Hydrogenation of graphite, diamond, carbonates and iron carbides as the source of hydrocarbons in the upper mantle

I.A. SOKOL[1,*], A.G. SOKOL[1], P.A. ZAIKIN[2], A.A. TOMILENKO[1] AND T.A. BUL'BAK [1]

[1] V.S. Sobolev Institute of Geology and Mineralogy of RAS, 3 Koptyug Ave., Novosibirsk, 630090 Russia (*correspondence: isokol0x5a@gmail.com)

[2] N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of RAS, 9 Lavrentiev ave., Novosibirsk 630090, Russia

Formation of hydrocarbons by reactions of hydrogen-bearing fluids with carbon [1] (^{13}C soot, graphite, or diamond), carbonate-bearing pelites [2] and iron carbides (Fe_3C and Fe_7C_3) [3] was simulated at 5.5-7.8 GPa and 1100-1400°C, fH_2 in Pt and Au capsules being controlled at the $Mo+MoO_2+H_2O$ or $Fe+FeO+H_2O$ equilibria. For the first time, formation of hydrocarbons from inorganic compounds was proved by the reaction of ^{13}C with hydrogen, which yielded isotopically pure alkanes. The greatest amounts of HCs ($CH_4/C_2H_6 < 1$, CH_4/C_3H_8 and $CH_4/C_4H_{10} \leq 10$) formed at 1400°C in the 10-hr run. The amount of HCs synthesized at 1200°C was twice smaller. The rate of HCs formation was slowest in runs with diamond. At 1200 °C, light alkanes ($C_1 \approx C_2 > C_3 > C_4$) formed either by direct hydrogenation of Fe_3C or Fe_7C_3, or by hydrogenation of graphite/diamond in the presence of Fe_3C, Fe_7C_3. The CH_4/C_2H_6 ratio in the fluids decreased from 5 to 0.5 with decreasing iron activity and the C fraction increased in the series: $Fe–Fe_3C \rightarrow Fe_3C–Fe_7C_3 \rightarrow Fe_7C_3$–graphite→graphite–$Fe_3C$–magnesite and $Fe_3C–H_2O–CO_2$ systems at 1200 °C yielded magnesiowüstite and wüstite, respectively, and both produced C-rich Fe_7C_3 and mainly light alkanes ($C_1 \approx C_2 > C_3 > C_4$). In the experiments containing pelites methaneimine (CH_3N) was found to be the main N-bearing compound. The experiments have provided the first unambiguous evidence that volatile-rich and reduced mantles of terrestrial planets (at fO_2 near or below IW) provided favorable conditions for abiotic generation of complex hydrocarbon systems that predominantly contain light alkanes. The conditions favorable for HC formation exist in earth mantle, where slab-derived H_2O-, CO_2- and carbonate-bearing fluids interact with metal-saturated mantle.

[1] Sokol et al. (2019) *PEPI* **291**, 12. [2] Sokol et al. (2019) *Minerals* **9**, 712. [3] Sokol et al. (2020) *Minerals* **10**, 88. The research was performed by a grant of the Russian Science Foundation (16-17-10041).