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Metal Speciation Controls Nitrogenase Activity in Euxinic and Ligand-Rich Environments

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Nitrogen is an essential nutrient for life, and biological nitrogen fixation (BNF) is the only pathway that converts atmospheric dinitrogen (N_2) into bioavailable ammonia (NH_3). This process is catalyzed by nitrogenase enzymes that predominantly require molybdenum (Mo) as a cofactor, although alternative vanadium (V)- and iron (Fe)-only nitrogenases can function under specific environmental conditions. These alternative enzymes are generally less efficient and are thought to have evolved later, potentially in response to fluctuations in metal availability in ancient oceans.

Emerging evidence suggests that metal bioavailability is governed not only by bulk concentration but also by mineralogical association and chemical speciation. Our previous work demonstrated that diazotrophs can mobilize metal ions directly from Mo, V, and Fe minerals to sustain nitrogenase expression and nitrogen fixation through diverse strategies. More recently, we observed that even in euxinic environments characterized by Fe–S-mediated Mo sequestration and elevated dissolved V concentrations, conditions traditionally assumed to favor alternative nitrogenases, anoxygenic phototrophs can still mobilize Mo via metallophore production and maintain Mo-nitrogenase activity. In contrast, within the overlying water column where Mo is removed, isotopic signatures and functional gene analyses indicate activation of V-nitrogenase. We further found that, in the presence of organic ligands such as metallophores, the methanogen *Methanosarcina acetivorans* was unable to directly utilize metal-metallophore complexes to fix N_2, leading to reduced metal bioavailability and a likely shift toward expression of alternative nitrogenases. Metallophore addition also reshaped transcriptional profiles associated with metal transport systems and cellular energy metabolism in these anaerobic diazotrophs. Notably, when mineral phases such as molybdenite and basalt were introduced, nitrogen fixation activity was restored despite the presence of metallophores, indicating that mineral can buffer ligand-induced metal limitation and sustain diazotrophic function. Together, these findings highlight the central role of metal speciation in regulating nitrogenase utilization and biological nitrogen fixation in ancient redox-stratified environments.