

Minerals to support biological nitrogen fixation on early Earth

YIZHI SHENG¹, XINYI ZHOU¹, XIAOWEN ZHANG²,
DONGYI GUO³, SHUAIDI WANG¹ AND HAILIANG
DONG¹

¹China University of Geosciences, Beijing

²China University of Geosciences Beijing

³Miami University

Nitrogen is a vital nutrient for life on Earth, and biological nitrogen fixation plays a crucial role in converting atmospheric nitrogen (N₂) into bioavailable ammonia (NH₃). This process relies on nitrogenase enzymes, which primarily use molybdenum (Mo) as a cofactor, although iron (Fe) and vanadium (V) can serve as alternatives. While the origin of nitrogenase was once debated, evidence suggests that Mo-based nitrogenase dates back to the Archean, despite the low concentrations of Mo in early oceans. Less efficient Fe and V nitrogenases are thought to have evolved about a billion years later, with Mo possibly being less bioavailable than Fe and V in certain environments, thus enabling activation of these alternative enzymes. Although hydrothermal vents may supply some trace metals, the bioavailability of mineral-bound Mo is crucial for nitrogen fixation in shallow seas and coastal environments, where ancient diazotrophs could access it.

This study examined the bioavailability of Mo, Fe, and V in minerals and rocks by incubating them with anaerobic diazotrophs. The results demonstrated that these microorganisms were able to extract metal ions from minerals to express nitrogenase genes and fix nitrogen through various mechanisms. The efficiency of nitrogen fixation was influenced by the rate of microbial weathering of minerals, with some bacteria secreting metallophores—metal-binding compounds that facilitate metal acquisition from minerals. Methanogens, which do not produce metallophores, were still able to utilize Mo from minerals and rocks for nitrogen fixation, likely due to the metal-chelating compounds and redox reactions on mineral surfaces. However, metallophores produced by other bacteria likely inhibited methanogen growth, suggesting competition for trace metals. These findings underscore the significance of mineral-bound transition metals in supporting biological nitrogen fixation in ancient environments.

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[2] Zhou, X., Sheng, Y., Zheng, Y., Jiang, M., Wang, M., Zhu, Z., Li, G., Baars, O. and Dong, H., 2024. Bioavailability of molybdenite to support nitrogen fixation on early Earth by an anoxygenic phototroph. *Earth and Planetary Science Letters*, 647, 119056.