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Serpentinizing systems and hydrogen activation in early metabolism

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Hydrogen gas, H_2, is generated in alkaline hydrothermal vents from reactions of iron containing minerals with water during a geochemical process called serpentinization. It 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 (*1*). H_2 is the electron donor for the most ancient route of biological CO_2 fixation, the acetyl-CoA pathway and abiotic, geochemical organic syntheses resembling segments of the pathway occur in hydrothermal vents today (*2*).

These recurring parallels between biochemistry and geochemistry were put to test in a laboratory experimental setting. We were able to show that minerals found in serpentinizing systems such as magnetite (Fe_3O_4) or awaruite (Ni_3Fe) catalyse the fixation of CO_2 with H_2 at 100 °C under alkaline aqueous conditions via the surface activation of H_2 (so the formation of mineral bound hydrides). The products were formate, acetate, pyruvate, methanol, and methane. These compounds are important educts, products and intermediates of the acetyl-CoA pathway, shedding light on both the nature of abiotic formate and methane synthesis in modern hydrothermal vents and the geochemical origin of microbial metabolism (*3*).

In metabolism itself, H_2 is being transformed into biochemical electron donors, cofactors such as NADH, which are simply hydride (H^-) donors (*4*). We successfully used the mineral bound hydrides mentioned above to reduce NAD^+ to NADH under alkaline aqueous conditions at temperatures found at the cooler end of serpentinizing systems. These results underline the connection between central molecular transitions in metabolism and abiotic, geochemical catalysis with hydrogen as a common denominator.

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