Supporting Information For:

Photocatalytic Reduction of Fumarate to Succinate on ZnS Mineral Surfaces

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*Ruixin Zhou and Marcelo I. Guzman**

Department of Chemistry, University of Kentucky, Lexington, KY 40506

*Corresponding author's email: marcelo.guzman@uky.edu

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Content **Pages**

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Context to the Origin of Life

The origin of life is one of the most important unsolved questions of science,[1] which combines several diverse disciplines, including physical chemistry. In this context, the large number of evolutionary scenarios that have been considered for the origin of life can be constrained by simultaneously considering bioenergetic, physical, and geological factors.[2] The connection between the origin of life and anabolism was recognized by Hartman, who introduced the concept of early metabolism by speculating a set of reactions conductive to the origin of life.[3] Before the discovery of the rTCA cycle, early metabolism was proposed as driven by UV light to fix N_2(g) and CO_2(g).[3] An autocatalytic rTCA cycle acting as a central biosynthetic pathway was introduced for a different model for driving redox reaction of thioacids powered by the oxidative formation of pyrite (FeS_2).[4] Despite the chemical energy source considered in those studies, the emerging concept of universal metabolism connecting all metabolic pathways is valid across all early metabolism models.[5-6] In addition, the autocatalytic rTCA cycle of thioacids powered by FeS_2 formation[4] was proposed as important for catalysis of slow reactions.[4] However, fast and efficient conversions within putative prebiotic metabolic systems for the rTCA cycle and redox systems lack any experimental support.[7] Instead, photocatalyzed reactions have been proposed as fundamental for the origin of life by directly providing carboxylic acids to the rTCA cycle.[7]

Our work advances a proposed evolutionary scenario that satisfies the known constraints for the emergence of life on Earth powered by UV solar radiation activating compartmentalized photocatalytic minerals such as sphalerite (ZnS) found around shallow water hydrothermal systems first proposed by Guzman and Martin.[8-9] The Zn world hypothesis has improved such a system as the driver of CO_2 reduction to yield the building blocks for the first biopolymers, which serve as templates for the synthesis of longer biopolymers while acting as a protective shield that

prevents photo-degradation.[2, 10] In addition, predictions from the Zn world hypothesis about the role of Zn^{2+} ions in modern organisms have been successfully tested.[10] Several reactions of the rTCA cycle can be driven by illuminated ZnS at circumneutral pH and 288 K due to the reducing power of conduction-band electrons poised at -1 V vs NHE.[7] ZnS is believed to have been prevalent in the waters of early Earth[11] and possess a large band gap (E_{BG} = 3.59 eV).[12] Thermodynamically, ZnS has the potential to facilitate all reductions in the rTCA cycle (varying from -0.2 to +0.15 vs NHE)[13] to proceed in the presence of a scavenger to poise the valence-band hole at +2.6 V vs NHE. The photochemical model has the advantage to harvest energy from the sun to open new reaction pathways by the interactions of excited-state species and radicals. This work does not assume a direct utilization of photochemical energy to just boost reducing power from other pathways but highlights the unique role that photocatalysis may have played in the origin of life.

A final consideration is given to the problem of thermodynamic control, as given by the free-energy difference of the reaction. Thermodynamic control does not play a role in determining the formation of succinic acid during the photocatalyzed reduction of fumaric acid in ZnS colloidal suspensions. Instead, the reaction selected is kinetically controlled, and the rate of formation of succinic acid is a key limitation. Furthermore, the reaction product is formed irreversibly, probably because succinic acid lacks the ability to interact with the surface of ZnS at the C_2-C_3 position for the reverse reaction to proceed. As a result, the consecutive removal of two hydrogens is mechanistically unfavorable.

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