

Abiotic hydrocarbons in Earth's crust: a phantom?

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Abiotic production of methane and its higher chain homologues (C₂₊) has been postulated to occur within the Earth's crust. Apparent evidence for abiogenesis was based on carbon isotope distribution patterns between methane and the C₂₊ as well as on apparent CH₄-CO₂ and CH₄-H₂ isotopic temperatures. We present a global survey of carbon and hydrogen isotope data on hydrocarbons in discharges from geothermal wells and volcanic-hydrothermal systems. The range of total variation in δ¹³C decreases with increasing chain length, and the carbon isotopic composition of the longest n-alkanes (propane, n-butane) brackets the range characteristic for modern marine and terrestrial organic matter. Methane of a non-microbial origin describes a trend in δ¹³C and δD similar to thermogenic methane from sedimentary systems, but is shifted to higher δ¹³C relative to the latter. These patterns are in agreement with methane and C₂₊ hydrocarbons deriving from open-system pyrolysis of modern organic matter at relatively high temperatures. Organic matter is supplied to the hydrothermal systems and associated rocks through infiltrating seawater and meteoric waters.

During open system thermogenic degradation of organic matter methane can become unusually enriched in ¹³C. It seems that carbon isotope partitioning between CH₄ and CO₂ only fortuitously corresponds to equilibrium. Hydrogen isotopes might attain overall equilibrium in the CH₄-H₂O-H₂ system only at temperatures >250°C. At lower temperatures, hydrogen isotope exchange proceeds in the H₂O-H₂ subsystem exclusively. As a consequence, the CH₄-H₂ geothermometer cannot be applied to low temperature natural emissions. Hydrocarbons previously postulated to be abiotic match our observed trend of δ¹³C vs δD and our observed range of δ¹³C-C₂₊. These results challenge the dogma of crustal production of abiotic hydrocarbons.