

**HYDROTHERMAL MINERAL-ASSISTED ORGANIC TRANSFORMATIONS OF CARBOXYLIC**

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**Introduction:** Carboxylic acids are found across diverse natural environments including hydrothermal systems, carbonaceous chondrites and inside the cells of organisms. The goal of this project is to understand the organic transformations of carboxylic acids in natural environments, and to contribute toward understanding their involvement in pre-biotic chemistry. We have performed experiments under hydrothermal conditions (300°C and 1000 bar) to analyze the effects of minerals on carboxylic acids, as well as their reactivity in water alone. Previous studies of carboxylic acid reactivity with minerals have focused on simple molecules such as acetic acid and valeric acid [1] and [2] and have shown that iron bearing minerals increase the rate of decomposition for these small molecules. The carboxylic acids used in this study differ from those in the previous work by the addition of a phenyl ring, which facilitates the investigation of mechanistic pathways for product formation. Decarboxylation (i.e.,  $\text{RCO}_2\text{H} \rightarrow \text{RH} + \text{CO}_2$ ) is the major reaction pathway for carboxylic acids in the absence of minerals under hydrothermal conditions, but new additional products are formed in the presence of minerals.

**Results in water:** The compounds studied include phenylacetic acid ( $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ) and hydrocinnamic acid ( $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{COOH}$ ), which differs from phenylacetic acid by the addition of a  $\text{CH}_2$  group between the phenyl ring and the carboxyl group. This additional carbon linkage allows us to investigate a compound more like lipids or other carboxylic acids with longer aliphatic chains. The addition of this alkyl carbon drastically changes the rate of reaction, slowing down the overall rate of conversion. The major products are toluene and ethyl benzene, from phenylacetic acid and hydrocinnamic acid respectively. Phenylacetic acid reaches ~80% conversion within ~50 hours [3] while hydrocinnamic acid reaches only ~20% conversion in ~1000 hours. For phenylacetic acid, the only product is toluene. The major product for hydrocinnamic acid is ethyl benzene and additional minor products result from intramolecular reactions.

**Results with minerals:** The presence of magnetite ( $\text{Fe}_3\text{O}_4$ ) in hydrothermal experiments results in additional products of larger size than the parent acids. In experiments with phenylacetic acid, the presence of

magnetite did not enhance the rate of toluene production from decarboxylation, but did activate additional product pathways including the formation of diphenyl alkanes, alkenes and ketones. In addition, benzoic acid, a carboxylic acid one  $\text{CH}_2$  group shorter than the parent compound was produced. The hydrocinnamic reaction pathways were altered by the magnetite to a greater extent. A series of reactions over a prolonged duration (1000h at 300°C, 1 kbar) demonstrates that magnetite enhances the overall conversion of hydrocinnamic acid from ~20% in water alone to ~80%. In addition to forming the same variety of compounds as observed in the phenylacetic acid experiments, hydrocinnamic acid experiments also produced polymerization products as a result of the acid's aliphatic chain and an array of products resulting from secondary reaction pathways.

Magnetite facilitates the formation of larger products from phenylacetic acid and hydrocinnamic acid. Hematite ( $\text{Fe}_2\text{O}_3$ ) was capable of facilitating the same reactions observed for magnetite but to a much lesser extent. Not all minerals are capable of producing these kinds of organic transformations. Experiments with quartz ( $\text{SiO}_2$ ) did not differ from the results in water alone. Possible reasons for these differences include the zero point of charge which influences the charge distribution on the mineral's surface, mineral structures, redox states, available surface area and electron mobility along band gaps of specific minerals.

Investigations of this kind are fundamental to improve our understanding of how organic compounds can be transformed abiotically in natural environments on Earth and other worlds. The continued work involves investigating the mineralogical properties that variably affect organic reactions. Results of this study can provide clues as to the variety of organic processes and organic abundances available for emergent life.

**References:** [1] Bell J. L. S., Palmer DA, Barnes H. L., Drummond S. E. (1994) *Geochim Cosmochim Acta*, 58, 4155-4177. [2] McCollom T.M. and Seewald J.S. (2003) *Geochim Cosmochim Acta*, 19, 3645- 3664. [3] Glein C. R. (2012) *PhD Dissertation, Arizona State University*