samples but the volcanic samples run between 50 and 480 pA. Volcanic samples were run between 18 and 50 pA. A secondary electron multiplier was used for  $^{15}N^{15}N^+$ , with corresponding count rates ranging from  $1 \times 10^3$  to  $4 \times 10^4$  counts per second (cps), or 0.06 to 2.5 fA. Abundances of  $^{14}N^{14}N$ ,  $^{14}N^{15}N$ , and  $^{15}N^{15}N$  in atmospheric  $N_2$  are approximately 99.3%, 0.7%, and 14 parts per million, respectively. Typical mass resolving power (MRP) was near 50,000, calculated as the ratio of the ion mass and the mass difference between 95 and 5% of the peak height; for example,  $\text{MRP} = 30.00022 \text{ atomic mass unit (amu)}/0.0006 \text{ amu} = 50,000$ . Nearly baseline resolution is achieved between  $^{14}N^{16}O^+$  and  $^{15}N^{15}N^+$ , despite a mass difference of only 0.002 amu (fig. S2). Replicate  $\Delta_{30}$  measurements of air with  $^{14}N^{16}O^+$  ion currents ranging from  $10^4$  to  $10^5$  cps, afforded by having previously reduced the source surfaces with methane, were indistinguishable. The effect of the isobaric interference between  $^{12}C^{18}O^+$  and  $^{15}N^{15}N^+$  (mass difference, 0.001 amu) was evaluated using serial  $^{12}C^{18}O$  spike dilutions and found to be comparable to the uncertainty in the external reproducibility of the measurement (fig. S2).

Samples of  $N_2$  were purified using gas chromatography (GC) with methods described previously for methane (11). Briefly, a two-column setup at  $60^\circ\text{C}$  was used to separate  $N_2$  from other gases, first through a stainless steel molecular sieve 5A column [ $3 \text{ m} \times 1/8''$  outside diameter (OD)] followed by a stainless steel HaySep D column ( $2 \text{ m} \times 1/8''$  OD). This setup was interfaced with an all-stainless steel, oil-free high-vacuum line (base pressure  $\sim 10^{-6}$  mbar) through which samples were introduced

and recollected for analysis. Some air samples were purified on a separate, single-column GC system (30 to 60 cm  $\times$  1/8" OD molecular sieve 5A, 80/100 mesh) over a range of temperatures, interfaced with a glass vacuum line (19), with indistinguishable results.

### Calculations, instrument calibration, and testing

The bulk  $^{15}\text{N}/^{14}\text{N}$  ratio, in terms of  $^{14}\text{N}^{14}\text{N}$ ,  $^{14}\text{N}^{15}\text{N}$ , and  $^{15}\text{N}^{15}\text{N}$  abundances, is expressed as

$$^{15}R = \left( \frac{^{15}\text{N}}{^{14}\text{N}} \right) = \frac{^{14}\text{N}^{15}\text{N} + 2^{15}\text{N}^{15}\text{N}}{2^{14}\text{N}^{14}\text{N} + ^{14}\text{N}^{15}\text{N}} = \frac{^{29}R + 2^{30}R}{2 + ^{29}R} \quad (1)$$

Therefore, to obtain both a  $\delta^{15}\text{N} \equiv (^{15}R_{\text{sample}}/^{15}R_{\text{air}} - 1)$  value and a  $\Delta_{30}$  value, one must solve for  $^{15}R$  of the sample using  $^{29}R$  and  $^{30}R$ . Our method is one often used in clumped-isotope geochemistry, namely, to measure a  $\delta^{15}\text{N}$  standard (air;  $^{15}R_{\text{air}} = 0.003676$ ) and a  $\Delta_{30}$  standard ( $\text{N}_2$  isotopically equilibrated at 800°C; see fig. S1) against the same laboratory working standard gas and iterate  $^{29}R$  and  $^{30}R$  of that gas until its isotopic composition is found. Subsequent measurements are related to the  $\delta^{15}\text{N}$  and  $\Delta_{30}$  standards through this working gas.

We note in passing that Eq. 1 also shows how mixing between  $\text{N}_2$  reservoirs will alter  $^{15}R$  nonlinearly. Moreover, because  $\Delta_{30} \equiv ^{30}R/(^{15}R)^2 - 1$ ,  $\Delta_{30}$  values vary nonlinearly with mixing as well. A 50:50 mixture between components that both have  $\Delta_{30}$  values of zero, but with a 20‰ difference in  $\delta^{15}\text{N}$ , will have  $\Delta_{30} = +0.1\%$ . If the difference in  $\delta^{15}\text{N}$  of the two components is 40‰, then the gas will be characterized by  $\Delta_{30} = +0.4\%$ .

In order to reorder  $\text{N}_2$  toward high-temperature equilibrium, samples were expanded into either breakseals or valved quartz sample tubes containing strontium nitride ( $\text{Sr}_3\text{N}_2$ , a black powder; ESPI Metals and Materion) and heated in a horizontal tube furnace to 800°C for between 4 and 96 hours. Time-series experiments conducted at 400° and 800°C ( $\Delta_{30} = 0.21$  and  $0.07\%$  at equilibrium, respectively) showed a ninefold change in reordering rate (fig. S2), but we also found that this rate depended on the age of the solid catalyst; it decomposes slowly over time due to reaction with water to make ammonia. The condition of the catalyst and the relative proportions of catalyst to  $\text{N}_2$  gas allowed some variation of  $\delta^{15}\text{N}$  values of the equilibrated gas (table S1). We also reordered  $\text{N}_2$  from a 21-mbar electrolysis experiment ( $\Delta_{30} = -2\%$ ) to  $\Delta_{30} = 0.0 \pm 0.1\%$  on strontium nitride at 800°C. This experiment, combined with the time series described above, indicates that heating  $\text{N}_2$  over strontium nitride yields  $\text{N}_2$  with a nearly random distribution of isotopes.

In general, the catalyst is crucial to the isotopic reordering of  $\text{N}_2$ . An experiment using titanium nitride instead of strontium nitride as the  $\text{N}_2$ -reordering catalyst showed significantly slower reordering ( $\Delta_{30} = 19 \rightarrow 7\%$  in 7 days at 900° to 1000°C) with no change in  $\delta^{15}\text{N}$ . The experiment suggests that the  $\text{N}_2$  isotopes are not equilibrating on the quartz.

To verify instrumental accuracy with pure  $\text{N}_2$  samples, we performed pinhole-diffusion experiments using the same apparatus as that described previously for  $\text{O}_2$  (19). Briefly, 1 mbar of  $\text{N}_2$  in a 5-liter bulb was allowed to diffuse through a  $75 \pm 7.5 \mu\text{m}$  critical orifice, which was comparable to the mean free path of  $\text{N}_2$  at that pressure ( $\sim 95 \mu\text{m}$ ). The amount of undiffused gas remaining was determined manometrically, and both the diffused gas and the residue gas were analyzed to determine the difference in their  $\delta^{29}\text{N}_2$  and  $\delta^{30}\text{N}_2$  values.

Measured values were in agreement with those predicted for Rayleigh fractionation of gases separated according to Graham's law of effusion within typical analytical uncertainty ranges (that is,  $\pm 0.2\%$  in  $\delta^{30}\text{N}_2$ ) when a correction for back diffusion/viscous flow was included (table S6). The correction in which the effective fractionation factor  $\alpha_{\text{effective}}$  is related to Graham's law fractionation factor  $\alpha_{\text{effusion}}$  by  $(\alpha_{\text{effective}} - 1) = (\alpha_{\text{effusion}} - 1)(1 - P_{\text{ds}}/P_{\text{us}})$  has been described previously; the  $P_{\text{ds}}/P_{\text{us}}$  factor here is similar in magnitude to that found previously on the same apparatus for  $\text{O}_2$  diffusion (19). The consistency between theory and measurements for these experiments suggests that isotopic reordering on the tungsten filament in the mass spectrometer does not exceed analytical uncertainties over a range of  $\sim 40\%$  in  $\delta^{30}\text{N}_2$ .

Other potential impurities in natural samples included  $\text{O}_2$  and methane. We performed analyses of air- $\text{N}_2$  that included up to 14%  $\text{O}_2$  and found that  $\Delta_{30}$  values increase 0.5‰ at 3 to 4%  $\text{O}_2$  and 1.8‰ at 14%  $\text{O}_2$ , accompanied by 0.2 and 0.5‰ decreases in  $\delta^{15}\text{N}$  values, respectively. We estimate typical  $\text{O}_2$  content to be  $\ll 1\%$  after GC purification. In the volcanic  $\text{N}_2$  samples, small amounts of methane ( $< 10\%$ ) were identifiable and collected in the tail of the  $\text{N}_2$  peak. To examine the effect that this methane impurity may have on the  $\text{N}_2$  isotopologue ratios, we made a 10% methane/ $\text{N}_2$  mixture of similar sample size and purified it. We did not observe any difference in  $\Delta_{30}$  value from the methane-free tank gas.

Finally, we tested for potential analytical artifacts due to variations in  $\text{N}_2$  sample size. Air- $\text{N}_2$  samples ranging from 5 to 160  $\mu\text{mol}$  in size were prepared and analyzed over a range of ion currents. Bulk isotope composition exhibited larger variability at small sample sizes, about  $\pm 0.2\%$  in  $\delta^{15}\text{N}$  versus  $\pm 0.05\%$  for larger samples. The  $\Delta_{30}$  values were indistinguishable up to  $\sim 250$  pA on  $m/z = 28$  (smaller samples had larger analytical uncertainty because of counting statistics). Above 250-pA ion currents, the  $\Delta_{30}$  values for air- $\text{N}_2$  decreased by as much as  $\sim 0.4\%$  when the ion current was 400 pA on  $m/z = 28$ . The origin of this effect is enigmatic: No dependence on ion current intensity was observed for heated gases, and ion-counting rates ( $10^4$  cps) were lower than typical rates that one expects would require dead-time corrections. A possible explanation for this effect is isotope exchange between  $\text{NO}$  and  $\text{N}_2$  in the ion source, similar to the exchange reaction observed for  $\text{N}_2\text{O}$  (39). Whatever the source of this ion-intensity effect, it was only relevant for  $\text{N}_2$  dissolved in seawater (the largest samples), and the effects are small. We therefore report  $\Delta_{30}$  values for those samples before and after correcting for this ion-intensity effect based on the air- $\text{N}_2$  measured at similar ion currents (table S1). On the basis of the comprehensive analytical tests above, we estimate an overall accuracy of  $\pm 0.3\%$  in  $\Delta_{30}$  values.

### Natural samples

Sampling procedures for UCLA air and the stratospheric sample have been described previously (14, 19). The stratospheric sample was #3-A01-R(1141) from a scientific balloon flight in 2004 (Fort Sumner, New Mexico; 32.3 km) that has also been characterized for a variety of other trace gases and isotope ratios (14, 19, 40, 41). The stratospheric air samples were purified at UCLA. Seawater samples were collected from the San Pedro Ocean Time-series site (33°33'N, 118°24'W), a coastal site near Los Angeles, on 12 April 2017. They were siphoned from 10-liter Niskin flasks into prepoisoned, pre-evacuated ( $< 10^{-3}$  mbar) bottles according to established methods (42). The bottles were allowed to degas and equilibrate on an orbital shaker (110 rpm) for 48 hours before the water was removed, and the headspace gas was collected onto silica gel for purification. Dissolved  $\text{N}_2$  was separated

from the other gases at Rice University on a molecular sieve 5A column (3.05 m × 1/8" OD, 80/100 mesh) at  $-80^{\circ}\text{C}$  and recollected on a silica gel U-trap using a method described previously (41). We also isolated atmospheric  $\text{N}_2$  using this method, and the results were indistinguishable from gases collected and purified at UCLA.

## Biological culturing conditions and experiments

### Denitrifying bacteria

*P. stutzeri* and *P. denitrificans* were cryogenically stored ( $-80^{\circ}\text{C}$ ) in tryptic soy broth (TSB; Caisson Labs) and sterile glycerol 1:1 (v/v). Stock cultures were reestablished in 5 ml of TSB amended with sodium nitrate ( $\text{NaNO}_3$ , 10 mM; Sigma-Aldrich) under aerobic conditions at a constant temperature with continuous agitation (18 hours). Denitrifier cultures were grown at  $30^{\circ}\text{C}$ . Individual colonies were obtained from reestablished stock cultures by the streak-plate technique on tryptic soy agar (Caisson Labs) amended with  $\text{NaNO}_3$  (10 mM). Streak-plate cultures were sealed with parafilm and incubated (aerobic,  $30^{\circ}\text{C}$ ). The plates were stored at  $4^{\circ}\text{C}$  for up to 2 weeks before establishment in liquid medium for experiments.

The two species were established with one colony from stored stock culture plates in 5 ml of TSB amended with  $\text{NaNO}_3$  (10 mM) in a 20-ml culture tube (Thermo Fisher Scientific). Cultures were grown aerobically with agitation ( $30^{\circ}\text{C}$  for 18 hours) to late exponential phase (optical density at 600 nm = 2.0). Culture turbidity was determined with a Spectronic 20 spectrophotometer (Bausch and Lomb). Two 160-ml sterile serum bottles containing 50 ml of carbon minimal medium (CMM; 10 mM  $\text{NaNO}_3$  and 10 mM sodium succinate; Sigma-Aldrich) (43) were each inoculated with 200  $\mu\text{l}$  of the aerobic culture. The bottles were stoppered (Geomicrobial Technologies Inc.) and crimp-sealed, and the headspace was sparged with ultrahigh purity (UHP) helium for 20 min. Cultures were incubated ( $30^{\circ}\text{C}$  for 18 hours) with agitation. The cells were transferred to 50-ml conical Falcon tubes (Corning) and centrifuged (3000g for 30 min). The cell pellet was washed in CMM lacking carbon and nitrogen and centrifuged (3000g for 30 min). The supernatant was decanted, and the cells were dispersed in CMM lacking a carbon or nitrogen source (optical density at 600 nm = 0.2). The cells were aliquoted (9.6 ml) into sterile flasks outfitted with a vacuum "sidearm" valve (160 ml), and a carbon source was added (30 mM sodium succinate). The flask was stoppered (Geomicrobial Technologies Inc.) and crimp-sealed, and the sidearm closure was sealed. An anaerobic environment was created by sparging the cells (UHP He, 60 min). Sparging was accomplished by inserting one sterile stainless steel needle (#20, Thomas Scientific) carrying He gas through the stopper into the medium while a second sterile stainless steel needle was inserted through the stopper and into the headspace to allow gas to exit. Following sparging, the flasks were allowed to reach atmospheric pressure and then the reactions were initiated by injecting the nitrogen source (30 mM USGS34 potassium nitrate) with a gas-tight syringe. Individual reactions were stopped by injecting 10 M sodium hydroxide (400  $\mu\text{l}$ ).

### Nitrogen-fixing cyanobacteria

*A. variabilis* [American Type Culture Collection (ATCC) 29413] was cultivated in BG-11 medium (44) from lyophilized samples as per ATCC instructions. Cultures were maintained by streaking onto BG-11 agar under a 12-hour light/12-hour dark regime at  $25^{\circ}\text{C}$ .

Cyanobacterial cultures were started from streak plates of *A. variabilis* by adding culture to 10 ml of BG-11 medium and incubating aerobically ( $22^{\circ}\text{C}$ , 12-hour light/12-hour dark regime). Cultures were transferred to larger vessels twice in 1:10 dilutions to reach a final culture volume of 250 ml. Transfers were conducted only when cultures reached a

chlorophyll-a density of greater than 1  $\mu\text{g}/\text{ml}$  (45). The cells were centrifuged (4000g for 15 min) and washed 1 $\times$  in 50 ml of BG-11 medium without nitrogen (BG-11<sub>0</sub>). The cells were resuspended in 250 ml of BG-11<sub>0</sub> medium, which had been allowed to equilibrate with laboratory air for 1 day with gentle stirring. Contamination of outside agents was prevented by fitting a sterile cotton plug to the flask opening and covering this with sterile tin foil. Laboratory equilibration of the medium served to ensure that atmospheric  $\text{N}_2$  was the only source of nitrogen in the medium. The culture was then transferred to a sterile "Emerson" flask with a sterile gravity syphon. The Emerson flask (200 ml) was filled beyond the neck and then sealed shut to remove any headspace. Before stoppering the flask, the seal was sterilized with 70% ethanol and rinsed with Milli-Q water. Nitrogen fixation reactions were considered to have begun once the Emerson bottle was stoppered. Reactions were conducted in an environmental chamber ( $22^{\circ}\text{C}$ , 12-hour light/12-hour dark regime), and the flasks were turned over once a day to provide gentle agitation. After between 2 and 7 days, the dissolved  $\text{N}_2$  was transferred by equilibration following established protocols (42). After allowing the culture to settle to the bottom of the bottle, 150 ml of culture medium was transferred to an evacuated Emerson bottle (300 ml) with a sterile syphon. The transferred medium was allowed to equilibrate for at least 6 hours before isolation.

### Isolation and trapping of $\text{N}_2$ for analysis

Quantitative distillation of  $\text{N}_2$  from samples was achieved under high vacuum (4.5  $\mu\text{mHg}$ ). A metering valve and two stainless steel liquid  $\text{N}_2$  cryogenic traps (OD = 6.35 mm) preceded the sample bottle. The first cryogenic trap condensed and separated water from gases, whereas the second trap was filled with coarsely crushed silica to trap all remaining gases (15 min). Isolated  $\text{N}_2$  was cryogenically transferred to a 30-cm Pyrex tube (OD = 6.35 mm) containing 50 mm of crushed silica gel for 15 min. To accomplish this, the second cryogenic trap was isolated from the first cryogenic trap and the vacuum line was evacuated. The system was then isolated from the vacuum system and the isolated gases were desorbed from the silica by heating with warm tap water. Pyrex sample tubes were sealed with an acetylene torch while still under cryogen conditions. All silica gel traps were conditioned under high vacuum at  $200^{\circ}\text{C}$  (24 to 48 hours) before sampling.

The specific method for isolation of  $\text{N}_2$  from sidearm flasks for denitrification experiments differed slightly from the previous method. Sidearm bottles were attached to the vacuum line with ultra-torr Cajon fittings. The sidearm bottle was opened to the vacuum line while the metering valve remained closed. The metering valve was then slowly opened to maintain a vacuum (50 to 70  $\mu\text{mHg}$ ) while the sample passed through the cryogenic traps, until high vacuum was again achieved (35 to 40 min). The cryogenically isolated gases were then desorbed from the silica as previously described.

### Analytical correction for air contamination

During the *P. denitrificans* experiments, a procedural blank was performed, which revealed a small residual gas pressure equal to 1 to 5% of the experimental  $\text{N}_2$  gas yield, depending on reaction progress. This blank (0.8  $\mu\text{mol}$ ) was presumed to be entirely  $\text{N}_2$  with atmospheric isotopic composition. The reported isotopic composition for both the *P. denitrificans* and the *P. stutzeri* experiments includes a correction for this blank. We cannot rule out a difference in blank amount between the two experiments. However, the more fully reacted experiments had larger  $\text{N}_2$  gas yields and therefore a smaller contamination from this blank; thus, their  $\Delta_{30}$  values are more likely to reflect those intrinsic to bacterial denitrification.

### Samples of opportunity from anammox bioreactors

Water from a semi-batch-fed anammox bioreactor at the University of Utah (17) was sampled into 60-ml septa vials (bubble-free, until they overflowed, ensuring no gas headspace) and poisoned with 600  $\mu$ l of saturated ZnCl<sub>2</sub> solution. Samples were shipped back to Michigan State University for isolation of the dissolved gases.

### Electrolysis experiments and modeling

#### Laboratory electrolysis

Electrolysis experiments were performed in a valved-off Bayart-Alpert ion gauge with one lead (the ion collector) attached to the Oudin coil and the others grounded (fig. S3). The chamber was preconditioned initially by applying a voltage to the electrical lead under vacuum for  $\geq 1$  hour to degas the filament and then applying a voltage under N<sub>2</sub> atmosphere for  $\geq 1$  hour to replace the adsorbed species with nitrogen. In the experiments, voltage was applied to the electrical lead until continuous visible emission was observed in N<sub>2</sub> or an O<sub>2</sub>/N<sub>2</sub> mixture. The same analog setting (that is, rotating dial position at the base of the coil) was used for all samples. The reaction was allowed to proceed for 1 hour.

The emission field changed color and expanded as pressure was varied (fig. S3). The colors and patterns were similar for both N<sub>2</sub> only and O<sub>2</sub>/N<sub>2</sub> mixtures. These changes suggest that local electron and ion concentrations and electron energies also varied with pressure. Consequently, we expect that ion production rates, energy-dependent product branching ratios, wall reaction rates, and the rates of reactions dependent on these quantities likely varied with total pressure as well. Because of the potential variability in reaction rates expected in the experiments, our kinetic model was aimed at determining the most important N–N bond-altering mechanisms in the gas phase rather than explaining the laboratory results quantitatively.

#### Model of electrolysis experiments

The model contained 41 reactions for the O<sub>2</sub>–N<sub>2</sub> system, including charge transfer reactions (table S4). It was run at 298 K for 1 hour of simulated time using the program Kintecus (29). Electron temperatures were held constant at 10,000 K. Only positive ion chemistry was included except for electron impact and recombination processes. Electronic states were not specified; ground electronic states and thermal vibrational states for all reactions and products were assumed unless otherwise noted. Surface chemistry was not explicitly included. Electron impact ionization was only included for N<sub>2</sub> and O<sub>2</sub>, with prescribed (but adjustable) branching ratios between ionization and fragmentation channels (typically 3:1). A more explicit description would render the number of variables unmanageable for this conceptual model. In a similar vein, electron densities were prescribed and held constant within each simulation as a way to specify the total rate of electron impact processes.

Gross rates of N–N bond-altering processes were tracked by including “dummy” products in those reactions that did not affect other variables such as temperature or pressure. Rates of electron impact ionization and dissociation were varied over a large range, but rates of at least 10<sup>13</sup> to 10<sup>14</sup> cm<sup>3</sup> s<sup>−1</sup> were required for the fastest N–N bond-altering processes to reorder an amount of N<sub>2</sub> equal to the experiment’s inventory between 1 and 10 mbar (2.5 × 10<sup>16</sup> to 2.5 × 10<sup>17</sup> cm<sup>−3</sup>). For the N<sub>2</sub>-only experiments, only electron impact and the termolecular N + N + M → N<sub>2</sub> + M reaction would be relevant to the destruction and formation of N<sub>2</sub> unless some other trace oxygenated constituent were present (for example, NO). We note that tungsten surfaces can catalyze isotope exchange between N<sub>2</sub> molecules

(28); at low pressures, therefore, these reactions likely influenced  $\Delta_{30}$  values resulting from electrolysis, driving them down toward isotopic equilibrium values in competition with gas-phase isotopic fractionation.

Sample results for three different electron number densities are shown in fig. S4. In all cases, electron impact fragmentation of N<sub>2</sub> is the only important N<sub>2</sub> bond-breaking mechanism by an order of magnitude except at low pressures. At low pressures, N<sub>2</sub><sup>+</sup> + O becomes comparable in rate. The importance of this channel decreases at higher pressures. Of the bond-making reactions, N + NO is the most important by at least a factor of 100 in all cases.

#### Determining the atmospheric N<sub>2</sub> recycling time scale

Globally integrated rates of N<sub>2</sub> bond-altering processes in moles per year were calculated from monthly-averaged outputs of the WACCM-X model (30) for model year 2001 (1.9° latitude × 2.5° longitude grid). The data were outputs of present-day control runs of the Community Earth System Model version 1.0 (data set f.e10.FWX.f19\_f19.control.001) available from the Earth System Grid (www.earthsystemgrid.org). Globally integrated species concentrations and reaction rates were calculated using methods similar to those previously described (41). Briefly, reaction rates were calculated at each grid point using monthly-averaged species mixing ratios, temperatures, and pressures. Because N<sub>2</sub> is not an explicit field in this version of the model, its concentrations were calculated by subtracting the number densities of O and O<sub>2</sub> from the total number density. Reaction rates were then integrated over grid volumes covering all 81 atmospheric levels using the latitude, longitude, and mean geopotential height of each grid point as the vertical coordinate. Accuracy checks on this integration scheme included reproducing the total atmospheric N<sub>2</sub> inventory (1.40 × 10<sup>20</sup> mol N<sub>2</sub> modeled versus 1.4 × 10<sup>20</sup> mol N<sub>2</sub> expected) and total atmospheric volume (2.74 × 10<sup>14</sup> km<sup>3</sup> modeled versus 2.76 × 10<sup>14</sup> km<sup>3</sup> using a 500-km exobase). Weighting for residence time in different regions of the atmosphere was not included because the time scale for whole-atmospheric mixing [ $\ll 10^6$  years based on cross-homopause and intrathermosphere diffusion coefficients of  $>10^{-5}$  km<sup>2</sup> s<sup>−1</sup> (46)] should be much faster than the time scale found for atmospheric N<sub>2</sub> bond recycling (10<sup>7</sup> years). The time scale for atmospheric N<sub>2</sub> recycling in years is defined as the total N<sub>2</sub> inventory divided by the globally integrated rate of N–N recombination assuming a steady state between N<sub>2</sub> destruction and recombination.

#### Mass balance of volcanic N<sub>2</sub>

Mixing fractions of air N<sub>2</sub>, recycled-sediment N<sub>2</sub>, and mantle N<sub>2</sub> in volcanic N<sub>2</sub> samples (that is,  $f_{\text{air}}$ ,  $f_{\text{RS}}$ , and  $f_{\text{mantle}}$ , respectively) are calculated from N<sub>2</sub>/He ratios and  $\delta^{15}\text{N}$  values using the end-member compositions shown in table S5 and the mass balance equations (36)

$$\begin{aligned} (\text{N}_2/\text{He})_{\text{sample}}^{-1} = & f_{\text{air}}/(\text{N}_2/\text{He})_{\text{air}} + f_{\text{RS}}/(\text{N}_2/\text{He})_{\text{RS}} \\ & + f_{\text{mantle}}/(\text{N}_2/\text{He})_{\text{mantle}} \end{aligned} \quad (2)$$

$$\delta^{15}\text{N}_{\text{sample}} = f_{\text{air}}\delta^{15}\text{N}_{\text{air}} + f_{\text{RS}}\delta^{15}\text{N}_{\text{RS}} + f_{\text{mantle}}\delta^{15}\text{N}_{\text{mantle}} \quad (3)$$

$$f_{\text{air}} + f_{\text{RS}} + f_{\text{mantle}} = 1 \quad (4)$$



Alternatively, they are calculated using Eqs. 4 to 6 and  $\delta^{15}\text{N}$  and  $\Delta_{30}$  values for each end-member (converted to  $^{29}\text{R}$  and  $^{30}\text{R}$  using Eq. 1)

$$^{29}\text{R}_{\text{sample}} = f_{\text{air}} ^{29}\text{R}_{\text{air}} + f_{\text{RS}} ^{29}\text{R}_{\text{RS}} + f_{\text{mantle}} ^{29}\text{R}_{\text{mantle}} \quad (5)$$

$$^{30}\text{R}_{\text{sample}} = f_{\text{air}} ^{30}\text{R}_{\text{air}} + f_{\text{RS}} ^{30}\text{R}_{\text{RS}} + f_{\text{mantle}} ^{30}\text{R}_{\text{mantle}} \quad (6)$$

In both methods, only  $f_{\text{air}}$ ,  $f_{\text{RS}}$ , and  $f_{\text{mantle}}$  are unknown, and they can be computed using a set of three equations.

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/11/eaao6741/DC1>

### Supplementary Text

fig. S1. Theoretical  $\Delta_{30}$  values at isotopic equilibrium ( $\Delta_{30,\text{equil}}$ ) as a function of temperature, from Wang *et al.* (7).

fig. S2. Analytical tests of  $\Delta_{30}$  accuracy.

fig. S3. Changes in visible emission properties during electrolysis experiments.

fig. S4. Modeled gross rates of bond-breaking (black symbols) and bond-making (red symbols) reactions in the electrolysis experiments.

table S1. Isotopic data for air samples and heated gases.

table S2. Isotopic data for biological experiments.

table S3. Data for electrolysis experiments.

table S4. Reactions used in the model of the electrolysis experiments.

table S5. Data for volcanic  $\text{N}_2$  samples and end members used to derive mixing fractions  $f_{\text{RS}}$  and  $f_{\text{mantle}}$ .

table S6. Results from diffusion experiment for verifying instrumental accuracy.

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