

BIOGENIC VS. ABIOGENIC ISOTOPE SIGNATURES OF REDUCED CARBON COMPOUNDS: A LESSON FROM HYDROTHERMAL SYNTHESIS EXPERIMENTS. J. Horita¹, D.E. Allen², M.E. Berndt², and W.E. Seyfried, Jr.², ¹Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O.Box 2008, MS 6110, Oak Ridge, TN 37831-6110 (horitaj@ornl.gov) and ²Department of Geology and Geophysics, University of Minnesota, MN 55455-0219.

Introduction: With growing interest in and demonstrated cases of inorganic hydrothermal synthesis of reduced or organic carbon compounds from CO and CO₂, it becomes crucial to establish geochemical criteria to distinguish reduced/organic carbon compounds of abiogenic origin from those of biogenic origin with overwhelming abundances on the surface and in subsurface of the Earth. Chemical and isotopic compositions, particularly ¹³C/¹²C ratios, of reduced/organic carbon compounds have been widely utilized for deducing the origins and formation pathways of these compounds. An example is isotopic and C₁/(C₂+C₃) ratios of natural gases, which have been used to distinguish bacterial, thermogenic, and possible abiogenic origins. Another example is that ancient graphitic carbon with δ¹³C values <-25‰ has been considered of biogenic origin. Although these criteria could be largely valid, growing data including those from our hydrothermal experiments suggest that a great caution must be exercised.

Experimental Data:

Light hydrocarbons. We demonstrated that minerals and alloys enriched in native transition metals (Fe, Ni) can catalyze hydrothermal reduction of HCO₃⁻(aq) to methane and other light hydrocarbons under conditions similar to midocean ridges ([1], [2]). It was found that abiogenic CH₄ thus formed at 200-300°C has very low δ¹³C values (-20 to -54‰) and high C₁/(C₂+C₃) ratios (>10³), which are essentially indistinguishable from those of microbial CH₄. Kinetic ¹³C/¹²C fractionation associated with abiogenic CH₄ formation (-35 to -50‰) are as large as those by methanogenic bacteria. Literature data on Fisher-Tropsch reactions (CO Ψ light hydrocarbons in dry conditions) also exhibited large negative kinetic fractionations ([3], [4]). ¹³C/¹²C distributions among abiogenic methane and its homologs (ethane, propane) can be either normal (C₁<C₂<C₃) or inverse (C₁>C₂>C₃) ([4], [5]).

Organic acids. We also investigated ¹³C/¹²C fractionation during the formation of formate (HCOO⁻) from HCO₃⁻(aq) at 200-400°C. The formate was depleted in ¹³C by 3‰ (400°C) to 25‰ (200°C) compared to HCO₃⁻(aq). These large kinetic fractionations produced formate with low δ¹³C values (<-25‰). To our knowledge, no isotopic fractionation has been determined for the synthesis of other organic acids, but it is known that intramolecular ¹³C/¹²C fractionation be-

tween methyl and carboxyl carbons is normal, δ¹³C(CH₃-)<δ¹³C(-COOH), for natural acetic acids, and is inverse for synthetic ones [6].

Amino acids and other organic compounds. Virtually no isotopic study has been conducted for inorganic synthesis of complex organic compounds. Intramolecular isotopic heterogeneity and site-specific isotope fractionation are reported for many organic compounds [7]. However, no intramolecular ¹³C/¹²C fractionation is observed in synthetic glycine [8].

Conclusions:

Limited experimental results from our studies and the literature demonstrated that abiogenic processes during the formation of reduced/organic carbon compounds can involve larger negative isotope fractionation. Thus, the isotopic composition of individual compounds alone is not sufficient to distinguish biogenic and abiogenic origins. A combination of multiple isotopes (¹³C/¹²C, D/H, ¹⁵N/¹⁴N, ¹⁸O/¹⁶O) and intramolecular/site-specific isotope fractionation of single compounds hold greater promise for this purpose. We need to better understand not only the mechanisms and processes, but also isotopic fractionation during the abiogenic formation of organic compounds.

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