## The Effect of Magnetite upon the Transformations of Carboxylic Acids at Hydrothermal Conditions

KRISTIN JOHNSON<sup>1</sup> LYNDA WILLIAMS<sup>2</sup> IAN GOULD<sup>1</sup> HILAIRY HARTNETT<sup>1,2</sup> EVERETT SHOCK<sup>1,2</sup>

 <sup>1</sup>School of Molecular Sciences, Arizona State University, Tempe 85287-1404
<sup>2</sup>School of Earth and Space Exploration, Arizona State University, Tempe 85287-1404

Natural organic transformations occur in the presence of minerals in hydrothermal systems, sedimentary basins, and meteorite parent-bodies, and organic transformation pathways at mineral surfaces differ dramatically from reactions in water alone [1]. In the present study, we explored the hydrothermal (300°C, 100 MPa) effects of magnetite (Fe<sub>3</sub>O<sub>4</sub>) on transformations of phenylacetic (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>COOH; PAA) and hydrocinnamic acids (C<sub>6</sub>H<sub>5</sub>(CH<sub>2</sub>)<sub>2</sub>COOH; HCA). We find that magnetite opens new reaction pathways, not available in water alone, which can lead to the generation of more complex organic compounds. PAA and HCA differ by the addition of a phenyl ring from the acetic and valeric acids used in previous mineral-organic studies [2,3]. Aromatic ring structures facilitate the investigation of mechanistic pathways for product formation and provide analogs for lipids and lignin. In the absence of minerals, decarboxylation is the major hydrothermal reaction pathway and the products formed are smaller than the reactants. Specifically, PAA reaches 80% conversion in 50 h and forms only toluene [4] while HCA reaches only 20% conversion after 1000 h and primarily yields ethyl benzene. In the presence of magnetite new reaction pathways yield organic products that are larger than the reactants. In the case of PAA, the magnetite-activated product pathways lead to larger diphenyl alkanes, alkenes, and ketones. Magnetite enhanced the overall conversion of HCA from 20% in water alone to 80% (1000 h). In addition to the compounds observed in the PAA experiments, magnetite-activated HCA experiments also produced polymerization products and an array of new compounds resulting from secondary reaction pathways. The new reaction pathways may be a result of hydrogen atoms attracted to the magnetite surface. If so, affiliation of the carboxyl group with the protonated surface would create an environment where molecules readily interact in ways that are not possible in water alone. These results demonstrate how mineral surfaces can guide hydrothermal organic reactions to greater complexity, which may be common in natural mineral-organic systems.

[1] Shipp JA et al. (2014) *PNAS* [2] Bell JLS et al. (1994) *GCA* [3] McCollom TM and Seewald JS (2003) *GCA* [4] Glein CR (2012) *PhD Dissertation*, *Arizona State University*