## Following the fundamentals of serpentinization: an experimental approach to mineral and organic reaction pathways at serpentinizing conditions

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Before life on Earth, organic compounds and minerals coexisted in geologic settings. Different geologic processes likely shaped the metabolic pathways we see today. But what geologic processes altered the first organic matter? If an essential geologic process is common throughout the universe, could it play a part in the formation of new life on other worlds? Of geologic processes, serpentinization is potentially the most common water-rock reaction in our solar system. The progressive hydration from ultramafic silicates to serpentine minerals provides an array of alkaline and redox active chemical environments that could facilitate different organic chemical reactions. The impact that these newly formed minerals and the resulting fluid chemistry can have on organic reactions is still largely unknown. Understanding the mechanisms of organic reactions in the presence of minerals will give a better overview of the chemistry available in abiotic environments and ideas for how metabolisms, as we know them, could be connected.

By performing simplified experiments using both hydrothermal and electrochemical methods, I can determine the role of minerals in abiotic organic reactions. The experimental mixtures contain only one organic compound as the starting material and one pure mineral phase so that detailed kinetic studies can be investigated. By focusing on a singular functional group, the exact reactions can be pursued as a component of the overall reaction web for many different functional groups. My focus is the reaction pathways of carboxylic acids. Carboxylic acids are prevalent in Earth-based metabolism and abundant in abiotic samples such as the Murchison meteorite [1]. Previous work has demonstrated that at hydrothermal conditions, phenylacetic acid ( $C_6H_5CH_2COOH$ ; PAA) in the presence of magnetite (Fe<sub>3</sub>O<sub>4</sub>) or hematite (Fe<sub>2</sub>O<sub>3</sub>) results in the formation of several different organic product pathways at hydrothermal conditions (300°C, 100 MPa) [2]. Dibenzyl ketone (( $C_6H_5CH_2$ )<sub>2</sub>CO; DBK) and benzoic acid ( $C_6H_5COOH$ ; BA) were both observed products in these experiments. It was proposed that the reaction path to form BA from PAA was a stepwise oxidation through the reaction intermediates of benzyl alcohol (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH) and benzaldehyde (C<sub>6</sub>H<sub>5</sub>CHO) by the loss of electrons to redox active metal cations in solution or at the surface of a mineral [2,3]. Magnetite, a promininate mineral product of serpentinizing reactions with iron-containing starting minerals, may serve as an electron conductor during hydrothermal reactions. The exact mechanism is unknown and the extent to which magnetite and hematite differ as potential electron acceptors during organic reactions is unclear.

I performed experiments with propanol ( $CH_3(CH_2)_2OH$ ) and propionaldehyde ( $CH_3CH_2CHO$ ) as analogs to the benzyl alcohol and benzaldehyde intermediates hypothesized in hydrothermal experiments. Propanol and propionaldehyde, unlike aromatic compounds, are soluble in room temperature water and have been used previously in experiments to investigate the formation of acetic acid in oil field brines [4]. I will discuss the results of preliminary experiments to probe the use of magnetite as a catalyst for the electrochemical oxidization of propanol to propanoic acid ( $C_3H_5COOH$ ) at the basic pH conditions of serpentinization. I am conducting complimentary hydrothermal experiments starting with butanoic acid ( $CH_3(CH_2)_2COOH$ ) to see if propanoic acid will still form in hydrothermal conditions. In this way, electrochemistry can be used as a tool to understand the mechanisms of hydrothermal reactions and the role that minerals can play as electron acceptors for carboxylic acid reaction pathways.

[1] Martins Z. (2011) *Elements* [2] Johnson KN (2017) *PhD Dissertation, Arizona State University* [3] Yang Z (2015) *J. Org. Chem* [4] McCollom TM and Seewald JS (2003) *GCA* 

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