Compound specific hydrogen and carbon isotopes as a tool to distinguish abiogenic from biogenic hydrocarbons

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Recent reports of methane in the atmosphere of Mars raise the possibility of bacterial methanogenesis on Mars. Resolving the question of the origin of methane on Mars is even more challenging given that distinguishing abiogenic versus biogenic sources of methane in the terrestrial subsurface is still controversial. Deep subsurface gases in Precambrian Shield rocks have been suggested to have been formed by processes of abiogenic water-rock interaction such as Fischer-Tropsch synthesis or mineral-surface catalyzed polymerization. Compound specific carbon and hydrogen isotopic analysis of methane and other light hydrocarbons is a potentially powerful tool to distinguish between biogenic and such abiogenic sources.

In contrast to the majority of hydrocarbon deposits in the Earth's crust, isotopic measurements of methane and C2-C4 alkanes in Precambrian Shield rocks suggest an abiogenic source for a portion of the hydrocarbons *via* polymerization of methane precursors. It has been proposed that with increasing molecular mass, the hydrocarbons become increasingly depleted in 13C (due to the faster reaction rate of 12CH4 relative to 13CH4 to form chains) and enriched in 2H (due to the preferential cleavage of the weaker 12C-1H relative to 12C-2H). However, there is at present very little laboratory verification of the isotopic fractionation factors involved in abiogenic hydrocarbon formation.

Experiments have been carried out to abiogenically synthesize higher molecular weight hydrocarbons by polymerization from methane, using electrical spark discharges. Separation and analysis of the compounds is ongoing, and the results should aid distinguishing between abiogenic and biogenic hydrocarbons on both Earth and Mars.