

## Fumarate Photoreduction by Zinc Sulfide Nanoparticles: Ultrafast Studies of Prebiotic Photochemistry

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Photochemical reactions at mineral surfaces have been proposed as essential steps in the origins of life. In particular, the photoexcitation of semiconductor minerals such as sphalerite (ZnS) by ultraviolet light generates electrons capable of driving reduction reactions in the reverse tricarboxylic acid (rTCA) cycle [1]. The rTCA cycle has been proposed as a precursor to the oxidative cycle found in modern mitochondria.

We used liquid chromatography coupled to mass spectrometry (LCMS) to investigate possible side reactions in the ZnS photocatalyzed steps of the rTCA cycle, finding a diversity of end products in most cases. However, the proton-coupled, two-electron reduction of fumarate to succinate occurred in high yield with no alternative products. We chose this system to investigate the roles of solution conditions, surface structure and reagent chemistry in controlling the outcome of a plausible prebiotic interfacial multi-electron redox reaction.

We studied the timescale for interfacial one-electron transfer using ultrafast optical spectroscopy. We observed a significant reduction of the fluorescence lifetime of photoexcited ZnS in the presence of fumarate, indicating that interfacial electron transfer occurs on the picosecond timescale. Transient optical spectroscopy showed complex kinetics on the same timescale, suggesting a role for surface sites in charge transfer. We developed two candidates for the reaction mechanism that we are evaluating using studies of reaction kinetics, ZnS surface properties and the affinity of organic metabolites on zinc sulfide surfaces. By establishing the mechanistic controls on fumarate reduction, we seek to provide constraints on the early Earth environments that could permit photochemical transformation of metabolic organic molecules.

[1] X.V. Zhang *et al* (2006) *J. Photochem. and Photobiol.* **185**, 301-311