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Evaluating the plausibility of an electrochemical source of free cyanide in low-temperature prebiotic aqueous environments

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Reactions involved in the cyanosulfidic protometabolism could have plausibly generated precursors of RNA, proteins, and lipids required for first life on Earth from cyanide and its reactive derivatives. Because it was likely a common on prebiotic rocky planetary surfaces, this scheme has partially fueled the search for life elsewhere in the universe. It crucially depends on the availability of free cyanide (i.e., as HCN or CN^-) as a feedstock both early and late in the reaction sequence, and therefore demands a sustainable reservoir that can stockpile cyanide for subsequent generation and reaction. Researchers have proposed evaporative precipitation and sedimentary accumulation of sodium ferrocyanide salts in alkaline lakes, where elevated pH inhibits cyanide loss to the atmosphere, as a means to amass ferrocyanide ($Fe(CN)_6^{4-}$). However, because UV-driven decomposition of ferrocyanide in alkaline solutions to free cyanide is frustrated by efficient nighttime backreaction, thermal metamorphism of sodium ferrocyanide salts has become the leading proposed mechanism to liberate cyanide in its required, free form. Yet, this essential confluence of extreme geologic processes challenges the plausibility of this aspect of the reaction scheme.

In this study, we hypothesize that prebiotically relevant galvanic redox couples operating under alkaline aqueous conditions could have driven electrochemical processing of dissolved ferricyanide ($Fe(CN)_6^{3-}$) in low temperature aqueous settings to yield free cyanide without extreme thermal processing of ferricyanide evaporites. Experiments show that dissolved ferrocyanide can be reversibly converted to dissolved ferricyanide via UV photoemission; the cyanosulfidic protometabolism requires (bi-)sulfite sourced from atmospheric SO_2 to recycle the ferricyanide back to ferrocyanide and promote continued reaction. Here, we show that this ferricyanide, generated through the previously acknowledged UV photoemission route, or, alternatively, electrochemical oxidation, can be a ready source of free cyanide. Our proof-of-concept experiments show that concentrations of tens of millimolar ferricyanide can electrochemically yield millimolar concentrations of free cyanide in under 5 hours at high electrochemical potentials. Thus, electrochemical reactions could represent a sustained free cyanide source in alkaline environments, provided that elevated electrical potentials are achieved. Continued examinations of these reactions under more geologically relevant conditions will permit further evaluation of their potential role in prebiotic chemistry.