

DISSOLVED CARBON MONOXIDE IN HYDROTHERMAL FLUIDS ON SOLAR SYSTEM BODIES: EXPERIMENTAL STUDY OF REACTIVITY AND ORGANIC SYNTHESIS.

M. Yu. Zolotov¹, J. S. Seewald², and T. M. McCollom³,
¹Department of Geological Sciences, Arizona State University,
Tempe, AZ 85287, zolotov@asu.edu; ²Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543; ³LASP, University of Colorado, Boulder, CO 80309.

Introduction: Carbon monoxide was the major carbon gas in the solar nebula and was involved in the formation of comets and some bodies in the outer solar system (e.g., Triton, Pluto). Heating of bodies containing CO and H₂O ices should have led to interaction of CO with liquid water. At low temperatures this interaction results in formation of formic acid, but at higher temperature CO₂ and H₂ form via the water-gas shift reaction: CO + H₂O → HCOOH (formic acid) → CO₂ + H₂ (1). We conducted experiments to investigate the rate of reaction (1) in liquid water and observe formation of organic by-products of the CO-H₂O interaction.

Hydrothermal experiment: A 1200-hour experiment was conducted in a flexible gold-titanium cell apparatus at 350 bar and 150°C, 200°C, and 300°C without a mineral phase. The apparatus [1] allows sampling and injection of fluid during runs. A 150 mmolar solution of isotopically enriched (99% ¹³C) formic acid in deionized water was initially heated at 300°C. During the experiment, changing temperature, injections of deionized water, and injection of CO gas perturbed the C-O-H system. Following formic acid decomposition, the concentration and isotopic composition of CO₂(aq), H₂(aq), aqueous hydrocarbons, carboxylic acids, and alcohols were monitored with GC, GC-MS, and IC.

Results: At 300°C, comparison of measured CO, CO₂, and H₂ concentrations with values predicted at thermodynamic equilibrium for reaction (1) in liquid water indicate equilibration on time scales of hours. Perturbation of the system by decreasing the temperature from 300°C to 200°C resulted in fast (<24 h) re-equilibration among aqueous CO, CO₂, and H₂. After a temperature decrease from 200°C to 150°C, the concentration of CO decreased slightly toward an equilibrium value but had not attained equilibrium after 63 h. Following injection of CO and deionized water at 150°C, we observed a decrease in CO concentration and an increase in CO₂ and H₂ concentrations according to Eq. (1). Although reaction (1) is relatively sluggish at 150°C, the half-life (*t*_½) for conversion of CO to CO₂ and H₂ is estimated at about 550 hours, which is very rapid on a geologic time scale. The rate of reaction (1) increased after temperature was elevated from 150°C to 200°C. At 200°C, *t*_½ is ~25 h. Aqueous CO, CO₂, and H₂ reached equilibrium concentrations in ~300 hours after the last temperature increase. At 300°C and 200°C, measured concentrations of formic acid corresponded to calculated equilibrium amounts. At 150°C, the equilibration of formic acid was not attained during the time of the experiment. Although ¹³C-labeled CH₄ and methanol were detected, measured concentrations are much lower than at chemical equilibrium. Production of C₂₊ organic compounds was not observed.

Discussion: Heating of H₂O- and CO-bearing solar system bodies would have rapidly converted CO-rich solutions to H₂- and CO₂-rich solutions. If H₂ escapes owing to low solubility, the remaining aqueous solution becomes more oxidizing and CO₂-rich. Reaction (1) could have contributed to oxidation of bodies in the other solar system and, to a lesser extent, parent bodies of chondrites.

References: [1] Seyfried W. E. et al. (1987) In *Hydrothermal Experimental Techniques*, John Wiley and Sons, N. Y., 216-240.