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Abiogenic hydrocarbons produced under upper-mantle pressure-temperature conditions

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There are growing evidences for abiogenic pathways of the petroleum production in the deep Earth. The laboratory experiments under extreme pressures and temperatures provide direct information about the chemical reactivity and stability of the natural oil components. Here we present new results on formation of hydrocarbons at high pressures and temperatures generated in diamond anvil cells (DAC). We use *in situ* Raman spectroscopy in laser heated diamond anvil cells to monitor the chemical reactivity; Raman spectroscopy and synchrotron x-ray diffraction are used to determine the reaction products quenched to ambient temperature. We have explored chemical reactions in the system consisting of $CaCO_3$-H_2O with either of the following mantle minerals: San Carlos olivine, peridodite, and Rockport fayalite. We also studied chemical reactivity of methane and ethane to explore possible routes to generate heavier hydrocarbons. The pressure range of the experiments (3-6 GPa) are similar to those studied by Kenney *et al*. [1] and Scott *et al*. [2] but temperatures up to 2500 K were generated. At pressures in the 5-6 GPa range, methanogenesis was observed in the olivine-calcite-water, fayalite-calcite-water system at temperatures greater than 2300 K and less than 800 K, respectively. We find that methane at 2-5 GPa and 1000-1500 K partially reacts and forms saturated hydrocarbons (C_2-C_4alkanes), molecular hydrogen and graphite. Formation of methane in similar experiments on ethane suggests reversibility of hydrocarbon formation. These results support proposals of abiogenic pathways for the formation of hydrocarbons in the Earth's upper mantle.

[1] Kenney, J. F., Kutcherov, V. G., Bendeliani, N. A. & Alekseev, V. A. The Evolution of Multicomponent Systems at High Pressures: VI. The Thermodynamic Stability of the Hydrogen-Carbon System: The Genesis of Hydrocarbons and the Origin of Petroleum. *Proc. Natl. Acad. Sci. U.S.A.* **99,** 10976-10981 (2002).

[2] Scott, H.P., Hemley, R.J., Mao, H-K., Herschbach, D.R., Fried, L.E., Howard, W.M., and Bastea, S. Generation of methane in the Earth's mantle: In situ high pressure-temperature measurements of carbonate reduction, *Proc. Nat. Acad. Sci.* **39**, 14023-14026 (2004).