

Implications for the origin of nitrogenase: Trace metals from pyrite as cofactors for biological nitrogen fixation

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Molybdenum nitrogenase (Nif), the enzyme that catalyzes the reduction of N_2 to bioavailable NH_3 , is recognized as the most widely distributed and oldest form of nitrogenase. The origin of Nif can be dated to an ancestor of methanogenic archaea before the Great Oxidation Event (GOE), despite the depletion of dissolved Mo in the ancient oceans. Mo was locked in the sulfide minerals such as pyrite. Here, we showed that the mineral-bound trace Mo from pyrite was available to a diazotrophic methanogen (*Methanosarcina acetivorans*) as a cofactor for nitrogen fixation. Both cell growth yields and N_2 fixation rates were enhanced in the cultures with smaller mineral particle sizes than the larger particle sizes under diazotrophic conditions, as measured by the total protein content and ^{15}N -labelled assay, respectively, suggesting the bioavailability of metals in the pyrite was dependent on particle sizes. A physical contact between the cell and pyrite was necessary for metal extraction. X-ray photoelectron spectroscopy (XPS) analysis showed that the valence states of Mo and sulfur (S) on the surface of pyrite changed from reduced to oxidized state after interacting with cells, indicating a possible redox reaction-driven dissolution of pyrite to release Mo. These observations suggest that mineral-bound trace metals may be bioavailable for methanogens to fix nitrogen in the ancient oceans, and anoxic environments were favorable for the evolution of Mo-nitrogenase.