# Photocatalytic Mineral-Promoted Protometabolic Pathway

PUNAM DALAI[1] AND NITA SAHAI[2, *]

[1]Department of Polymer Science, University of Akron, Akron, OH 44325-3909. pdalai@uakron.edu
[2]Department of Polymer Science, University of Akron, Akron, OH 44325-3909. *sahai@uakron.edu

The emergence of metabolism in protocells, the earliest life-like entities, is one of the central questions in the origins of life field. The crux of the issue is how were metabolic pathways catalyzed before the evolution of enzymes? Here we developed a synthetic protocell system capable of a rudimentary photoheterotrophic metabolism catalyzed by photocatalytic minerals. We show that photocatalytic minerals could have played the role of "prebiotic enzymes" by catalyzing a transmembrane electron transfer chain while generating a transmembrane pH gradient and reducing NAD to NADH inside the model protocell. This system is analogous to the development of a modern cellular proton motive force with acidification of the extracellular region and reduction of NAD to NADH in the interior of the cell.

In detail, our model protometabolism is composed of palmitoyl-oleoyl-phosphocholine (POPC) or oleic acid (OA) vesicles as model protocells; terminal electron acceptor, $NAD^+$; electron mediator, $Rh(bipy)_3^{3+}$, encapsulated in the vesicles; electron shuttle, naphthopyrene or perylene, embedded in the lipid bilayer; photocatalytic minerals (CdS, $FeS_2$, CdSe, $TiO_2$, or ZnO); and terminal electron donor, (serine, glycine or isopropanol) present in the extra-vesicular medium. The system is irradiated with UV light and the generation of NADH is monitored by fluorescence spectroscopy. The generation of the pH gradient is determined by co-encapsulating puranine, a pH-senstive fluorscent dye, in the vesicles and monitoring the change in fluorescence emission.

The results show the ability of various photocatalytic minerals present in the extravesicular medium to drive redox chemistry inside vesicles, while simultaneously generating a transmembrane pH gradient and reducing $NAD^+$ to NADH within the vesicle (model protocell). The enzymatically active NADH formed in the experiments could then potentially drive subsequent biochemistry in a complex metabolic pathway. Thus, we have demonstrated a part of a rudimentary photoheterotrophic protometabolic pathway.