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Mineral-Bound Mo, V, and Fe as Cofactors for Anaerobic Biological Nitrogen Fixation

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Nitrogen acts as a critical nutrient for the origin and survival of living organisms on Earth. Through the process of biological nitrogen fixation (BNF) by a specialized group of diazotrophic prokaryotes, atmospheric nitrogen (N2) is converted into bioavailable ammonia (NH3). BNF requires nitrogenase enzymes that commonly use Mo as a metallocofactor and alternative cofactors V and Fe are also viable. N2 fixation was once believed to have evolved during the Archean-Proterozoic times using Fe as a cofactor. However, both geological and bioinformatic evidence suggest an ancient origin of Mo-based nitrogenase, despite the low concentration of dissolved Mo in the Archean oceans. This apparent paradox would be resolvable if mineral-bound Mo were bioavailable for nitrogen fixation by ancient diazotrophs under anoxic condition. Fe and V are also sequestered within minerals in various modern environments, and thus are considered not readily bioavailable.

In this study, the bioavailability of mineral-bound Mo, V, and Fe was determined by incubating different anaerobic diazotrophs with Mo-, V-, and Fe-bearing minerals (e.g., molybdenite, pyrite, cavansite, ferrihydrite) and rocks (e.g., basalt, peridotite, black shale) under diazotrophic conditions. The results showed that these diazotrophs utilized and bioaccumulated mineral-associated metals to express respective nitrogenase genes and fix nitrogen. The extent of metal mineral weathering directly controlled the efficiency of nitrogen fixation. Some diazotrophs could secrete metal-chelating molecules and metallophores to extract metals from the minerals and rocks, as measured by Orbitrap liquid chromatography-mass spectrometry (LC-MS) and liquid chromatography-inductively coupled plasma mass spectrometry (LC-ICP-MS). As a result of microbial weathering, surface sensitive techniques demonstrated that mineral surface chemistry significantly changed, owing to the surface coating by microbial exudates and metallophores for metal extraction. These results provide important support for the ancient origin of Mo-based nitrogenase and the bioavailability of Fe and V minerals, with profound implications for coevolution of the biosphere and geosphere.