An Approach to Mimicking Abiotic Hydrogenation of Carbon Dioxide in Alkaline Hydrothermal Vents

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Biotic chemistry has the unique ability to drive certain reactions at highly improbable rates. Such rates can only be achieved through a combination of catalysis and energy. Chemiosmosis provides the energy needed to power unfavorable reactions. Chemiosmosis derives that energy by utilizing the proton-motive force that results from sharp differences in pH (plants) or ionic concentration (animals) across membranes. From the perspective of evolution, chemiosmosis enables life to out-compete abiotic chemistry[1]. All life today takes advantage of this chemiosmotic strategy to survive.

Early in history the Earth was covered in a warm mildly acidic (pH 5.5) ocean. That ocean had natural-convection, alkaline hydrothermal vents, similar to those seen today at Lost City[2]. These mounds are divided into finely chambered structures by a combination of insulating materials (e.g. calcium carbonate, amorphous silica and hydrolyzed silicates) and thin metal sulfide membranes that are both proton and electron conductive. The slow, percolating flow through such hydrothermal mounds is stable for hundreds of thousands of years[2]. The range of temperatures (100°C to 20°C) and acidity (pH 10 to 5.5) in these mounds is perfect for production of organic molecules and for their products to accumulate and interact....eventually leading to life.

Their formation was driven partly by exothermic serpentinization reactions and partly by the geothermal gradient. Serpentinization provided a hydrogen-, ammonia- and, on occasion, bisulfide-bearing flow that formed catalytic nanocrystallites and thin chambers. These chambers were divided by semiconductive and conductive membranes of minerals such as mackinawite and greigite ensconced within electrically insulating carbonate and hydrosilicate structures.[3] There is a significant proton-motive force where fluids of differing pH and ionic concentration are separated by a proton conductive membrane. Such a proton-motive force could have provided the energy necessary to drive membrane-catalyzed reactions (in particular the proton-assisted hydrogenation of carbon dioxide) in an abiotic analog to chemiosmosis.

An interesting question to study is whether the natural proton-motive and chemiosmotic forces seen in alkaline hydrothermal vents were purely coincidental or if they had a real bearing on how life emerged. Microfluidic channels could potentially be used to mimic the pH and redox gradients at the boundary between a natural-convection, alkaline hydrothermal vent (pH ~10), as it interfaced the ancient acidic ocean (pH 5.5) through inorganic membranes. This is inherently a problem at the nanoscale: a length scale where local charge, steric effects, confined volumes and the surface energetics of nanocrystalline inclusions uniquely combine to define reaction rates and the potential for catalysis. By growing these membranes over nanofabricated interfaces, the emergence of chemiosmotic processes in an essentially pre-biotic world could be studied.

The key benefit of a microfluidic approach is that relaxation times to nonequilibrium steady-states will be short due to small volume diffusion times and high surface area-to-volume ratios, enabling rapid acquisition of comparative data sets. Fluid pressures between 1 MPa and 10 MPa (equivalent to the hydrostatic pressure at 100 to 1000 m ocean depth) at temperatures up to 100°C will be used. These high pressure and temperature requirements preclude the use of 'soft' materials (i.e. PDMS) commonly used in microfluidics. To be relevant, the microfluidic environment requires interstitial ultra-small reaction volumes featuring thin proton and electron conducting mineral membrane interfaces with specific catalytic properties separating a fluid mimicking a low pH ocean from one mimicking the alkaline hydrothermal vent fluid.

Detailed characterization of membrane structure and activity, as well as atomistic simulation of the metal sulfide nanocrystallites present in high concentration, both as membrane inclusions and simple cofactor sites for proto-enzymes, would be crucial to gain insight into the film characteristics most critical for achieving high catalytic rates of CO_2 hydrogenation.

This system achieves some of the capabilities of mitochondria and chloroplasts at a time prior to the evolution of lipids, proton pumps and ion-selective transmembrane protein channels. Such microfluidic devices offer an opportunity to study the chemiosmotic mechanisms that enabled the synthesis of increasingly complex organic molecules and that eventually enabled respiration by living organisms. This experiment provides a stringent test of the alkaline hydrothermal vent theory of the origins of life.

Results from such a study would significantly add to our understanding of origins of biological functionality at the nanoscale. Such knowledge is crucial for distinguishing biotic chemistry from normal chemical processes. As such it is relevant to defining biosignatures for planetary exploration and selecting relevant landing sites.

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