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### Title

News About Nitrogen

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increases. Solder connections are limited to spheres with an aspect ratio of 1:1 (height:diameter), making connections with high aspect ratios (large chip-to-substrate stand-off distances) very difficult to fabricate. This causes difficulties with flow in the placement of underfill (a stress-distributing layer around the solder balls). Fragile on-chip interlayer dielectrics require lower-stress I/O so as not to cause fracture.

The next frontier is an all-copper chip-tosubstrate interconnect, which would eliminate many of the problems with solder. Copper has superior electrical properties relative to solder with respect to both electrical conductivity and electromigration resistance. It also has superior mechanical properties, such as yield stress and elastic modulus, that allow for the design of mechanically compliant interconnect structures. Having no tin-based materials present eliminates the formation of brittle intermetallics, thus leading to an improvement in the thermomechanical reliability of the device. Finally, copper interconnects are capable of forming high aspect ratios because they are not melt-cast and therefore don't need to be spherical in shape. This will pave the way for finepitch interconnects with higher stand-off distances and complex shapes, such as shielded coaxial structures, which can support high-frequency I/O. Copper-to-copper bonding via methods that are compatible with temperaturesensitive substrate materials has been reported using surface-activated bonding (3) and electroless deposition and annealing (4). The left panel of the figure shows two (short) copper pillars joined by the all-copper electroless process. Such copper bonding facilitates connections for low-loss high-frequency operation that is not possible with solder.

Substrate and board-level signaling are particularly challenging because of the longer wires that require small  $\gamma$  to maintain adequate voltages. Conventional board-level wires, etched copper traces on fiberglass and epoxy substrates, suffer from large losses due to substrate capacitance and conductance. Improved performance can be achieved with more expensive ceramic substrates that offer comparable capacitance loss while reducing dielectric conductance. Such ceramics offer mechanical benefits due to the lower coefficient of thermal expansion.

Substrate capacitance can be reduced through the use of polymer dielectrics, although this typically is associated with an increase in substrate conductance. Further reduction of the coupling capacitances and conductances can be achieved by incorporating gaseous cavities in the material, via either a porous matrix or a continuous air cavity supported by a dielectric (5). At higher frequencies, such nonhomogeneous dielectric layers are undesirable, as propagation at different velocities through different media leads to distortion of the electric field. Copper surface roughness can also degrade performance at high frequencies because of the longer path length along the surface, where charge concentrates at higher frequencies as a result of the skin effect. Surface undulations due to glass fibers in epoxy-fiberglass substrates pose challenges to both electrical and optical systems ( $\delta$ ).

System-level integration of air-insulated copper lines will remain difficult until a variety of mechanical, thermal, and electrical considerations are addressed. Mechanical integrity of copper lines is important to maintain reliability and prevent failure due to stress and electromigration (7). Inclusion of air insulation thus poses a particular challenge, as the lack of confining stress allows copper surface diffusion to proceed with greater ease (8). The right panel in the figure shows a microstrip copper signal line on a substrate with its return path separated by an air-polymer gap. Moisture absorption into air cavities is particularly troublesome because it can increase the capacitance and conductance, which may result in short circuits. Air-insulated circuits will require surface treatments or hermetic sealing to circumvent these challenges. Maximized electrical performance ultimately corresponds to minimized thermal performance, as air is also an ideal thermal insulator. This increase in thermal resistance may limit heat removal from the package and prevent further improvements in system performance.

Any advances in integrated circuit performance will need to be matched by performance enhancements at the package level. Work is under way toward providing cost-effective high-speed chip-to-chip communication.

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#### BIOGEOCHEMISTRY

# **News About Nitrogen**

#### M. Claire Horner-Devine<sup>1</sup> and Adam C. Martiny<sup>2</sup>

Discoveries of microbial pathways, players, and population dynamics challenge conventional models of the nitrogen cycle.

Understanding of microbial diversity and interactions is crucial for quantifying fluxes in nutrient cycles and forecasting ecosystem responses to global environmental changes. This is particularly true for the nitrogen cycle. In contrast to the carbon cycle, none of the steps in the nitrogen cycle can be measured at a global scale on the basis of satellite data. Instead, global biogeochemical models rely on field measurements of nitrogen concentrations and fluxes, combined with rate constants from a few known organisms, to balance the net flux of nitrogen. Thus, incomplete knowledge of microbial diversity and ecological dynamics may mislead estimates of fluxes in the nitrogen cycle.

Three discoveries illustrate how much scientists are still learning about the nitrogen cycle. First, ammonia oxidation by microbes was thought to proceed only in the presence of oxygen. However, bacteria have been shown to be capable of oxidizing ammonium anaerobically, using nitrite rather than oxygen as the electron acceptor, resulting in the production of  $N_2$  gas (1). Although this "anammox" reaction was theoretically predicted, finding anammox organisms has helped to explain deviations between models of the marine nitrogen cycle and observed ammonia concentrations and  $N_2$  production in anaerobic marine environments (2).

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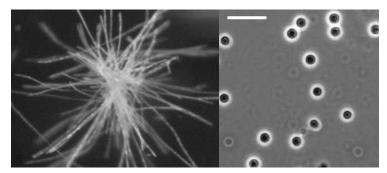
Second, archaea-previously thought to inhabit only extreme environments-have been shown to constitute a substantial proportion of marine plankton worldwide (3, 4). Some archaea have the genetic capacity for ammonia oxidation, as evidenced by an archaeal version of the ammonia monooxygenase (amoA) gene (5, 6). Perhaps more important, the cultivation of an ammonia-oxidizing archaeon in the laboratory allowed researchers to establish a link between the presence of the amoA gene and archaeal ammonia oxidation (7).

Field studies show that archaea likely contribute substantially to nitrification in marine and terrestrial environments (8-11).

Third, researchers have found several new lineages responsible for nitrogen fixation. *Trichodesmium* (see the figure, left panel) and symbionts of diatoms were long thought to be the major nitrogen fixers or diazotrophs in the open ocean; the discovery of this trait in unicellular cyanobacteria (see the figure, right panel) suggests that this is not the case. Researchers have found novel lineages of N<sub>2</sub> fixers in hot springs, including cyanobacteria and archaea (*12, 13*). These findings suggest that the ability to fix nitrogen is widely distributed among bacteria and archaea.

From a biogeochemical perspective, one might argue that all this diversity may not matter to our understanding of nutrient fluxes. Microbial ecologists will likely continue to discover new lineages capable of a given reaction, but incorporating all these groups into ecosystem models would be intractable. However, the discovery that such disparate groups are involved in ammonia oxidation, nitrogen fixation, and other steps in the nitrogen cycle calls for a reevaluation of the assumptions made in biogeochemical models and field experiments (14). Many rate constants used in models are based on only a few taxa. These rate constants may be very different from those of newly discovered taxa, and some of these new players may have very different nutrient or energy requirements.

For example, two dominant marine  $N_2$  fixers—*Trichodesmium* and unicellular cyanobacteria (see the figure)—may have vastly different phosphate uptake kinetics due to differences in cell size and physiology (15). This could be important for predicting the response of diazotrophs to a shift from a nitrogen- to phosphorus-controlled ocean environment in the North Pacific Subtropical Gyre (16). In addition, several assays used to measure nitrogen transformation rates were based on



**New players.** *Trichodesmium* (**left**), which forms floating colonies ~1 to 4 mm in diameter (colony example shown in the picture), is a key nitrogen fixer. Recent studies have shown that unicellular cyanobacteria, such as *Crocosphaera* (**right**), may be competing for this role. Scale, 10  $\mu$ m.

known taxa (for example, nitropyrene addition to block nitrification), but these assumptions may not hold up against new lineages.

In addition to new pathways and players, understanding of the global nitrogen cycle has recently benefited from work at a smaller scale of organization: the interaction between populations. Experiments in wastewater bioreactors revealed that the dynamics of two guilds involved in nitrification are tightly linked to nitrogen transformation rates. Guilds of ammonia- and nitrite-oxidizing bacteria were prone to chaotic behavior, resulting in marked temporal variation in nitrification (17). Increasing variation in the abundance of ammonia-oxidizing bacteria was associated with large, destabilizing variations in nitrite-oxidizing bacterial abundance, resulting in the extinction of Nitrospira and the breakdown of nitrification (18). Thus, complexity and dynamics at these small scales of organization can have important consequences for local nitrogen transformation rates.

The above results suggest critical gaps in our knowledge of the relationship between microbial composition and nutrient fluxes. Changes in community composition in a particular microbial functional group can be associated with changes in nutrient cycling rates (19–21), implying that all microbes in a functional group are not functionally redundant. We must understand when, where, and at what scale of organization it is necessary to consider complex dynamics and shifts in composition in ecosystem models. Nitrogen cycle monitoring and modeling may require more sophisticated representations of microbial communities, as was recently proposed for marine phytoplankton (22).

Novel ways of understanding and incorporating new pathways, players, and population dynamics may be particularly pertinent for forecasting nutrient dynamics in the face of human disturbances. Human activities increasingly dominate nitrogen input in many regions of the world. Combined with climate change, these perturbations are globally altering nitrogen dynamics (23) and are likely changing microbial community composition and activity (24). Our ability to forecast ecosystem responses to human disturbances would benefit from a coordinated effort of both observational and experimental studies and integration of this know-

ledge into biogeochemical models. The scientific community must better understand how changes in community and population dynamics are related to nitrogen transformation rates and how both the players and the processes respond to disturbances. Only by understanding nitrogen cycling at a range of scales of biological organization can scientists predict how anthropogenic pressures will influence local and global nitrogen dynamics.

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