

## The Formation of Ferrocyanide Evaporites on Early Earth

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Cyanide plays a central role in recent origin of life hypotheses because it simultaneously forms ribonucleotides, amino acids, and lipid precursors [1]. Hydrogen cyanide likely formed in Earth's early atmosphere due to atmospheric photochemistry [2] and comet/asteroid impacts [3]. Patel et al. [1] hypothesize that this cyanide accumulated in surface environments by: (1) complexing with ferrous iron ( $\text{Fe}^{2+}$ ) as ferrocyanide ( $\text{Fe}(\text{CN})_6^{4-}$ ), (2) precipitation from evaporating closed-basin brines as ferrocyanide salts, and (3) thermal decomposition to form free cyanides. Although steps 1 and 3 are supported by theory and experiments [1,4], plausible early Earth conditions leading to salt precipitation from ferrocyanide brines have not been explored.

To determine if ferrocyanide salts could accumulate on early Earth, we developed a numerical model of aqueous ferrocyanide in the Na-K-Ca-Mg-Fe-H-OH-Cl-CO<sub>3</sub>-HCO<sub>3</sub>-CO<sub>2</sub>-CN-HCN-Fe(CN)<sub>6</sub> system, and applied this model to closed-basin evaporation. We also measured ion activities in Na<sub>4</sub>Fe(CN)<sub>6</sub>, Ca<sub>2</sub>Fe(CN)<sub>6</sub>, and Mg<sub>2</sub>Fe(CN)<sub>6</sub> brines, which are needed because ferrocyanides are poorly characterized at high concentrations. To develop our model, we used the Pitzer ion interaction approach in FREZCHEM [5] as a basis, and added in cyanide and ferrocyanide chemistries.

By applying the model to plausible early Earth conditions ( $T = 0 - 25^\circ\text{C}$ ,  $p\text{CO}_2 = 0.1 - 1$  bar,  $p\text{HCN} = 10^{-8} - 10^{-5}$  bar), we find that ferrocyanide salts form only in concentrated carbonate solutions, and preferentially at low temperatures. Furthermore, we predict that evaporating solutions will form a salt sequence of Na<sub>4</sub>Fe(CN)<sub>6</sub>·10H<sub>2</sub>O followed by sparingly soluble mixed K-Mg and/or K-Ca ferrocyanides. Total aqueous cyanide concentrations (as ferrocyanide) can be up to 1–2 mol kg<sup>-1</sup>. Such carbonate environments form in closed-basin lakes in contact with ultramafic rocks and so our results suggest a very specific environment for prebiotic chemistry. Further work will test the thermal decomposition products of predicted salt assemblages.

Ref: [1] Patel et al. (2015) *Nature Chemistry* 7(4): 301-307. [2] Zahnle (1986) *JGR* 91: 2819-2834. [3] Fegley et al. (1986) *Nature* 319: 305-308. [4] Keefe and Miller (1996) *Orig. of Life and Evo. of the Bio.* 26(2): 111-129. [5] Marion et al. (2003) *GCA* 67(22): 4251-4266.