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# The Evolution and Future of Earth's Nitrogen Cycle

Donald E. Canfield,<sup>1\*</sup> Alexander N. Glazer,<sup>2</sup> Paul G. Falkowski<sup>3</sup>

Atmospheric reactions and slow geological processes controlled Earth's earliest nitrogen cycle, and by ~2.7 billion years ago, a linked suite of microbial processes evolved to form the modern nitrogen cycle with robust natural feedbacks and controls. Over the past century, however, the development of new agricultural practices to satisfy a growing global demand for food has drastically disrupted the nitrogen cycle. This has led to extensive eutrophication of fresh waters and coastal zones as well as increased inventories of the potent greenhouse gas nitrous oxide (N<sub>2</sub>O). Microbial processes will ultimately restore balance to the nitrogen cycle, but the damage done by humans to the nitrogen economy of the planet will persist for decades, possibly centuries, if active intervention and careful management strategies are not initiated.

Nitrogen, the fifth most abundant element in our solar system, is essential for the synthesis of nucleic acids and proteins—the two most important polymers of life. Indeed, the nitrogen requirements for life are enormous; depending on the life form, for every 100 atoms of carbon incorporated into cells, between 2 and 20 atoms of nitrogen follow (1). The biogeochemistry of nitrogen is almost entirely dependent on reduction-oxidation (redox) reactions primarily mediated by microorganisms (2), and to a lesser extent on long-term recycling through the geosphere [e.g., (3)]. Despite the importance of nitrogen and its overwhelming abundance in the atmosphere, N<sub>2</sub> is virtually inert; hence, fixed inorganic nitrogen [most commonly nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) ions] often limits primary productivity in both marine and terrestrial ecosystems (2, 4, 5). Here, we review the nitrogen cycle on Earth, its evolutionary history, its interactions and feedbacks with other key elements, and the disruption of the cycle by humans over the past century.

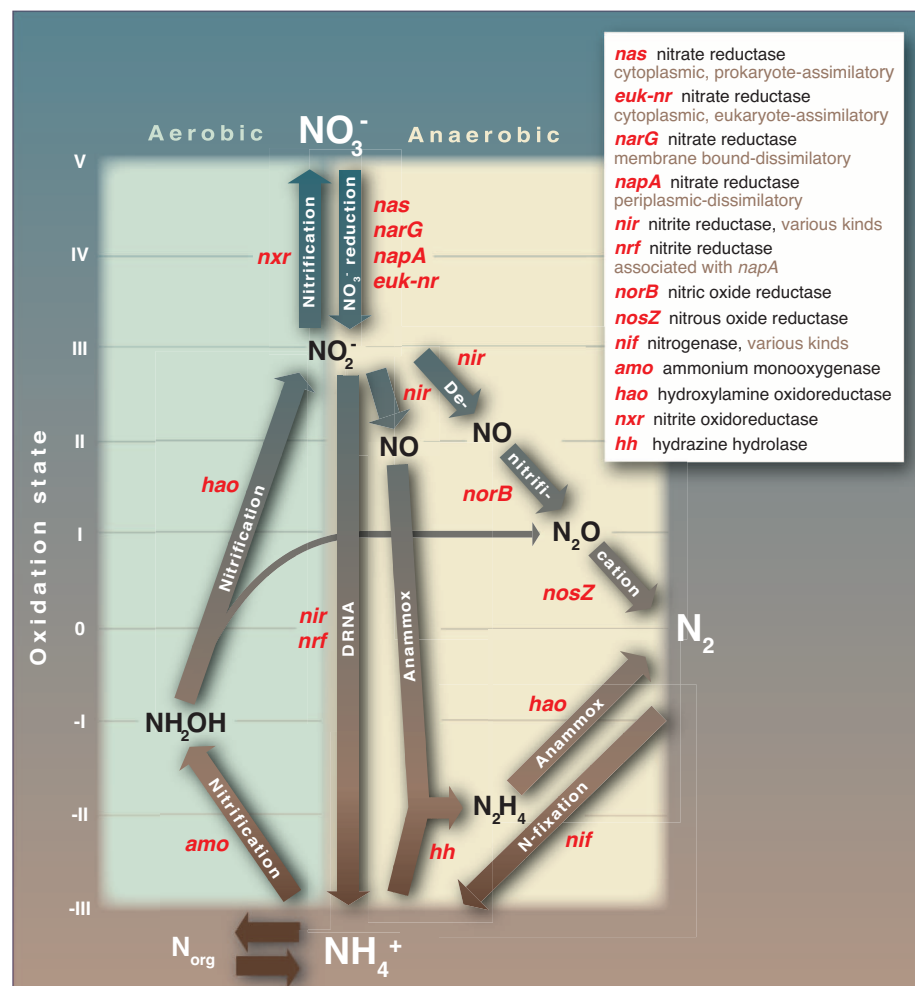
## What Is the Metabolic Basis of the Modern Nitrogen Cycle?

An active biosphere ultimately requires incorporation of nitrogen into biological molecules through nitrogen fixation, a process where prokaryotes in the bacterial and archaeal domains reduce nitrogen gas (N<sub>2</sub>) to ammonium (Fig. 1). Some eukaryotes (e.g., legumes and termites) also support nitrogen fixation, but only in symbiotic association with nitrogen-fixing prokaryotes. Although the reduction of N<sub>2</sub> is an exergonic reaction, the activation energy required to break its N≡N bond is formidable, and the reaction

requires a catalyst to overcome the energy barrier. The heterodimeric enzyme complex, nitrogenase, serves this role by hydrolyzing ~16 adenosine

triphosphate (ATP) molecules per molecule of N<sub>2</sub> fixed. Nitrogenase is an α<sub>2</sub>β<sub>2</sub> tetramer, in which each of the two α subunits catalyzes the ATP-dependent reduction of N<sub>2</sub> to NH<sub>3</sub>. In its most common form, each α subunit contains a MoFe<sub>7</sub>S<sub>9</sub> metal cluster (the MoFe cofactor) that donates electrons to N<sub>2</sub> (6), with the electrons coming from the respiration of organic carbon. The genes encoding the two nitrogenase subunits are highly conserved but are widely dispersed across many phyla of bacteria and archaea, which suggests that nitrogen fixation evolved once and subsequently spread by vertical inheritance and by horizontal gene transfer (5, 7–9, 41).

Although nitrogenase is widely distributed among prokaryotic lineages, most organisms cannot fix nitrogen but rather obtain their nitrogen directly as NH<sub>4</sub><sup>+</sup> (or organic nitrogen) from the environment, or from the reduction of NO<sub>3</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup> through assimilatory nitrate reduction. Both prokaryotes and eukaryotes are able to mediate



**Fig. 1.** The major biological nitrogen transformation pathways are linked by their associated enzymes [adapted from (63)]. Genes encoding enzymes that conduct the important transformations include those for various nitrate reductases (*nas*, *euk-nr*, *narG*, *napA*), nitrite reductases (*nir*, *nrf*), nitric oxide reductase (*norB*), nitrous oxide reductase (*nosZ*), nitrogenase (*nif*), ammonium monooxygenase (*amo*), hydroxylamine oxidoreductase (*hao*), nitrite oxidoreductase (*nxr*), and hydrazine hydrolase (*hh*).

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this process. Ammonium is returned to the environment when organisms die, and its fate (and the variety of subsequent forms of nitrogen) depends on whether the local environment contains oxygen (Fig. 1). In the presence of oxygen,  $\text{NH}_4^+$  is sequentially oxidized to  $\text{NO}_3^-$  by specific groups of bacteria and archaea. In this pathway, known as nitrification, organisms containing the enzyme ammonium monooxygenase first oxidize  $\text{NH}_4^+$  to hydroxylamine, which is subsequently oxidized to  $\text{NO}_2^-$  by hydroxylamine oxidoreductase, and finally the  $\text{NO}_2^-$  is oxidized to  $\text{NO}_3^-$  by nitrite oxidoreductase (Fig. 1). The electrons and protons derived during ammonium and nitrite oxidation are used by the microbes to fix inorganic carbon in the absence of light (i.e., chemoautotrophy) (10). The greenhouse gas  $\text{N}_2\text{O}$  is a by-product in this process; indeed, nitrification from both marine and terrestrial environments is an important source of atmospheric  $\text{N}_2\text{O}$  (11, 12).

In the absence of oxygen,  $\text{NO}_3^-$  can be used by many microbes as a respiratory electron acceptor. Nitrate reduction is coupled to the anaerobic oxidation of organic carbon (Fig. 1), producing either  $\text{NH}_4^+$  in a process known as dissimilatory nitrate reduction to ammonium (DNRA) or, more commonly,  $\text{N}_2$  gas during denitrification (Fig. 1). Denitrifiers include representatives of more than 60 genera of Bacteria and Archaea, as well as some eukaryotes (e.g., fungi, protozoa, and benthic Foraminifera and Gromiida) (13, 14). The process involves four metalloenzymes: dissimilatory nitrate reductase, nitrite reductase, nitric oxide reductase, and nitrous oxide reductases.  $\text{N}_2\text{O}$  is an obligate intermediate (Fig. 1), and some ultimately escapes to the atmosphere, making denitrification another important source of this greenhouse gas from both marine and terrestrial environments (15–17).

An alternative route from fixed nitrogen to  $\text{N}_2$  is found among a group of bacteria known as a planctomycetes, where  $\text{NH}_4^+$  oxidation is coupled to  $\text{NO}_2^-$  reduction in a process called anammox (anaerobic ammonium oxidation), an exergonic reaction used for chemoautotrophic growth (18). This process dominates  $\text{N}_2$  production in many marine environments, but, unlike classical denitrification, it does not lead to the production of  $\text{N}_2\text{O}$  (18). Together, denitrification and anammox close the nitrogen cycle by returning  $\text{N}_2$  gas back to the atmosphere (Fig. 1).

### What Controlled Earth's Earliest Nitrogen Cycle?

The form(s) of nitrogen delivered during planetary accretion, the rate of accretion, and the secondary atmosphere arising from volcanism controlled the prebiotic nitrogen cycle. Planetary accretion models generally assume that nitrogen was delivered to the protoplanet as solid (ice)  $\text{NH}_3$ , amino acids, and other simple organics. These reduced forms of nitrogen subsequently became oxidized via high-temperature reactions in the upper mantle with iron and other transition elements to form atmospheric  $\text{N}_2$ , which outgassed from

volcanoes (19). Indeed, a sizable (but poorly constrained) proportion of the nitrogen on Earth is still associated with the mantle (Fig. 2). These abiotic processes are extremely slow, yielding an estimated turnover time for the nitrogen cycle of about 1 billion years (3).

Current models suggest that in the early Earth atmosphere, heat shock associated both with lightning (20, 21) and high-energy meteorite impacts (22) produced  $\text{NO}$ , which would have converted to  $\text{NO}_3^-$  and  $\text{NO}_2^-$  through a series of subsequent photochemical and aqueous phase reactions (23, 24). The conversion of  $\text{N}_2$  to  $\text{NH}_3$  by these processes was probably extremely slow, with estimates ranging from  $\sim 2 \times 10^8 \text{ mol N year}^{-1}$  (assuming a low  $\text{CO}_2$  atmosphere) to  $\sim 2 \times 10^{10} \text{ mol N year}^{-1}$  (assuming a high- $\text{CO}_2$  atmosphere)

probably the most important (31). However, as a result of the limited  $\text{H}_2$  supply and its escape to space, primary productivity was lower than contemporary rates by a factor of 1000 or more (Fig. 3) (31). Even so, heat shock processes may have kept pace with the demands of the emerging biosphere, especially if microorganisms evolved an early means (i.e., assimilatory nitrate reduction) to reduce any environmental  $\text{NO}_3^-$  to  $\text{NH}_4^+$  within the cell.

Early in biological evolution, anoxygenic photosynthetic organisms evolved and harnessed the Sun's energy to oxidize substrates such as  $\text{H}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{Fe}^{2+}$  (but apparently not  $\text{NH}_4^+$ ) and to use the reducing equivalents for carbon fixation. If fixed inorganic nitrogen was not limiting in the earliest prephotosynthetic biosphere, it almost cer-

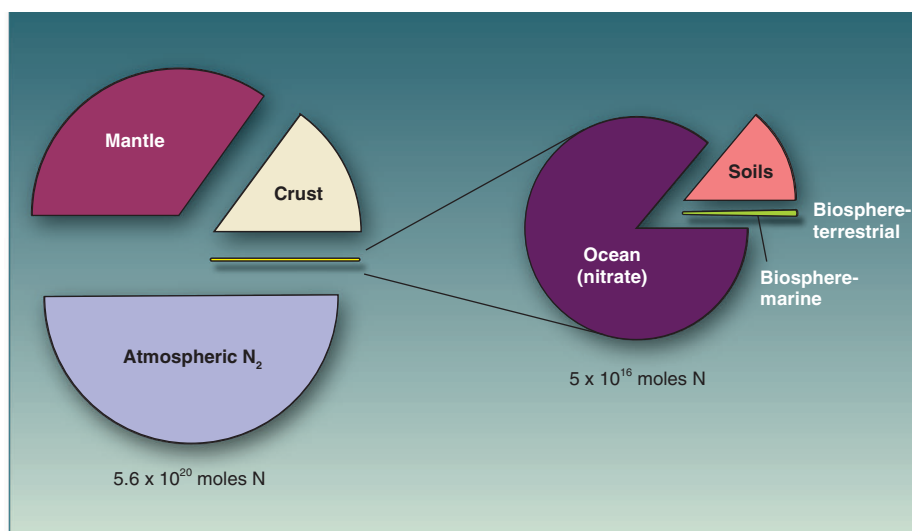


Fig. 2. The size of nitrogen reservoirs on Earth is highly variable. (44, 64–67).

(24). These estimates are lower than modern rates of biological nitrogen fixation in the oceans by a factor of 50 to 5000 (25). In principle,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{N}_2$  can be abiotically reduced to  $\text{NH}_4^+$  at high temperatures through interactions with metallic Fe, magnetite, or iron sulfide minerals (26, 27); however, no appreciable flux of  $\text{NH}_4^+$  is apparent in modern hydrothermal vent systems where such reactions should occur. Nitrite is also readily reduced to  $\text{NH}_4^+$  by  $\text{Fe}^{2+}$  at  $\text{pH} > 7.3$  (28), which may have been of particular importance on the early Earth when the oceans were likely rich in  $\text{Fe}^{2+}$  (29). Because ultraviolet oxidation of atmospheric  $\text{NH}_3$  (in equilibrium with  $\text{NH}_4^+$  in the oceans) would have formed  $\text{N}_2$  (30),  $\text{N}_2$  gas remained the dominant form of nitrogen in the atmosphere (Fig. 3). Ammonium and possibly some  $\text{NO}_3^-$  dominated ocean chemistry, whereas  $\text{NO}_2^-$  would have been a minor phase (Fig. 3).

### How Did the First Organisms Influence the Nitrogen Cycle?

The earliest organisms on Earth likely gained energy from chemically reduced compounds delivered from Earth's interior, of which  $\text{H}_2$  was

tainly became limiting after the evolution of anoxygenic photosynthesis. Estimates suggest that anoxygenic phototrophs increased the flux of nutrients and carbon through the biosphere by a factor of up to 100 (31) (Fig. 3), with the oxidation of  $\text{Fe}^{2+}$  yielding potentially the highest rates of primary production. Nitrogen limitation would have provided strong selection pressure for the evolution of biological  $\text{N}_2$  fixation to allow anoxygenic phototrophs to fully make use of the reducing substrates available to them in the environment. Indeed, the ability to fix  $\text{N}_2$  evolved early in biological evolution (8), possibly in anaerobic photoautotrophs, all of which are in the domain *Bacteria*.

With anoxygenic photosynthesis, chemical stratification would have developed for the first time in the global ocean. Ammonium would have accumulated deep in the oceans, and intense productivity at the base of photic zone (analogous to the deep chlorophyll maximum in the modern oceans) would have removed both  $\text{NH}_4^+$  and  $\text{Fe}^{2+}$ . Because primary production would have been limited by  $\text{Fe}^{2+}$  availability, a  $\text{NH}_4^+/\text{Fe}^{2+}$  ratio of 2/3 in the deep waters would have been expected

from the stoichiometry of anoxygenic photosynthesis with  $\text{Fe}^{2+}$  (4  $\text{Fe}^{2+}$  per  $\text{CH}_2\text{O}$  fixed as organic carbon), and a C/N ratio of 6/1 in organic matter. On the basis of this stoichiometry, and given estimated Fe concentrations of 40 to 120  $\mu\text{M}$  in the deep ocean (29),  $\text{NH}_4^+$  levels would have been 27 to 80  $\mu\text{M}$ .

### How Did the Nitrogen Cycle Respond to Changes in Earth's Surface Chemistry?

Both the evolutionary history of nitrogen metabolisms as well as their intensity depended on the evolution of Earth's surface chemistry. Hence, although the anaerobic process of nitrogen fixation likely evolved early in biological evolution, the efficiency of this process and its importance in regulating the nitrogen inventory of the oceans depended on the evolution of ocean chemistry (9, 32). Thus, before ~2.5 billion years ago, the oceans were rich in dissolved  $\text{Fe}^{2+}$  (29), which accumulated under very low atmospheric oxygen concentrations (33). Some nitrogen fixers contain paralogous genes that encode two alternative nitrogenases, where V or Fe replaces Mo. These alternative and less efficient forms are expressed when Mo is unavailable (34), and given the abundant availability of Fe on the early Earth and the lack of soluble Mo under conditions of low atmospheric oxygen, it is likely that the Fe form

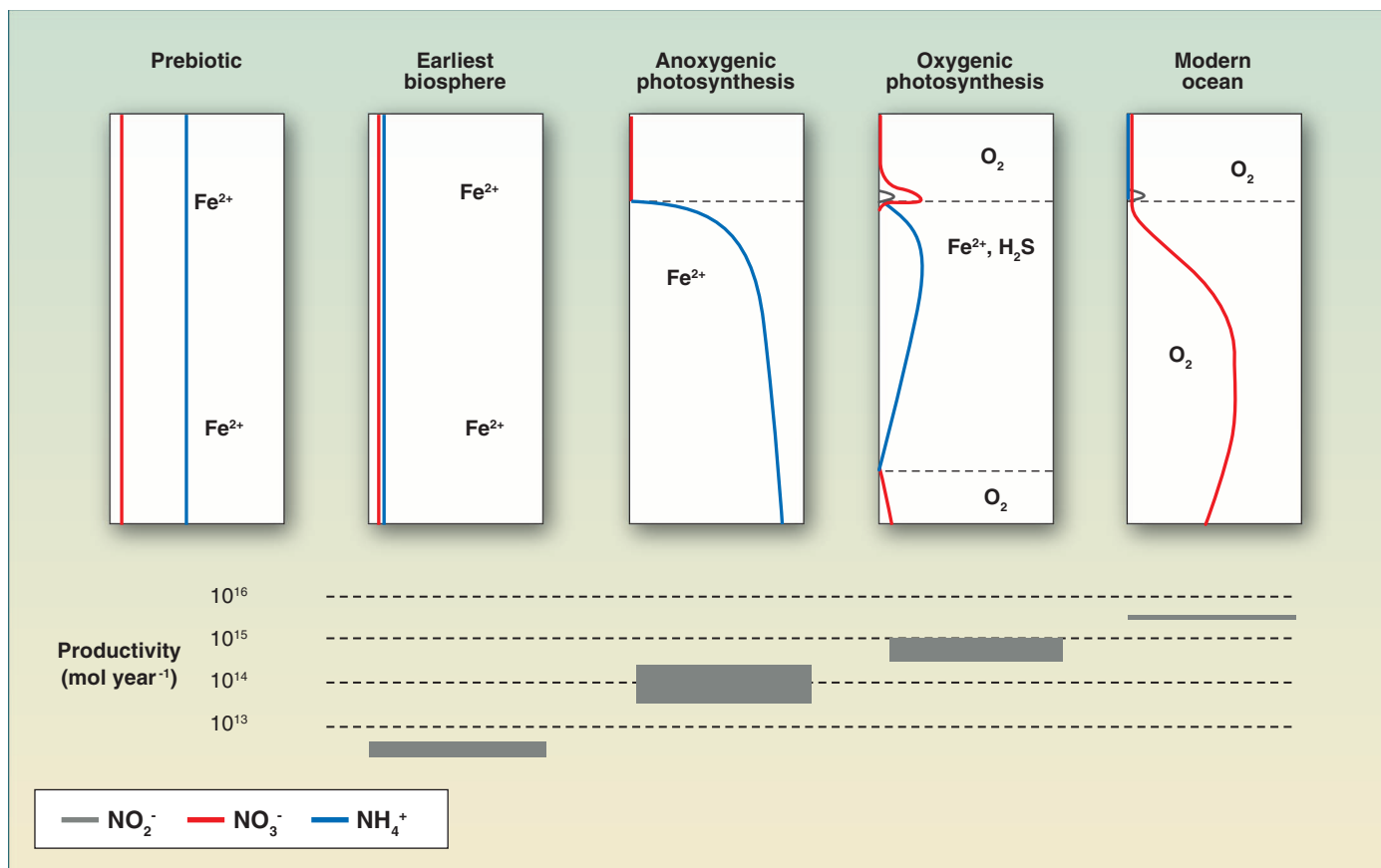
dominated under these conditions. Indeed, the more efficient Mo form may not have become widely distributed until some 500 to 600 million years ago, after oxygenation of the deep ocean led to an increase in soluble Mo concentrations (35). All known nitrogenases, however, are irreversibly inhibited by molecular oxygen. Hence, to operate in the presence of oxygen, organisms evolved means to shield the enzyme complex by scavenging oxygen to low concentrations and/or by restricting its diffusion to the complex.

It is unclear when the other critical anaerobic processes in the nitrogen cycle, denitrification and anammox, evolved. If these processes evolved before oxygen-producing photosynthesis by cyanobacteria, they only became important after cyanobacterial evolution, because molecular oxygen appears to be requisite for the biological production of  $\text{NO}_3^-$ . Indeed, nitrification is the critical aerobic process in the nitrogen cycle (Fig. 1); once it evolved, the modern nitrogen cycle emerged.

The timing of cyanobacterial evolution is unclear, but periodic oxygenation of the surface environment occurred at least 200 to 300 million years before pronounced atmospheric oxygenation around 2.3 to 2.4 billion years ago [e.g., (33, 36, 37)]. Even after this, it was not until ~600 million years ago [e.g., (35, 38, 39)] that widespread oxygenation of the deep ocean occurred. During this

transition period of ~1.8 billion years, oxygenic phototrophs in the surface ocean resided above anoxygenic phototrophs at the transition between  $\text{H}_2\text{S}$  or  $\text{Fe}^{2+}$  in the deeper ocean layers (38–40). In such a situation,  $\text{NH}_4^+$  would have been present in the deeper anoxic parts of the ocean, whereas  $\text{NO}_3^-$  and  $\text{NO}_2^-$  would have been concentrated at the oxic-anoxic transition as a result of nitrification just above and denitrification just below (Fig. 3). This situation is analogous to modern stratified basins such as the modern Black Sea, but some ventilation of the ocean interior may have accompanied the downwelling oxygen-enriched waters at high latitudes, as happens in the contemporary ocean.

While global rates of primary production increased markedly with the evolution of oxygenic photosynthesis (31) (Fig. 3), feedbacks among the nitrogen, carbon, and oxygen cycles potentially contributed to the retardation of Earth's surface oxidation. Thus, massive loss of fixed nitrogen from the oceans through anammox and denitrification are predicted during periods of deep-water anoxia (9, 31), potentially limiting the availability of fixed inorganic nitrogen. With nitrogen limitation, the burial of organic carbon would have been reduced, and hence net oxygen accumulation would have been retarded [i.e., a negative feedback (9, 31)].



**Fig. 3.** The marine nitrogen cycle responded to changes to biological evolution and ocean chemistry through geologic time. The five major biological innovations are indicated by different vertical profiles of ocean chemistry. Rates of oceanic primary production ( $\text{mol C year}^{-1}$ ) also increased as they changed in response to the evolving biosphere and the oxygenation of the oceans.



Stable isotopes provide some temporal constraints on the emergence of interactions between biogeochemical cycles. In the water column, both denitrification and anammox lead to an isotopic fractionation between the two stable isotopes of N; the lighter isotope,  $^{14}\text{N}$ , is preferentially converted to  $\text{N}_2$ , leaving the pools of fixed inorganic nitrogen enriched in  $^{15}\text{N}$ . Indeed, isotopic analyses from late Archean shales (about 2.7 billion years ago) reveal organic matter with strong enrichments in  $^{15}\text{N}$  (41), suggesting that the nitrogen cycle had either an anammox or classical denitrification pathway. The expression of these pathways required active nitrate production through nitrification, which suggests that molecular  $\text{O}_2$  and the complete nitrogen cycle were present in the upper ocean for several hundred million years before the widespread oxygenation of the atmosphere (7).

### How Did the Modern Nitrogen Cycle Evolve?

Oxygen rose to its modern levels over the last 550 million years [e.g., (42)], aided by the rise of terrestrial plants (43). With the oxygenation of the ocean interior,  $\text{NO}_3^-$  became the dominant nitrogen species, with minor concentrations of  $\text{NH}_4^+$  and  $\text{NO}_2^-$  in the water column. On the modern Earth, rates of net primary production are nearly equally balanced between the land and sea at about  $4 \times 10^{15} \text{ mol year}^{-1}$  each (44), and although current estimates are not well constrained, the natural, pre-industrial nitrogen cycles are also of a similar magnitude on land and in the sea (45) (Fig. 4).

A curious feature of the modern terrestrial nitrogen cycle is that denitrification and nitrogen fixation are largely balanced. A sizable fraction of the nitrogen transfer from the land to the sea results from a combined loss of anthropogenic nitrogen inputs through rivers and atmospheric transport of gaseous phases (e.g.,  $\text{NO}_x$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$ ) from the continents to the oceans (45, 46). There is apparently also a large annual storage of nitrogen on the continents (46). In the oceans, rates of denitrification appear to be higher than those of nitrogen fixation and terrestrial input, suggesting an imbalance in the system (45, 46) (Fig. 4). Overall, denitrification in the oceans is governed by oxygen supply (47). In coastal sediments, and in regions of low oxygen in the water column (such as in the eastern tropical Pacific, southwest Africa, and the Arabian Sea), denitrification is extensive. In contrast,  $\text{N}_2$  fixation is primarily found in the tropical and subtropical regions of the Northern Hemisphere where continents deliver a biologically available dust source of iron (48). Assuming an average molar ratio for nitrogen and phosphate of 16/1 in organic matter

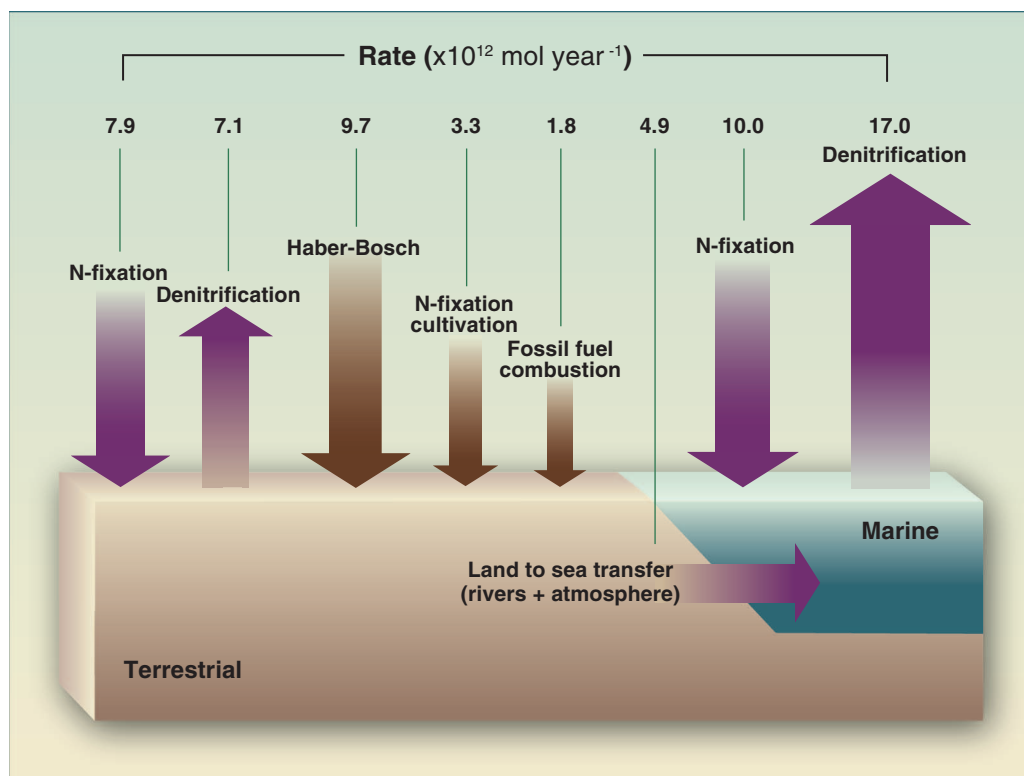
(i.e., the Redfield ratio), there is a  $\text{NO}_3^-$  deficit of  $\sim 2 \mu\text{mol/liter}$  in the contemporary ocean, presumably reflecting a slight imbalance between  $\text{N}_2$  fixation and denitrification (2). Because nitrogenase has a high absolute Fe requirement, and because Fe availability is variable from place to place in the oceans, nitrogen deficits may have been the norm in the global ocean, with nitrogen fixation lagging to fill the demands of the biosphere as necessitated by fixed nitrogen loss through denitrification.

### Has Human Activity Created an Imbalance?

In the 20th century, humans began to have an enormous impact on the global nitrogen cycle by developing industrial processes to reduce  $\text{N}_2$  to  $\text{NH}_4^+$ , by implementing new agricultural practices that boost crop yields, and by burning fossil fuels (49). Agriculture alone contributes about

use efficiency is typically below 40%, meaning that most applied fertilizer either washes out of the root zone or is lost to the atmosphere by denitrification before it is assimilated into biomass. Given the rising costs of synthetic fertilizer production, this overuse is not only economically expensive, but also initiates a cascade of large-scale environmental impacts (52). Worldwide, nearly 90% of nitrogen fertilizer is  $\text{NH}_4^+$ , where nitrifying bacteria can convert it to highly mobile  $\text{NO}_3^-$ , which in turn can leach into rivers, lakes, and aquifers. This results in nitrogen loss and leads to eutrophication of coastal waters, creating huge hypoxic zones around the world (53).

Under anoxic conditions (e.g., as found in wet soils), denitrification forms mainly  $\text{N}_2$  but also forms  $\text{N}_2\text{O}$ , a fraction of which is lost to the atmosphere and increasingly contributes to the rise in atmospheric  $\text{N}_2\text{O}$  concentrations (54). As



**Fig. 4.** Rates of nitrogen flux in the modern nitrogen cycle depend on the efficiency of the transformations between reservoirs. Arrow size reflects relative size of the flux. The dark brown arrows represent anthropogenic inputs (25, 45, 46, 52, 53, 68, 69).

$2.4 \times 10^{12} \text{ mol N year}^{-1}$  because of cultivation-induced nitrogen fixation, primarily from fodder legumes (46). During 2008 alone, the Haber-Bosch process of  $\text{NH}_4^+$  production supplied  $9.5 \times 10^{12} \text{ mol}$  (50), and fossil fuel combustion generated another  $1.8 \times 10^{12} \text{ mol}$  (45). Together, anthropogenic sources contribute double the natural rate of terrestrial nitrogen fixation, and they provide around 45% of the total fixed nitrogen produced annually on Earth (Fig. 4).

From 1960 to 2000, the use of nitrogen fertilizers increased by  $\sim 800\%$  (51), with wheat, rice, and maize accounting for about 50% of current fertilizer use. For these crops, the nitrogen

a greenhouse gas,  $\text{N}_2\text{O}$  has 300 times (per molecule) the warming potential of  $\text{CO}_2$ , and it also reacts with and destroys ozone in the stratosphere (55). Because nitrification also produces  $\text{N}_2\text{O}$  as an intermediate, agricultural systems represent huge sources of  $\text{N}_2\text{O}$  to the atmosphere, accounting for about one-quarter of global  $\text{N}_2\text{O}$  emissions (56).

### What Will the Future Nitrogen Cycle Look Like?

Humans may have produced the largest impact on the nitrogen cycle since the major pathways of the modern cycle originated some 2.5 billion

years ago. Natural feedbacks driven by microorganisms will likely produce a new steady state over time scales of many decades (i.e., excess nitrogen added from human sources will no longer accumulate, but will be removed at rates equivalent to rates of addition). However, because of the projected increase in human population through at least 2050, there will be demand for a concomitant increase in fixed nitrogen for crops to feed this population. One potential consequence of increased fixed nitrogen use will be increased fluxes of riverine nitrogen to coastal zones (57), leading in turn to enhanced biological productivity, increased coastal anoxia, detrimental impacts on water quality, and increased fluxes of N<sub>2</sub>O to the atmosphere.

Several new approaches and a much wider use of more sustainable time-honored practices, however, can decrease nitrogen use substantially. These include (i) systematic crop rotation [e.g., legume cropping in maize-based systems supplies the nitrogen otherwise provided by synthetic fertilizers (58)], (ii) optimizing the timing and amounts of fertilizer applied to increase the efficiency of their use by crops (59), (iii) breeding or developing genetically engineered varieties for improved nitrogen use efficiency (60), (iv) improving the ability of economically important varieties of wheat, barley, and rye to produce nitrification inhibitors through traditional breeding techniques (60, 61), and (v) further developing cereals and other crops with endosymbiotic nitrogen-fixing bacteria to supply their nitrogen needs [e.g., (62)]. Market forces may drive these improvements because the rising economic and environmental costs of nitrogen fertilizers will accelerate a demand for increased nitrogen use efficiency in agriculture (17). Thus, humans can do something about managing the nitrogen cycle, and microbial processes will ensure that a new balance in the cycle will be reached. However, even with management, the future cycle will likely be different from the one that preceded the Industrial Revolution.

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