

INVESTIGATING THERMAL CATALYTIC CONVERSION OF A POLYCYCLIC AROMATIC HYDROCARBON (PAH) TO A BIOLOGICALLY EXTANT QUINONE ON PLANETARY RELEVANT MINERAL SUBSTRATES: IMPLICATIONS FOR ORIGINS OF LIFE. S. Sharma¹, S. M. Drummond², C. M. Maloney², S. Gonzalez Henao³, V. Karanauskas³, L. R. Dewitt², C. Mulu², A. Omran⁴, J. Weber⁵, L. M. Barge⁵, P. Videau^{6,7}, M. O. Gaylor², ¹Blue Marble Space Institute of Science, Seattle, WA, USA, ²Dakota State University, Madison, SD, USA, ³Instituto de Astrobiología de Colombia, Bogotá, Colombia, ⁴University of North Florida, Jacksonville, FL, USA, ⁵NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA, ⁶Southern Oregon University, Ashland, OR, USA, ⁷Bayer Crop Science, Chesterfield, MO, USA

Introduction: Polycyclic aromatic hydrocarbons (PAHs) are abundant in astrochemical environments and are dispersed into planetary environments via extra-terrestrial infall where they may undergo thermal-catalyzed reactions on mineral surfaces to produce biomolecular precursors (e.g., quinones) that may have influenced origins of life chemistries [1,2,3].

To address the reasonableness of this idea, and seeking to build upon earlier foundational work [1], we assessed the catalytic potential of the planetary minerals montmorillonite (hereafter MONT), kaolinite (hereafter KAO), a Mohave Mars Simulant (hereafter MMS), and a carbonaceous asteroid simulant (hereafter AST) to catalyze conversion of the representative cosmic PAH anthracene (hereafter ANTH) to 9,10-anthraquinone (hereafter ANTHQ), a secondary metabolite in e.g., bacteria, fungi, lichens, higher plant taxa, and some insect taxa. We assessed the kinetics of ANTHQ conversion, as well as ANTH and ANTHQ loss over a wide range of temperatures encompassing diverse astrochemical environments (25-500°C).

And inspired by our interests in the PAH (or Aromatic) World Hypothesis and its core tenet that PAHs may undergo pi stacking to produce oligomers that could have plausibly served as primitive information coding molecules, and upon observing production of dimers of ANTH and its isomer phenanthrene (hereafter PHEN) in early experiments with the AST, we assessed the kinetics of production and loss of the dimers 9,9'-bianthracene (hereafter BIANTH) and 9,9'-biphenanthrene (hereafter BIPHEN) over this temperature range. To the best of our knowledge, this is the first report of the kinetics of production/loss of ANTH, ANTHQ, BIANTH, and BIPHEN on planetary relevant mineral phases in the context of origins of life studies.

Results: Apparent rates of ANTHQ production on MONT, KAO, and AST exhibited sigmoidal behavior over the temperature range, while ANTHQ production on MMS exhibited quadratic behavior. We hypothesized that saturation of catalytic sites, combined with loss of ANTH and ANTHQ, likely accounted for this trend. To test this idea, we assessed the production/loss of ANTHQ from the substrates at the median 250 °C over a 60 min interval. ANTHQ production occurred in the order AST > MONT > KAO > MMS, while ANTHQ loss occurred in the order MMS > KAO > AST

≈ MONT. We then assessed the kinetics of ANTH and ANTHQ loss from the substrates. Loss of ANTH and ANTHQ was quadratic over the temperature range. ANTH loss occurred in the order MMS > MONT > KAO, while ANTHQ loss occurred in the order MONT >> KAO > MMS. In contrast, apparent rates of loss of ANTH and ANTHQ from the AST were sigmoidal.

We observed appreciable production of the ANTH dimers BIANTH and BIPHEN on the AST substrate, but observed only trace amounts on the other substrates. Apparent rates of production of BIANTH were significantly greater than BIPHEN above 100 °C on the AST.

Conclusions: ANTHQ production on the mineral substrates assessed demonstrates plausible non-enzymatic routes to biological quinones in prebiotic environments encompassing a wide range of plausible thermal regimes. Loss of ANTH and ANTHQ with temperature accounts in part for the observed rates of ANTHQ production on the substrates. AST catalyzed conversion of ANTH to BIANTH and BIPHEN dimers in appreciable yields, while the other substrates did not do so. ANTH Dimer production on AST presents a plausible prebiotic route to stacked PAH oligomer formation on carbonaceous asteroid substrates that could serve as information coding molecules for emergent biochemistries in prebiotic environments (in support of the Aromatic World Hypothesis). Loss of ANTH and ANTHQ from the substrates with temperature demonstrates a plausible dispersal pathway for seeding emergent biochemistries at distant locales in prebiotic planetary environments.

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