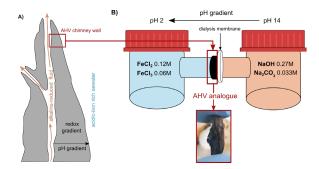
Fe²⁺ disproportionation within ironrich alkaline vent analogues reveals proto-bioenergetic systems

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Alkaline hydrothermal vents are very plausible environments for emergence of life on Earth. Reactive iron oxyhydroxides minerals present in the walls of such hydrothermal chimneys on the early Earth may have carried out proto-bioenergetic processes driven by redox and pH-gradients as hypothesized in the past [1] [2] [3] [4]. Studying the formation process of iron (oxy-hydr)oxides-containing barriers at the interface between an acidic Fe2+- and Fe3+-rich solution and a basic medium resembling conditions prevailing in primitive alkaline vents, we obtained experimental evidence of the previous hypothetical scenario. Over time, the initial pH gradient precipitates iron (oxy-hydr)oxides (magnetite, green rust and amakinite) and yields extremely reducing conditions, enabling the production of metallic iron Fe⁰ at ambient temperature via the disproportionation of Fe2+ into Fe3+ and Fe0. The close association of Fe⁰ with magnetite suggests the coupling of the thermodynamically favorable Schikorr reaction producing Fe³⁺ and H₂ through Fe(OH)₂ oxidation, with the thermodynamically unfavorable reduction of Fe²⁺ into Fe⁰. We interpret this coupling of exergonic and endergonic reactions as a proto-bioenergetic mechanism reminiscent of the process of electronic bifurcation, increasing the out of equilibrium reduction state of the system.

- [1] Russell, Hall & Martin (2010), Geobiology 8, 355-371.
- [2] Nitschke & Russell (2009), *Journal of Molecular Evolution* 69, 481-496.
- [3] Nitschke et al. (2022), Electrochemical Science Advances 3, e2100192.
 - [4] Duval et al. (2019), Interface Focus 9, 20190063.



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