

## **Carbon and energy first: Hydrothermal vents and the origin of microbial metabolism**

William F. Martin

University of Düsseldorf, Germany

Life is a chemical reaction. All cells require carbon, energy, and electrons for growth. One very ancient pathway serves all three needs simultaneously. In the acetyl-CoA pathway,  $H_2$  reduces  $CO_2$  to pyruvate for carbon supply, while methane (archaea) or acetate (bacteria) synthesis are coupled to ion pumping and energy conservation via the rotor-stator ATP synthase. Simplicity and thermodynamics implicate the acetyl-CoA pathway as the most ancient route of carbon assimilation. Fe, Co, and Ni in the active sites of its enzymes are relics of origins. Using  $Fe^0$  or  $Ni^0$  as catalysts, aqueous  $H_2$  and  $CO_2$  react specifically to formate, acetate, methane, methanol, and pyruvate overnight at 100 °C in the laboratory. Solid state  $Ni^0$  alone can replace the function of 140 enzymes required to convert  $H_2$  and  $CO_2$  to pyruvate and methane in cells,  $Ni^0$  can also catalyze reductive aminations of 2-oxoacids, while  $Fe^0$  reduces the 4Fe4S clusters of ferredoxin—an evolutionary precursor of flavin-based electron bifurcation. The alkaline conditions (pH 8-11) of serpentinizing ( $H_2$ -producing) hydrothermal systems generate very reducing conditions ( $E_0'$  up to  $-900$  mV), depositing  $Fe^0$ ,  $Co^0$ , and  $Ni^0$  as metals. These are precisely the metals that i) reduce  $CO_2$  with  $H_2$  in the laboratory and ii) are present at the active sites of enzymes in the acetyl-CoA pathway. Organic synthesis from  $H_2$  and  $CO_2$  on solid state metals unites hydrothermal environments, ancient microbial metabolism, and inorganic catalysts, converging on the origin of metabolism.