

Nanometric and hydrophobic green rust minerals upon exposure to amino-acids and nickel as prerequisites for a primitive chemiosmosis

NIL GAUDU¹, CHLOE TRUONG¹, ORION FARR^{1,2},
 ADRIANA CLOUET¹, OLIVIER GRAUBY², DANIEL
 FERRY², GEORGES ONA-NGUEMA³, FRANÇOIS
 GUYOT^{4,5}, WOLFGANG NITSCHKE¹ AND SIMON
 DUVAL¹

¹Bioénergétique et Ingénierie des Protéines (BIP) UMR 7281

²Centre Interdisciplinaire de Nanoscience de Marseille (CINAM) UMR 7325

³Institut de Minéralogie, Physique des Matériaux et Cosmochimie, CNRS UMR 7590

⁴Museum National d'Histoire Naturelle et Institut Universitaire de France (IUF)

⁵IMPMC, Muséum National d'Histoire Naturelle, Sorbonne Université, CNRS UMR 7590 (Paris)

Geological structures known as alkaline hydrothermal vents (AHVs) likely displayed energy dynamic characteristics analogous to current cellular chemiosmosis [1,2]. The chimney wall precipitating at the interface of the internal reducing alkaline fluid and the oxidizing iron-rich ocean contained iron-oxyhydroxide green rusts in the early Earth [3]. Under specific conditions, those minerals could have acted as non-enzymatic catalysts in the development of early bioenergetic chemiosmotic energy systems while being integrated in the membrane of AHV-produced organic vesicles [4,5]. Here, we show that the simultaneous addition of two probable AHV components, nickel and the amino-acid tryptophan, impacts green rust's physicochemical properties, especially those required for its incorporation in lipid vesicle's membranes. Firstly, they synergistically decrease the mineral size down to the nanometer scale, making it match with the thickness of organic dielectric barriers such as lipid membranes. Secondly, hydrogen bonding-mediated tryptophan adsorption at the surface of the crystals increases their hydrophobicity. These results suggest that such hydrophobic nano green rusts could fit into lipid vesicle membranes and could have functioned as a primitive, inorganic precursor to modern chemiosmotic transmembrane metalloenzymes, facilitating both electron and proton transport in early life-like systems.

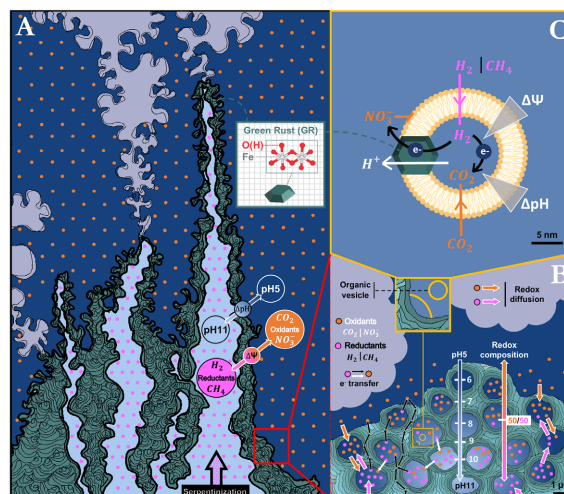
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Depiction of the Alkaline Hydrothermal Vent (AHV) setup close to life's emergence displaying:
 A) The physico-chemical and mineralogical properties of the vent: an internal reducing alkaline fluid (light blue fluid) springing from serpentinization processes and containing reducers such as H₂ and CH₄ (pink dots) at an alkaline pH11 value circulates upwards and mixes with the outside weakly acidic (pH5) and oxidative ocean (dark green fluid) containing oxidants such as CO₂ and NO₃ (orange dots) as well as high iron concentration, leading to the precipitation of iron-oxy-hydroxides such as green rust. This precipitate constitutes the chimney wall separating the internal reducing alkaline fluid from the external weakly acidic oxidizing seawater, thus building up apparent ΔpH (dark to light blue gradient) and ΔΨ (orange to pink gradient) across the wall.

B) A closer look at the microporous network within the chimney walls

C) A closer look at the organic vesicles formed upon green rust redox reactivity within the micropores: under these conditions, a nanometric, hydrophobic green rust crystals could be embedded in the nanometer-sized vesicle membrane which would provide a perfect seat for a proto-chemiosmosis to happen, based on the formation of cross-membrane ΔpH and ΔΨ.