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Organic cofactors as connection between minerals and protometabolism

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The last universal common ancestor (LUCA) arose in an environment of rocks and water on the early Earth about 4 billion years ago. Top-down comparative bioinformatics reveal LUCA's carbon metabolism: the acetyl-CoA (or Wood-Ljungdahl) pathway, driven by CO_2 and H_2 gas[1,2]. Looking at abiotic, mineral-assisted organic syntheses occurring in hydrothermal vents today, we see how they resemble segments of the pathway[3,] possibly revealing LUCA's geochemical roots. In order to connect undirected, mineral-assisted catalysis with the complex enzymatic catalysis in LUCA (and extant biochemistry), we are zooming in on central metabolic organic cofactors, so helper molecules employed by enzymes. Examples also found in the acetyl-CoA pathway are nicotinamide adenosine dinucleotide (NAD), C1 donors and acceptors such as tetrahydrofolate (H_4F) or, the namesake of the pathway, coenzyme A (CoA). Cofactors have been hypothesized to predate enzymes[4,] so in other words: cofactors could be the missing link between abiotic and biotic (enzymatic) catalysis.

Here, we show how cofactors employed in the acetyl-CoA pathway can function under conditions found in serpentinizing systems, where iron-containing minerals transfer electrons to the protons of water, continuously producing hydrogen gas (H_2) – LUCA's main electron and energy source. Not only can we show how activated hydrogen on minerals found in serpentinizing systems reduce the central redox cofactor nicotinamide adenosine dinucleotide (NAD)[5], we can furthermore make assessments on how the structure of NAD enables specific reduction under geochemical conditions[6]. We were also able, only starting from H_2, CO_2 and Ni-containing minerals, to produce a cofactor-bound methyl-group – thus reproducing 50% of the acetyl-CoA pathway without enzymes, but with minerals and cofactors. These results show how organic cofactors could play a central role in the transition between mineral and enzymatic catalysis.

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