## Mineral-microbe interaction and coevolution across critical geological periods

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Mineral-microbe interactions play important roles in environmental change, biogeochemical cycling of elements, and formation of ore deposits. Minerals provide both beneficial and detrimental effects to microbes, resulting in mineral-specific microbial colonization. Microbes impact dissolution, transformation, and precipitation of minerals through their activity, resulting in either genetically-controlled or metabolism-induced biomineralization. Through these interactions, minerals and microbes coevolve through Earth history. The mineral-microbe interactions typically occur at microscopic scale but the effect is often manifested at global scale.

One example is on N<sub>2</sub> fixation. The largest reservoir of nitrogen on Earth is nitrogen gas (N<sub>2</sub>). To make it bioavailable, N<sub>2</sub> gas is fixed into ammonia by N<sub>2</sub>-fixing microbes. N<sub>2</sub>-fixation requires nitrogenases, within which Fe, Mo, or V serve as metal cofactors. Mo-based nitrogenase (Nif) is the most common and efficient. However, on early Earth Mo was bound in solids and presumably not bioavailable, yet nitrogen isotopes of sedimentary rocks and phylogenetic analysis suggest that Mobased nitrogenase was the predominant class of enzymes in Archaean oceans. Therefore, the emergence of the Mo-based nitrogenase before the Great Oxidation Event, raises an apparent paradox. By incubating N<sub>2</sub>-fixing microorganisms of different ages with Mo-bearing minerals and rocks, our results demonstrated that microorganisms can extract Mo from molybdenite and other minerals/rocks by molybdophores and by expressing Mo transport proteins. Significant changes in surface chemistry of Mo-bearing minerals/rocks occurred after their interaction with microbes. These findings provide novel explanations for the prevalence of Mo-nitrogenase on early Earth, with significant implications for nitrogen fixation in modern Mo-deficient environments.

The second example is focused on how Ni bioavailability affects the growth and function of methanogens by incubating crushed igneous rocks with a model methanogen *Methanosarcina acetivorans*. These rocks significantly promoted the growth and methanogenesis. The released trace metals from peridotite and basalt, especially Fe, Ni, and Co, accounted for the promotion effect. Proteomic analysis revealed that rock amendment significantly enhanced the expression of core metalloenzymes in the methylotrophic methanogenesis pathway. These results have important implications for evolution of methane flux over geological time and also for using enhanced rock weathering as an approach to sequester atmospheric CO<sub>2</sub>.