Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.16815

Mineral surfaces as protoenzymes: how to connect cofactors and heterogeneous catalysis

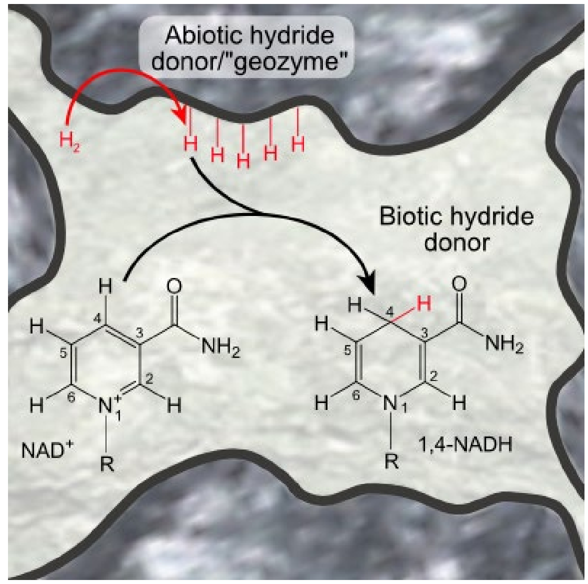
DELFINA PATRÍCIA HENRIQUES PEREIRA, MA[1,2], TUĞÇE BEYAZAY[3], KENDRA BELTHLE[3], HARUN TÜYSÜZ[3] AND **MARTINA PREINER**[1,2]

[1]Max Planck Institute for Terrestrial Microbiology

[2]Microcosm Earth Center

[3]Max Planck Institute for Coal Research

Presenting Author: martina.preiner@mpi-marburg.mpg.de



The last universal common ancestor (LUCA) arose in an environment of rocks and water on the early Earth about 4 billion years ago. We can connect LUCA's metabolism to its geochemical roots through top-down comparative bioinformatics[1] and through bottom up geochemical laboratory studies, using minerals and inorganic redox partners (H_2, metal ions) instead of catalysts as enzymes[2]. We aim to connect central metabolic cofactors and enzymatic reactions that were present in LUCA to early Earth geochemical reaction partners in order to better understand the transition from environmental reactions to genetically encoded metabolic functions. The hypothesis: cofactors are the missing link between abiotic and biotic (enzymatic) catalysis. Here, we show a connection between abiotic and biotic hydrogen (electron) transfer. Hydrogen gas, H_2, is generated in various geochemical settings, among them serpentinization, a water-rock interaction process during which iron-containing minerals transfer electrons to the protons of water. H_2 has been a source of electrons and energy since there was liquid water on the early Earth, and it fuelled early anaerobic ecosystems in the Earth's crust. It is also the electron donor for the most ancient route of biological CO_2 fixation, the acetyl-CoA pathway and abiotic, geochemical organic syntheses resembles segments of the pathway occur in hydrothermal vents today[3].

In metabolism itself, H_2 is being transformed into biochemical electron donors, cofactors such as the dinucleotide NADH which can be seen – simply put – as hydride (H^-) donors. We successfully activated hydrogen on minerals found in serpentinizing systems (awaruite Ni_3Fe, magnetite Fe_3O_4) reduce NAD^+ to NADH under aqueous conditions at temperatures found at the cooler end of serpentinizing systems[4]. We furthermore were able to conduct these principles onto other biochemical electron donors and acceptors (flavins such as F420, FAD and Riboflavin). These results underline the connection between central molecular transitions in metabolism and abiotic, geochemical catalysis with hydrogen as a common denominator.

1. M. C. Weiss *et al.* (2016) *Nat. Microbiol.* **1**, 16116.
2. M. Preiner *et al.* (2020) *Nat. Ecol. Evol.* **4**, 534–542.
3. S. Q. Lang, *et al.* (2010) *Geochim. Cosmochim. Acta*. **74**, 941–952.
4. D. P. Pereira *et al.* (2022) *FEBS J.* **289**, 3148–3162.