Diversity and evolution of nitric oxide reduction

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Nitrogen is essential for life, with the availability of fixed nitrogen limiting primary productivity in many ecosystems. The return of nitrogen species to the atmospheric N_2 pool is predominantly catalyzed by microbial denitrification (NO_3^- -> NO_2^- -> NO -> N_2O -> N_2). Incomplete denitrification can produce N_2O as a terminal product, leading to an increase in atmospheric N_2O, a potent greenhouse and ozone depleting gas. The biological production of N_2O is primarily catalyzed by nitric oxide reductase (NOR) enzymes, which are members of the heme-copper oxidoreductase (HCO) superfamily.

From emerging genomic and metagenomic datasets we identified a number of previously uncharacterized HCO families that perform nitric oxide reduction chemistry. These new NOR families have novel active-site structures demonstrating the mechanistic diversity of nitric oxide reduction chemistry. As an example, we will present experimental results that confirm the biochemical function of one of these new families, currently termed eNOR. Some of these new families, including eNOR, have conserved proton channels from the cytoplasmic surface of the enzyme, allowing them to couple nitric oxide reduction chemistry to energy conservation, a property not found in previously characterized NORs.

These newly described NORs also exhibit broad phylogenetic diversity and environmental distributions, greatly expanding the known biological diversity and environmental extent of denitrification in nature. Furthermore, phylogenetic analyses demonstrate that within the HCO superfamily, enzymes that perform nitric oxide reduction chemistry evolved multiple times, independently, from enzymes that perform oxygen reduction chemistry, strongly suggesting that aerobic respiration predated the emergence of classical denitrification.