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Fe^{2+} disproportionation within iron-rich 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 Fe^{2+}- and Fe^{3+}-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 Fe^0 at ambient temperature via the disproportionation of Fe^{2+} into Fe^{3+} and Fe^0. The close association of Fe^0 with magnetite suggests the coupling of the thermodynamically favorable Schikorr reaction producing Fe^{3+} and H_2 through $Fe(OH)_2$ oxidation, with the thermodynamically unfavorable reduction of Fe^{2+} into Fe^0. 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.

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