

ABIOTIC SYNTHESIS OF ORGANIC COMPOUNDS IN HYDROTHERMAL SYSTEMS:
DEHYDRATION REACTIONS BY SMECTITE CATALYSTS. P.A. O'Day, L.B. Williams,
J.R. Holloway, Arizona State Univ., Tempe, AZ, 85287-1404, and J.R. Delaney, Univ. of
Washington, Seattle, WA 98195

Since the discovery of a diverse, hydrothermally-supported biota at seafloor vents 20 years ago, mid-ocean ridge hydrothermal systems have been postulated as sites in which the abiotic synthesis of simple organic molecules might occur as precursors to the origin of life [1]. Previous work has focused on the role of sulfide catalysts in promoting carbon reduction and hydrocarbon synthesis, primarily by Fischer-Tropsch-type pathways [e. g., 2-3]. Clay minerals and zeolites have also been considered as templates for abiotic synthesis [e.g., 4]. The thermodynamics of a variety of dehydration reactions as a function of temperature and pressure were examined by Shock [5], but few studies have examined specific mechanistic pathways for organic synthesis by mineral catalysts under seafloor hydrothermal conditions.

In a previous study [6], we proposed that formation of C₁-C₄ alcohols may be possible metastable reaction products from seafloor diiking events that generate elevated concentrations of CO₂ + H₂. Alcohol formation may be catalyzed by phase separation and reaction with newly precipitated sulfide surfaces in the optimum temperature range of 200-300°C at sub-seafloor pressures (200-500 bars). Solubility of C₁-C₄ alcohols increases with decreasing temperature, allowing for subsequent aqueous reactions with mineral surfaces. Dehydration reactions among short-chain alcohols in the presence of a strong Brønsted-acid catalyst have been shown to produce C₂-C₅ alkenes and C₆-C₈ aromatic compounds [7]. One proposed reaction mechanism is the formation of surface methoxy intermediates from methanol adsorbed at acidic oxygen sites, followed by dehydration and formation of C-C double bonds [8]. Calculations (using SUPCRT92) show that overall methanol dehydration reactions are thermodynamically favored at hydrothermal temperatures (100-375°C) and pressures (100-500 bars) in aqueous solution, and are generally more favored with decreasing temperature. Smectite or other sheet silicates with exchangeable interlayer sites would serve as effective sorbents of alcohols and as strong Brønsted-acid catalysts at low to circum-neutral pH. Recent discovery of significant amounts of smectite within sulfide edifices recovered from MOR vents, in which sulfide minerals are mixed within clay pods, suggests the possibility of natural catalysis by this alcohol-initiated pathway. Results from laboratory experiments of alcohol reaction with smectite under hydrothermal conditions will be discussed.

[1] J. B. Corliss, J. A. Baross, S. E. Hoffman, *Earth. Ocean. Acta* **SP**, 55 (1981).

[2] G. Wächtershäuser, *Prog. Biophys. Molec. Biol.* **58**, 82 (1992).

[3] M. J. Russell, R. M. Daniel, A. J. Hall, J. A. Sherringham, *J. Mol. Evol.* **39**, 231(1994).

[4] A. G. Cairns-Smith, *Genetic Takeover and the Mineral Origins of Life*. Cambridge University Press (1982).

[5] E. L. Shock, *Geochim. Cosmochim. Acta* **57**, 3341 (1993).

[6] P. A. O'Day, J. R. Delaney, M. D. Lilley, J. R. Holloway, *EOS* **78**, F774 (1997).

[7] C. D. Chang, A. J. Silvestri, *J. Catal.* **47**, 249 (1977).

[8] W. W. Kaeding, S. A. Butter, *J. Catal.* **61**, 155 (1980).