Synthesis of hydrocarbons under upper mantle conditions: evidence for the theory of abiotic deep petroleum origin

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Abstract. A theory of abiotic deep petroleum origin explains that hydrocarbon compounds are generated in the upper mantle and migrate through the deep faults into the Earth’s crust. There they form oil and gas deposits in any kind of rock in any kind of the structural position. Until recently one of the main obstacles for further development of this theory has been the lack of reliable and reproducible experimental results confirming the possibility of the spontaneous synthesis of complex hydrocarbon systems at high pressure and temperature. Our experimental results demonstrate that abiotic synthesis of hydrocarbons under mantle conditions is a real chemical process. Different paths of hydrocarbon synthesis under mantle conditions are discussed. Obtained experimental results place the theory of the abiotic deep petroleum origin in the mainstream of modern experimental physics and physical chemistry.

1. Introduction
The theory of abiotic deep petroleum origin is an extensive body of the modern science which covers the subjects of the chemical genesis of the hydrocarbon molecules. The theory of the abiotic deep petroleum origin recognizes that natural gas and petroleum are primordial materials of deep origin which have migrated through the deep faults into the Earth’s crust. Until recently one of the main obstacles for further development of this theory has been the lack of reliable and reproducible experimental results confirming the possibility of the spontaneous synthesis of complex hydrocarbon systems under the conditions of the upper mantle.

In 1998 we have started the research program ”Deep Oil” to get answers the following questions:
• is an abiotic synthesis of hydrocarbon systems (deep fluids) possible at mantle conditions;
• if it is possible how deep fluid had converted in different oil-and-gas systems;
• how could the deep fluid migrate from the depth to the Earth’s crust.

The results of the first series of experiments [1, 2] gave an answer to the first question. The abiotic synthesis of hydrocarbons at mantle conditions is a real physical process. At pressure of 5 GPa with a temperature of 1200°C, the synthesis is due to the reaction as follows:

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\[ n\text{CaCO}_3 + (9n + 3)\text{FeO} + (2n + 1)\text{H}_2\text{O} \rightarrow n\text{Ca(OH)}_2 + (3n + 1)\text{Fe}_3\text{O}_4 + C_n\text{H}_{2n+2} \]  

(1)

A part of these results was confirmed by Scott et al. [3].

In the new series of experiments the following question should be answered:

- does the hydrocarbon synthesis under upper mantle conditions depend on the form of carbon and hydrogen donors;
- how does cooling rate of the fluid obtained at high thermobaric conditions influence on final content of hydrocarbon mixture;
- what are the possible reaction paths for hydrocarbon synthesis under conditions corresponding to the Earth's upper mantle.

2. Experimental details

Three different experimental methods were used: CONAC high-pressure chamber in a combination with mass-spectrometer and gas chromatograph; large-volume multi-anvil press apparatus BARS in a combination with gas chromatograph; in situ Raman spectroscopy in laser heated diamond anvil cell (DAC).

In CONAC and BARS experiments a filled ampule was placed into the high-pressure chamber, pressurized and then heated to given pressure and temperature. The treatment in the chamber was followed by cooling to room temperature at different rates (from 10-20 to several hundred degree per second), whereupon the pressure was decreased to normal pressure and the ampule was removed from the chamber. The composition of the reaction products was studied by gas chromatography and X-ray powder diffraction method. The procedures and experimental arrangement are fully described in [2 and 4]. The experiments were carried out in the temperature range 800-1500 K and at pressures up to 5 GPa.

Laser heated diamond anvil cell was combined with in situ Raman measurements and (in case of magnetite experiment) synchrotron X-ray diffraction of the products quenched to room temperature. Pressure was determined at room temperature using a conventional ruby manometer before and after laser heating (which was the same within the experimental error in most cases). The maximum coupler temperature was determined radiometrically by fitting the Planck function to the thermal radiation emitted. In in-situ experiment the Raman Stokes-to–anti-Stokes intensity technique was employed to determine the temperature of methane away from the heating spot. The method and experimental results were fully described in [5]. The experiments were made in the temperature range 900-2200 K and at pressures 2-5 GPa.

Initial components and experimental conditions are shown in table 1.

**Table 1** Initial components and experimental conditions

| №  | Initial substances | Pressure, GPa | Temperature, K | Cooling rate |
|----|-------------------|--------------|----------------|-------------|
| 1  | CaCO₃ + Fe + H₂O  | 5            | 1500           | quenching   |
| 2  | CaCO₃ + Fe + D₂O  | 5            | 1500           | quenching   |
| 3  | C + Fe + H₂O      | 5            | 1500           | quenching   |
| 4  | C + Fe + H₂O      | 5            | 1500           | 4 hours     |
| 5  | CH₄               | 2-5          | 900-2000       | in-situ     |
| 6  | CH₄ + Fe₃O₄      | 2-5          | 900-2000       | in-situ     |
3. Experimental results

3.1. Experiments in the CONAC high-pressure chamber

Experiment 1. CaCO$_3$ and H$_2$O were used as donors of carbon and hydrogen respectively. Favorable reducing conditions were created by the presence of Fe.

Experiment 2. There was one difference from the experiment 1: we replaced H$_2$O for D$_2$O.

The result of chromatographic analyses for both experiments is shown in table 2 and in figure 1. The result of the experiment from the first series where we used the CaCO$_3$ and H$_2$O as donors of carbon and hydrogen, but favorable reducing conditions were created by the presence of FeO is also shown in table 2. The X-ray diffraction pattern for the 1st experiment is presented on the figure 2. Data presented confirms the following:

- a reduction value of iron $+\text{II}$ or 0 does not influence the composition of the synthesized hydrocarbon mixture;
- replacement of H$_2$O by D$_2$O did not change qualitative and quantitative composition of the hydrocarbon mixtures;
- presence of clearly recognized Ca(OH)$_2$ lines on the XRD pattern without lines of CaCO$_3$ confirms the following path of the reaction:

\[
\text{experiment 1: } n\text{CaCO}_3 + (3n + 1)\text{Fe} + (2n + 1)\text{H}_2\text{O} \rightarrow n\text{Ca(OH)}_2 + (3n + 1)\text{FeO} + C_n\text{H}_{2n+2}
\]

\[
\text{experiment 2: } n\text{CaCO}_3 + (3n + 1)\text{Fe} + (2n + 1)\text{D}_2\text{O} \rightarrow n\text{Ca(OD)}_2 + (3n + 1)\text{FeO} + C_n\text{D}_{2n+2}
\]

| T, °C | CH$_4$ | C$_2$H$_6$/C$_3$H$_4$ | C$_3$H$_8$/C$_4$H$_8$ | C$_4$H$_8$/C$_5$H$_6$ | C$_5$H$_{10}$/C$_6$H$_6$ | H$_2$ | O$_2$ | H$_2$O | CO$_2$ | CO | N$_2$ |
|-------|-------|----------------------|----------------------|----------------------|----------------------|------|------|------|-------|-----|------|
| 120   | 310   | 210                  | 30                   | 4                    | 60                   | –    | 8000 | 0     | 0     | tr. |       |
| 200   | 0,6   | 0                    | 0,0                  | 0,0                  | 0,0                  | –    | 4200 | 2     | 0     | 0   |       |
| 300   | 2     | 0                    | 0,0                  | 0,0                  | tr.                  | 2    | –    | 8100  | 1     | 0   | 0     |
| 400   | 4     | 1                    | 0,8                  | 1                    | 40                   | –    | 4000 | 0     | 0     | 0   | 0     |
| 500   | 20    | 3                    | 4                    | 4                    | 40                   | –    | 4800 | 0     | 0     | 0   | 0     |
| 600   | 10    | 1                    | 0,4                  | tr.                  | 40                   | –    | 44000| 7     | 20    | 0   |       |
| 700   | 7     | 1,4                  | 0,8                  | 0,9                  | 50                   | –    | 4000 | 140   | 100   | 0   |       |

| T, °C | CH$_4$ | C$_2$H$_6$/C$_3$H$_4$ | C$_3$H$_8$/C$_4$H$_8$ | C$_4$H$_8$/C$_5$H$_6$ | C$_5$H$_{10}$/C$_6$H$_6$ | H$_2$ | O$_2$ | H$_2$O | CO$_2$ | CO | N$_2$ |
|-------|-------|----------------------|----------------------|----------------------|----------------------|------|------|------|-------|-----|------|
| 120   | 240   | 160                  | 30                   | 4                    | 80                   | –    | 34600| 0     | 0     | tr. |       |
| 200   | 2     | 0                    | 0,0                  | 0,0                  | 0,0                  | –    | 4000 | 0     | 0     | 0   | 0     |
| 300   | 4     | 0,5                  | 0,0                  | tr.                  | 30                   | –    | 3400 | 0     | 0     | 0   | 0     |
| 400   | 3     | 0                    | 0,4                  | 0,5                  | 60                   | –    | 4900 | 0     | 0     | 0   | 0     |
| 500   | 4     | 3                    | 3                    | 2                    | 1800                 | –    | 4300 | 0     | 0     | 0   | 0     |
| 600   | 8     | 1                    | 0,9                  | 1                    | 5400                 | –    | 4000 | 8     | 8     | 0   |       |
| 700   | 6     | 0                    | tr.                  | 0,0                  | 1600                 | –    | 4600 | 20    | 110   | 0   |       |

| T, °C | CH$_4$ | C$_2$H$_6$/C$_3$H$_4$ | C$_3$H$_8$/C$_4$H$_8$ | C$_4$H$_8$/C$_5$H$_6$ | C$_5$H$_{10}$/C$_6$H$_6$ | H$_2$ | O$_2$ | H$_2$O | CO$_2$ | CO | N$_2$ |
|-------|-------|----------------------|----------------------|----------------------|----------------------|------|------|------|-------|-----|------|
| 150   | 0,1   | 0                    | 0                    | 0                    | 0,9                  | 0    | –    | 143   | –     | tr. |       |
| 200   | 0,2   | 0                    | 0                    | 0                    | 1,1                  | 0    | –    | 54    | –     | tr. |       |
| 300   | 2,7   | 0,4                  | 0,7                  | 0,7                  | 7,3                  | 0    | –    | 389   | –     | tr. |       |
| 400   | 21,3  | 15,6                 | 18,9                 | 13,3                 | 507                  | 0    | –    | 457   | –     | tr. |       |
| 500   | 16    | 5                    | 5,6                  | 2,7                  | 370                  | 0    | –    | 68    | –     | tr. |       |
| 600   | 36    | 2,6                  | 2,1                  | 0,6                  | 488                  | 0    | –    | 348   | –     | tr. |       |
| 700   | 34    | 1,4                  | 0,8                  | 0,2                  | 672                  | 0    | –    | 2118  | –     | tr. |       |
Figure 1 Gas chromatograms of products mixture heating at different temperature: a - 1st experiment with water; b - 2nd experiment with heavy water

Absence of CO and CO$_2$ in the reaction products shows instability of C-O compounds at the experimental thermobaric conditions. CO$_2$ was detected during chromatographic analysis at heating up to 700°C at helium atmosphere (experiment 1). This tells us that CO$_2$ in some solid phase like carbonate or carbonate-hydrate could remain after the experiment in small quantities. It is necessary to add that absence of nitrogen in the reaction products confirms that contamination by air was prevented on all stages of the experiments.

Figure 2 X-ray diffraction pattern of 1st experiment products
3.2. *Experiments in the multi-anvil press apparatus BARS.*

In the experiments 3 and 4 CaCO$_3$ was replaced with graphite. H$_2$O was used as hydrogen donor. Favorable reducing conditions were created by FeO. The experiments were made in soldered 0.25 cm$^3$ platinum ampules at two different cooling rates. Results of chromatographic analysis of the reaction products made at 120°C are shown in table 3. XRD patterns for the experiment 3 and 4 are presented at figure 3 and figure 4.

|                    | CH$_4$ | C$_2$H$_6$/C$_2$H$_4$ | C$_3$H$_8$/C$_3$H$_6$ | C$_4$H$_{10}$/C$_4$H$_8$ | H$_2$ | O$_2$ | H$_2$O | CO$_2$ | CO | N$_2$ |
|--------------------|--------|-----------------------|-----------------------|-------------------------|------|------|-------|-------|----|-----|
| Experiment 3 (quenching) | 40     | 3                     | 0                     | 0                       | 7    | 0    | 0     | 0     | 0  | 0   |
| Experiment 4 (cooling during 4 hours) | 640    | 80                    | 8                     | 4                       | 530  | -    | 0     | 0     | 0  | 0   |

*Table 3* Results of chromatographic analysis made at 120°C for experiments 3 and 4

*Figure 3* XRD pattern of 3$^{rd}$ experiment products
Comparison of chromatographic data for experiment 1 (table 2, 120°C) and experiment 3 (table 3), that differ only by carbon donor nature: CaCO$_3$ and graphite correspondingly, confirms presence of hydrocarbon mixtures and general pattern of hydrocarbon distribution: concentration decreasing with molecular weight increasing. Thereby fact of genesis of hydrocarbons at conditions similar to conditions of Earth’s upper mantle does not depend on the form of carbon donors. The general path of the reaction could be summarized as follows: donor of carbon + donor of hydrogen + deoxidizer → hydrocarbons. Further investigation has to be carried out to establish accurate regularities of nature of donors factor influence.

The experiments 3 and 4 (table 3) were carried out at different cooling rates with other variables keeping constant. After quick cooling (quenching, experiment 3) CH$_4$ и C$_2$H$_6$/C$_2$H$_4$ were detected in the reaction products. At slower rate (4 hours, experiment 4) the amount of CH$_4$ и C$_2$H$_6$/C$_2$H$_4$ in the reaction products increased by tens times and more heavy saturated hydrocarbons up to C$_4$H$_{10}$ were fixed. Thus, cooling rate of the fluid synthesized at high pressure makes essential impact on its final composition. Decreasing of cooling rate leads to higher hydrocarbon yield and appearance of heavier hydrocarbons.

Analysis of XRD patterns for experiments 3 and 4 gives additional information. For the experiment 4 (figure 4, slow cooling) FeO signals (36, 42, 61) are absent, but they are fixed for the experiment 3 (figure 3, quenching). At the same time concentration of hydrogen in the reaction products increased by ten times in the case of the slow cooling. All this suggests following paths of reactions:

\begin{equation}
nC + (n + 2)Fe + (n + 2)H_2O = C_nH_{2n+2} + (n + 2)FeO + H_2
\end{equation}
experiment 4:
\[ 4nC + (3n+6)Fe + (4n+8)H_2O = 4C_nH_{2n+2} + (n+2)Fe_3O_4 + 4H_2 \]  

(5)

3.3. Experiments in laser heated diamond anvil cell
Transformation of methane under conditions corresponding to the Earth's upper mantle was investigated in the experiment 5 (pure methane) and 6 (pure methane with Fe$_3$O$_4$). These experiments were designed to check the following hypothesis: synthesis of hydrocarbons under the upper mantle conditions proceeds in two steps. In the first step methane is synthesized from carbon and hydrogen donors. In the second step a complex hydrocarbon mixture is synthesized from methane – “methane path”. Synthesis of methane under the upper mantle conditions was demonstrated previously [1, 3]. So, if our suggestion was correct we should obtain a mixture of saturated hydrocarbons from methane. Experimental results published recently [5] have confirmed our hypothesis and have demonstrated that according to thermobaric conditions (at corresponding depths) methane reacts to form saturated hydrocarbons (ethane, propane and butane) or dissociates to molecular hydrogen (or water in the experiment 6) and graphite. No other carbon or hydrogen containing products were observed (e.g. unsaturated hydrocarbons).

experiment 5:
\[ nCH_4 = H_2 + C_nH_{2n+2} \quad 900 < T < 1500 \text{ K}, \ p = 2-5 \text{ GPa} \]  

(6)

\[ CH_4 = C_{\text{graphite}} + 2H_2 \quad T > 1500 \text{ K}, \ p = 2-5 \text{ GPa} \]  

(7)

experiment 6:
\[ 4nCH_4 + Fe_3O_4 = 3Fe + 4C_nH_{2n+2} + 4H_2O \quad 900 < T < 1500 \text{ K}, \ p = 2-5 \text{ GPa} \]  

(8)

\[ 2CH_4 + Fe_3O_4 = 3Fe + 2C_{\text{graphite}} + 4H_2O \quad T > 1500 \text{ K}, \ p = 2-5 \text{ GPa} \]  

(9)

4. Conclusion
The following general conclusions could be made on the basis of the experimental results discussed above:

- the abiogenic generation of hydrocarbons in the mantle is a real physicochemical process. The «methane» path of hydrocarbons synthesis under mantle conditions has been proved experimentally,
- our suggestion that the fact of hydrocarbon synthesis at thermobaric conditions of the upper mantle does not depend on the type of carbon donor was confirmed. The general path of the reaction could be described as follows: donor of carbon + donor of hydrogen + deoxidizer → hydrocarbons,
- cooling rate of the fluid synthesized at high pressure makes essential impact on its final composition. Decreasing of cooling rate leads to higher hydrocarbon yield and appearance of heavier hydrocarbons.

5. References
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