Experimental investigation of hydrocarbons formation and transformation under Earth’s upper mantle conditions

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ABSTRACT

The theory of the abyssal abiotic petroleum origin considers oil and natural gas to be generated in the Earth’s upper mantle. Hydrocarbons migrate further through the deep faults into the Earth’s crust, where they can form oil and gas deposits in any kind of rock in any kind of structural position. Until recently one of the main obstacles for further development of this theory has been the lack of the data covering processes of generation and transformations of hydrocarbons.

Experimental data, presented in this thesis, confirms the possibility of hydrocarbons formation from mantle inorganic compounds (water, Fe, CaCO₃ or graphite) at temperature and pressure of the upper mantle (1500 K and 5 GPa). Experiments were carried out in CONAC high pressure device and multianvil apparatus BARS. Compositions of received gas mixtures were similar to natural gas. Quantity of hydrocarbons depended on the cooling regime of reaction mixture under pressure. Slow cooling favored higher quantity. We found that donor of carbon (CaCO₃ or graphite) determines formation of “dry” (methane-rich) gas or “wet” (light hydrocarbons-rich) gas.

Experiments in laser-heated diamond anvil cells showed that methane and ethane partially react under upper mantle thermobaric conditions (2-5 GPa, 1000-1500 K) to form mixture of hydrocarbons: methane, ethane, propane and n-bu tane – main compounds of natural gas. Similarity of final product mixture obtained from methane and ethane means thermodynamic stability of hydrocarbons in the thermobaric conditions of the upper mantle and equilibrium character of the observed processes.

Keywords: theory of deep abiotic petroleum origin, natural gas, hydrocarbons, methane, ethane, graphite, hydrogen, high pressure, high temperature, CONAC, BARS, diamond anvil cell, Raman, X-ray, gas chromatography.
PREFACE

The thesis is based on publications that are listed below and appended at the end of the thesis.


The contribution of Anton Kolesnikov is as follows:
• Paper 1: General planning together with V. Kutcherov, design of the experiments and realization together with A. Goncharov and independently, analyzing the data and making a substantial contribution in writing of the manuscript.
• Paper 2: Design of the parts of the experiments, building of the experimental setup and carrying out the experiments with A. Goncharov, commenting on the final manuscript.
• Paper 3: Planning of the experiments together with V. Kutcherov, making data analysis, writing and submitting the manuscript.

The material of the thesis has been presented by A.Kolesnikov at the following conferences:
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NOMENCLATURE

**latin**

- \( \text{fY}_{\text{buf}} \) fugacity of Y compound in buf(fer) reaction
- \( Z \) compressibility
- \( P \) pressure in the system, Pa
- \( P_y \) partial pressure of y, Pa
- \( V \) molar volume, m\(^3\)/mole
- \( T \) temperature, K
- \( X_y \) mole fraction of y compound in mixture
- \( a_y \) activity of y compound, mole/m\(^3\)

**greek**

- \( \gamma \) activity coefficient
- \( \lambda \) wavelength, nm

**abbreviations**

- MAA: multianvil apparatus
- BARS: pressless high-pressure equipment “Split Sphere”
- CONAC: high-pressure device based on toroid chamber with conical shape of the hole and small degenerated unsymmetric groove
- DAC: diamond anvil cell
- LHDAC: diamond anvil cell with laser heating
- IR: infrared
- MD: molecular dynamic
- AIMD: ab initio molecular dynamic
- EOS: equation of state
- FMQ: fayalite – magnetite – quartz

**chemistry of minerals**

- Olivine: \((\text{Mg}_{m}\text{Fe}^{2+}_{n})\text{SiO}_4\)
- Siderite: crust mineral \(\text{CaCO}_3\)
- Peridotite: igneous mantle consisting from olivine \((\text{Mg}_{m}\text{Fe}^{2+}_{n})\text{SiO}_4\) and pyroxene (Pyroxenes have the general formula \(\text{XY(Al,Fe}_{2+}\)Si\(_2\)O\(_6\) (X: Ca, Na, Fe\(^{2+}\), Mg, Zn, Mn, Li; Y: Cr, Al, Fe\(^{3+}\), Mn Mg, Sc, Ti, V, Fe\(^{2+}\)), but also can contain chromite \((\text{Mg}_{n}\text{Fe}_{m})\text{Cr}_2\text{O}_4\), plagioclase \((\text{NaAlSi}_3\text{O}_8\text{ to CaAl}_2\text{Si}_2\text{O}_6)\), and amphibole \((\text{Na}_6\text{Al}_8\text{Fe}^{2+}_{c}\text{Fe}^{3+}_{a}\text{Mg}_{b}\text{Si}_3\text{O}_11\text{(OH)}_y\text{Hal}_z)\)
- Serpentine: \((\text{Mg}_{a}\text{Fe}^{2+}_{b})_3\text{Si}_2\text{O}_5(\text{OH})_4\)
- Fayalite: crust mineral \(\text{Fe}_2\text{SiO}_4\)
- Iceland spar: crust mineral \(\text{CaCO}_3\)
- Biotite: \(K(\text{Mg,Fe}^{2+}_3(\text{Al,Fe}^{3+})\text{Si}_3\text{O}{}_{10}(\text{OH},\text{F})_2\)
INTRODUCTION

Petroleum, Oil and Natural Gas

According to the definition in the Schlumberger Oilfield Glossary\(^1\), petroleum is “a complex mixture of naturally occurring hydrocarbon compounds found in rock. Petroleum can range from solid to gas, but the term is generally used to refer to liquid crude oil”.

Petroleum consists of a great number of compounds. The main ones are different classes of hydrocarbons, carbon dioxide, sulphur and nitrogen compounds, helium, etc. The typical composition of natural gas is shown in (Table 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>70-98</td>
</tr>
<tr>
<td>Ethane</td>
<td>1-10</td>
</tr>
<tr>
<td>Propane</td>
<td>trace-5</td>
</tr>
<tr>
<td>Butanes</td>
<td>trace-2</td>
</tr>
<tr>
<td>Pentanes</td>
<td>trace-1</td>
</tr>
<tr>
<td>Hexanes</td>
<td>trace-0.5</td>
</tr>
<tr>
<td>Heptanes</td>
<td>0-trace</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>trace-15</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>trace-1</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>trace-5</td>
</tr>
<tr>
<td>Helium</td>
<td>trace-8</td>
</tr>
</tbody>
</table>

The hypothesis of organic petroleum formation suggests that oil and natural gas deposits were formed as a result of geological processes in organic sediments (Hunt et al. 2002). But there is an opposite viewpoint known as the theory of abyssal abiogenic origin of petroleum. According to this theory, hydrocarbon compounds are generated in the mantle of the Earth and migrate upwards through the deep faults into the crust of the Earth, where they form oil and gas deposits in any kind of rock. Today, this theory has begun to attract more and more attention. The fullest review of the main ideas, evidence, advantages and potential of this theory can be found in (Kutcherov and Krayushkin 2010).

OBJECTIVES

The purpose of this work was to conduct an experimental investigation of the processes of abiogenic petroleum formation and transformation under the same thermobaric conditions of the upper mantle of the Earth. Results of two main series of experiments are presented. In the first series of experiments the synthesis of complex hydrocarbon systems from inorganic substances under high pressures and high temperatures has been studied. In the second series, transformations of pure methane and ethane under upper mantle conditions have been investigated. Study of high pressure/high temperature methane and ethane transformation in situ, using Raman spectroscopy and X-ray analysis has been made.


The formation of hydrocarbons is still a debatable question, despite the worldwide industrial use of petroleum (oil and natural gas) for over a century. While the theory of organic petroleum formation found its place in the school textbooks, the theory of the abyssal abiogenic origin of petroleum begin to attract increasing attention.

The main postulates of the theory of the abyssal abiogenic origin of petroleum are the following (Figure 1-1) (Kutcherov and Krayushkin 2010, p. 2-3):

- “hydrocarbon fluids are generated in the upper mantle;
- where and when overlying rocks of the Earth’s Crust break up/fracture, petroliferous fluids rise from the Mantle through the deep faults and their feather joints or fissures;
- the petroliferous mantle fluids are injected at extreme high pressure from the faults and feathers into any rock with porous (sedimentary rocks) or fractured (basement rocks) pore space;
- the petroliferous fluids floods the reservoir.

The favorable conditions for the deep hydrocarbon generation are not available everywhere in the mantle. This explains the non-uniformity of spatial accommodation of hydrocarbon deposits on the Earth”.

While the main postulates were formulated in the 1950s in Russia and the Ukraine, the necessary experimental development of the theory did not occur.

Even the main postulate (possibility of hydrocarbons generation in the mantle) was not confirmed unquestionably till recently.

According to the theory, the following conditions are necessary for the synthesis of hydrocarbons in the Earth’s upper mantle:

- thermodynamically favorable thermobaric and oxidative-redox conditions;
- the availability of sources of carbon and hydrogen.

Theoretical calculations together with the reliable confirmation (Kenney et al. 2002) of the first high pressure experiments (Chekaluk et al. 1969) have established that the polymerization of hydrocarbons takes place at a 1000-1500 K temperature range and pressure of 2-5 GPa.
Figure 1-1 Visualization of the theory of deep abiogenic petroleum formation (Kutcherov and Krayushkin 2010).

According to (Carlson et al. 2005) these conditions correspond to the Earth’s depths of 70-250 km (Figure 1-2).

1.1. Thermobaric Conditions of the Earth’s Upper Mantle

The values for the temperature and pressure in the Earth’s interior are closely correlated (Carlson et al. 2005). This dependence is called the geotherm and is usually visualized versus depth. Continental and ocean geotherms are distinguished. In (Figure 1-2) one can see such geotherms that do not consider internal heat sources: 60 W/m² heat flow for the oceanic and 40 W/m² for the continental mantle (Pollack and Chapman 1977). Modern ideas about Earth’s the interiors conditions are based on seismographic data and the thermobarometry of minerals.
Seismic information from natural earthquakes or special artificial activity is used in laboratory experiments where different minerals are investigated for seismic waves patterns and following the building of an interior model.

Geothermometers and geobarometers are xenoliths – the mantle rocks – that have been brought to the surface during intensive volcanic activity. The minerals that the rock contains are studied in laboratories to establish the conditions of the phase transitions, saturation points, etc.

It is generally assumed that, at mantle temperatures, the transformation between minerals in exchange reactions is sufficiently fast to maintain equilibrium, and the swift migration of rocks to the surface during eruption does not disturb the equilibrium composition. Some exchange reactions are thermosensitive, while others are barosensitive (Brey et al. 1990; Finnerty and Boyd 1987). The accuracy of pressure determination via this method is usually 0.3 – 0.5 GPa, temperature – 30 – 180 K (Pearson et al. 2003).

The validity of a 40 mW/m² geotherm for South African Caapvaal to a 140 -180 km depth was confirmed for the first time by using geothermometry (Boyd 1973). Temperature and pressure values are different for continents (shield geotherm in Figure 1-2) and oceans (oceanic geotherm in Figure 1-2) but they may vary on the continents and, usually, the values of the real geotherms differ from those in the model. The coldest geotherms were found under stable platforms. The temperature at 100 km is in the range of 1050 – 1200 K (Finnerty and Boyd 1987).

It recently became possible to investigate large heterogeneities of composition and thermobaric parameters in the mantle by means of 3D seismography (Carlson et al. 2005) and we can expect new data about thermobaric parameters variations in the interiors. But today we can consider the conditions required for hydrocarbon synthesis to occur at a depth of 70 – 250 km, a pressure range of 2-5 GPa, and a temperature range of 1000-2000 K. The meaning of these values is stipulated by the experimental results of (Chekaluk et al. 1969).

1.2. The Oxidation-reduction Conditions of the Earth’s Mantle

To model mantle conditions completely, it is necessary to provide an appropriate chemical environment. Mantle minerals are usually used for this purpose in case of investigation of hydrocarbon synthesis. What concerns properties of individual hydrocarbons, then very little is done so far. The redox potential of the environment seems to be the first to be explored.

The parameter that is used to describe the redox properties of some minerals is oxygen fugacity. Oxygen is widely distributed in the Earth’s interior and can be written into a lot of generalized redox reactions, e.g. (1.1)-1.7. Oxygen fugacity can be easily converted to the equilibrium constant of a given redox process by simple thermodynamic correlations (see processes below and (1.8), (1.9)). The first method to determine minerals’ oxygen fugacities is a thermodynamic calculation with elements that constitute minerals and change the oxidation state (like iron or nickel). The second method is an experimental investigation with solid electrochemical cells, where oxygen fugacity can be measured almost directly.
Figure 1-2 Pressure-temperature conditions in laser heating experiments of this thesis in comparison to the model oceanic (60 mW/m²) and shield (40 mW/m²) geotherms (Pollack and Chapman 1977) and methane melting line (Yagi and Suzuki 1990).

To produce the necessary redox environment, a number of buffers are used, e.g.:

4 Fe₃O₄ + O₂ = 6 Fe₂O₃  
2 Ni + O₂ = 2 NiO  
3 Fe₂SiO₄ + O₂ = 2 Fe₃O₄ + 3 SiO₂  
3 Fe₁₋ₓO + O₂ ~ Fe₃O₄  
2(1-x) Fe + O₂ = 2 Fe₁₋ₓO  
2 Fe + SiO₂ + O₂ = Fe₂SiO₄  
3 Fe + 2O₂ = Fe₃O₄

MH magnetite – hematite  
NiNiO nickel – nickel oxide  
FMQ fayalite – magnetite – quartz  
WM wustite – magnetite  
IW iron – wustite  
QIF quartz-iron-wustite  
IM iron – magnetite

A buffer is a mixture of the reagents and products of the buffer reaction. The quantity of buffer components should be higher than that of the sample. In this case, when the reaction occurs in the sample with one of the buffer components, the buffer equilibrium (e.g. for iron-magnetite (1.7)) shifts to keep the content of the reacted compound, usually oxygen (1.8) and (1.9), constant.
\[ K = \frac{a_{Fe,O_3}}{a_{Fe} \times f_{O_2}} \]  
(1.8)

\[ \log f_{O_2} = \frac{1}{2}(-\log K + \log \left( \frac{a_{Fe,O_3}}{a_{Fe}} \right)) \]  
(1.9)

where \( K \) – equilibrium constant, \( f_{O_2} \) – oxygen fugacity, \( a_{Fe,O_3}, a_{Fe} \) – activities of \( Fe_3O_4 \) and \( Fe \), correspondingly.

Oxygen fugacity, as an empirical function of pressure and temperature (1.10), was published in (Huebner 1972).

\[ \log f_{O_2} = 8.99 - \frac{29260}{T} + 0.061 \times \left( \frac{P}{T} - 1 \right) \]  
(1.10)

A comparison of oxygen fugacity for different buffers (Table 2) shows the serious influence of temperature. Thus, for a wustite-magnetite (WM) buffer at 3 GPa and 1000 K \( \log f_{O_2} = -17.12 \), and at 1500 K \( \log f_{O_2} = -7.04 \). The value of iron-magnetite buffer changes from \( \log f_{O_2} = -18.44 \) to \( \log f_{O_2} = -9.30 \) in the same conditions. An increase in temperature for 500 degrees leads to the growth of oxygen fugacity by \( 10^6 \) - \( 10^9 \) times so, with the current accuracy of the temperature determination methods and our current state of knowledge, the choice of a buffer reaction and its investigation is less important than using proper thermobaric conditions.

**Table 2. Logarithm of oxygen fugacity for widespread buffers under conditions of potential hydrocarbon inorganic synthesis (Huebner 1972)**

<table>
<thead>
<tr>
<th>Buffer</th>
<th>0.1 MPa, 1000K</th>
<th>3 GPa, 1000K</th>
<th>3 GPa, 1500K</th>
<th>5 GPa, 1000K</th>
<th>5 GPa, 1500K</th>
<th>10 GPa, 1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>IM</td>
<td>-20.27</td>
<td>-18.44</td>
<td>-9.30</td>
<td>-17.22</td>
<td>-8.48</td>
<td>-14.17</td>
</tr>
<tr>
<td>IW</td>
<td>-20.65</td>
<td>-19.00</td>
<td>-10.47</td>
<td>-17.90</td>
<td>-9.74</td>
<td>-15.15</td>
</tr>
<tr>
<td>FMQ</td>
<td>-16.74</td>
<td>-13.98</td>
<td>-6.32</td>
<td>-12.14</td>
<td>-5.09</td>
<td>-7.54</td>
</tr>
<tr>
<td>MH</td>
<td>-10.67</td>
<td>-10.10</td>
<td>-2.08</td>
<td>-9.72</td>
<td>-1.82</td>
<td>-8.77</td>
</tr>
</tbody>
</table>

1.3. Content of the Potential Reagents for Hydrocarbon Synthesis in the Earth’s Mantle

For the synthesis of hydrocarbons, it is necessary to have donors of hydrogen and carbon (1.11). These elements are believed to exist in the mantle mostly in oxidized form so a reducer may be needed.

\[ \text{hydrogen donor} + \text{carbon donor} + (\text{reducer}) \rightarrow \text{hydrocarbons} \]  
(1.11)

The mantle contains a lot of peridotite (Carlson et al. 2005). This is an igneous mantle mineral, consisting of olivine (\( Mg_{m}Fe_{n}^{2+} \)SiO\(_4\)) and pyroxene.

Formula of olivine in another way can be presented as MgO-FeO-SiO\(_2\). FeO could be a reducer.

Pyroxenes have the general formula \( XY(Si,Al)_{2}O_{6} \) (\( X: Ca, Na, Fe^{+2}, Mg, Zn, Mn, Li; Y: Cr, Al, Fe^{3+}, Mn, Mg, Sc, Ti, V, Fe^{+2} \)), but also can contain chromite (\( Fe_{n}Mg_{n} \)Cr\(_2\)O\(_4\)), plagioclase (NaAlSi\(_3\)O\(_8\) to CaAl\(_2\)Si\(_2\)O\(_8\)), and amphibole (Na\(_8\)Al\(_9\)Fe\(_{2}^{2+}\)Fe\(_d^{3+}\)Ca\(_{10}\)Mg\(_{12}\)Si\(_4\)O\(_{12}\)(OH)\(_2\))\(_2\)).

The amphibole part of peridotite contains hydroxo-groups – a possible hydrogen donor, but more hydrogen can be stored in water.

Experiments carried out in recent years using high-pressure vessels showed that mantle minerals can contain a significant amount of water. In (Murakami et al. 2002), it was shown...
that Mg-perovskite and magnesiowustite each contain ~0.2% and Ca-perovskite 0.4 wt.% of H₂O. That supposes the mass of mantle water reservoir to be 5 times higher than the total quantity of the Earth’s oceans. Hydrogen during migration from the outer core, where it is supposed to saturate iron, can be oxidized by feeding the mantle minerals with water (Okuchi 1997).

Water may also be transported from the surface via the subduction of hydrated slabs, e.g. the hydrous magnesium silicate phase contains more than 10 wt% H₂O in cold slabs shallower than 1200 km (Shieh et al. 1998).

Wadsleyite and ringwoodite can contain 3.3 and 2.2 %wt. The amount of water in this reservoir is 6 times higher than that contained in the Earth’s oceans (Inoue 1995; Inoue 1998).

Carbon in the Earth’s mantle may occur in several forms: elemental – graphite or diamond - and in compositions – minerals, e.g. magnesite and dolomite, or fluids.

The quantity of carbon in the Earth interior is a very important and unexplored question that led to the establishment of the Deep Carbon Observatory project². (Biellmann et al. 1993) investigated magnesite carbonate and found it to be the major carbonate in the mantle. It is stable up to 80 GPa. (Isshiki et al. 2004) proposed that, at a p-T ratio of traditional geotherms, the dissociation of magnesite does not occur. Another carbonate that could be a carbon donor for hydrocarbon generation is CaCO₃, that was shown to be stable in relatively cold subduction slabs (Isshiki et al. 2004).

Carbon is also proposed to exist in deep fluids in the form of CO, CO₂ and CH₄.

**Conclusion**

Thermobaric conditions to a depth of 50-250 km are sufficiently well established. The presence of donors of carbon and hydrogen at these depths is not in doubt. The main question is the following: Could a complex hydrocarbon mixture be synthesized and be stable under the thermobaric conditions at these depths?

2. EXPERIMENTAL MODELLING OF ABIGENIC SYNTHESIS OF HYDROCARBONS UNDER UPPER MANTLE CONDITIONS

The first attempt of inorganic hydrocarbon synthesis under an upper mantle pressure of 1 – 7 GPa and temperature range of 1473 – 1973 K was made by (Chekaluk et al. 1969). Experiments at 1473 K and 1-1.2 GPa were carried out in a 50 ton press in a hermetic capsule with a volume of 2.5 cm$^3$ (Figure 2-1). The heating was done by an internal tungsten resistive heater. The time of exposition was 10-12 hours. The gas products of the reaction between CaCO$_3$, FeO and H$_2$O were collected by a water seal. Methane was found to occupy more than 80% of the volume of gaseous products. The presence of 2% CO$_2$ and air in the collecting system was the first evidence of the method imperfection. The authors estimated the total amount of gaseous products to be 100 cm$^3$ for 1cm$^3$ of the reaction mixture.

![Image](https://via.placeholder.com/150)

**Figure 2-1** High pressure chamber (Chekaluk et al. 1969). 1, 5 – 2 rings from 6 in assembled cylinder from 6 rings; 2 – thermo-insulating bush; 3 – reagents; 4 – graphite or metallic heater; 6 - sealing ring; 7 – tube.

Experiments at pressures of 7 GPa and a temperature of 2000 K were made with 3 MN and 4.9 MN presses in two chambers with a volume of 0.3 and 0.8 cm$^3$ correspondingly. The time of exposition was 10 minutes. The process of gas formation, its escape from the reaction chamber and mixing with hot air at the start of the heating, as the authors underlined, provided evidence of an incorrect method. Nevertheless, hydrocarbons from methane to pentane were observed in gaseous products and this qualitative result can be taken as a fact. Although the above-mentioned experiments could not be considered reliable, E.B. Chekaliuk was the first who demonstrated the possibility of hydrocarbons formation through inorganic synthesis at high pressure and high temperature conditions.

Series of similar experiments in different laboratories was carried out only 30 years later.

(Weng et al. 1999) reported the results whereby carbonate-containing material and water were exposed to high pressures and temperatures. All of the minerals were natural
samples: siderite, Iceland spar + biotite, serpentine + olivine. Three experiments were carried in a Mao-Bell diamond anvil cell with a rubber ring around the diamonds and gasket to collect gaseous products (Figure 2-2).

![Figure 2-2 DAC makeup in (Weng et al. 1999). After a cell quenching, a gas sample was derived from the inner of the rubber ring by syringe.](image)

In the experiment with water and siderite, a (1:8 vol.) pressure was calibrated by the known pressure-induced transition of water to ice-VI at about 1 GPa. In other experiments, the pressure was estimated from the length of DAC springs to be 1 GPa too. In fact, both of these methods lead to unsatisfactory accuracy in pressure determination. Heating was done by the YAG laser with a 30 μm laser spot. The temperature was measured only by the visible observation of the heating spot hue and the brightness was about 1000 – 1700 K. The time of the heating was 30 - 60 minutes. In case of experiments with serpentine, gas bubbles have appeared and the reactant has turned black. After quenching and syringe tapping through rubber, gas chromatographic analysis was performed. After several tappings, confirmation that the content of the methane is lower than the air background was obtained (in one of the experiments it was much bigger at the beginning). The authors have reported that about 1 ml of gas products was analyzed for hydrocarbons. The presence of CO and CO₂ was detected in the experiment with siderite only and the authors have propagated this result in two other experiments.

The quality of chromatographic analysis, such as signal-to-noise ratio and peak distribution, can be estimated by chromatogram analysis. The authors used chromatographic results for the diagrams (Figure 2-3) construction and put them into a table. Although the fact that the analyzed volume differs from the volume inside the rubber ring, no calculation was shown and no discussion was presented about the possible yields and conversions. X-ray analysis shows that wustite and magnetite formation was performed only for one experiment.
The first reliable and reproducible experimental results, confirming the possibility of hydrocarbons synthesis under upper mantle conditions, were published by (Kutcherov et al. 2002). The authors used a CONAC high-pressure chamber. The pressure in the chamber was estimated using calibration curves, which were preliminarily constructed by studying the phase transitions in reference substances (Bi, Tl, and PbTe). The reproducibility of the calibration curves was within 2%. Heating was performed by passing an alternating electric current through a graphite heater. The temperature was measured with a chromel/alumel thermocouple. A programmable temperature control made it possible to maintain the temperature to an accuracy of 5 K throughout the experiment. The temperature gradient in the sample did not exceed 10 K at 1500 K. The reaction cells were stainless-steel or platinum ampoules with a volume of 0.6 cm³. The procedure of filling an ampule with the initial reactants ruled out the presence of air in the sample, and the sealing technique ensured the air tightness at all steps of the experiment. The filled ampule was placed into the high-pressure chamber and was pressurized and then heated to a given pressure and temperature. The treatment in the chamber for the necessary time was followed by quenching to room temperature at a rate of the order of 500 K/s, 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 mass spectroscopy, gas chromatography, and X-ray. The initial reactants in the synthesis were chemically pure FeO (wustite), chemically pure CaCO₃ (calcite), and double distilled water. The particle size of the solid reactants was 10–50 mm. Tentative experiments showed that the synthesis is described by the reaction (showed only for alkanes for simplicity):

\[
n\text{CaCO}_3 + (9n + 3)\text{FeO} + (2n + 1)\text{H}_2\text{O} \rightarrow n\text{Ca(OH)}_2 + (3n + 1)\text{Fe}_3\text{O}_4 + C_n\text{H}_{2n+2} \quad (2.1)
\]

where n≤6. Relatively wide spectrum of hydrocarbons was observed: normal and branched alkanes, alkenes and alkynes.

Taking into a consideration the fact that all of the calcite in ampoule was converted either to Ca(OH)₂ or, through phase transition, to aragonite, the authors proposed an equilibrium regime of the observed processes.

Figure 2-3 Results of the chromatographic analysis of gas products by (Weng et al. 1999). (A) – air, (B) – siderite + water, (C) – iceland spar + biotite, (D) iceland spar + serpentine + olivine.
(Scott et al. 2004) used the diamond anvil cell method with laser and resistive heating to investigate in-situ the behaviour of the system \( \text{CaCO}_3 - \text{FeO} - \text{H}_2\text{O} \) at a pressure of 5-11 GPa and for a temperature range of 800 – 1500 K. Raman spectrometry and X-ray synchrotron diffraction methods were used for the analysis. Both CO\(_2\) and Nd:YLF lasers were used simultaneously in the laser heating experiments to produce temperatures higher than 1200 K. The pressure was measured by the ruby technique (Mao et al. 1986). Optical pyrometry (Boehler and Chopelas 1991b) was a method for temperature determination in laser heating experiments.

Methane was identified in the reaction products for 2972 cm\(^{-1}\) and no other hydrocarbons had been observed. Methane signal was registered at 5 GPa during heating up to 773 K and at 883 K, it became very intensive. The authors noted the interesting fact that the methane amount was higher in the lower temperature experiments. Bubble formation with weak methane signals was observed in all experiments during depressurization at room temperature. As the authors also pointed out, no successful Raman spectra was collected higher 10 GPa. Using X-ray, formation of Fe\(_3\)O\(_4\) was detected. At the same time, calcium containing compound was not found, and general formula CaFe was suggested to keep material balance. In general, the reaction scheme, proposed by (Kutcherov et al. 2002), was confirmed by Scott et al.’s experimental results:

\[
\text{CaCO}_3 + 12\text{FeO} + \text{H}_2\text{O} \rightarrow \text{CaO} + 4\text{Fe}_3\text{O}_4 + \text{CH}_4
\]  

(2.2)

A comparison of (Kutcherov et al. 2002) and (Scott et al. 2004)’s experimental results, where the same initial reactants and similar thermobaric conditions were used, shows us the following. In the case of Raman spectrometry in a diamond anvil cell (Scott et al. 2004) only methane was found. In relatively large volume experiments in the CONAC chamber (Kutcherov et al. 2002) a mixture of hydrocarbons up to hexane was detected. The difference may be explained by the microliter character of the DAC experiment and the obstacle to analyzing highly distributed products of the cell volume with the background of fluorescent iron-containing materials. Quantities of hydrocarbons higher than methane, on an analogy with (Kutcherov et al. 2002), should decrease with an increase in molecular weight. Another important fact is that the characteristic frequencies of hydrocarbons lie in the spectral range of 1000 and 1500 cm\(^{-1}\) but their intensities are less than stretching C-H vibrations.

In 2008, (Chen et al. 2008) have continued the work of the (Scott et al. 2004) group. They also used diamond anvil cells for high pressure experiments, Raman spectrometry for analysis, resistive heating, ruby technique for pressure determination, but gold liner separated samples from the rhenium gasket to exclude its catalytic influence. There were 4 different loadings (Table 3):

<table>
<thead>
<tr>
<th>#</th>
<th>Reagents and thermobaric parameters in (Chen et al. 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>CaCO(_3) + FeO (1:12) and H(_2)O pressure change after 2 h 853 K: 6.5 – 8.9 GPa</td>
</tr>
<tr>
<td>#2</td>
<td>CaCO(_3) + FeO + serpentinite (1:12:4) pressure change after 2 h 853 K: 6.5 – 8.9 GPa</td>
</tr>
<tr>
<td>#3</td>
<td>CaCO(_3) + fayalite (1:6) and H(_2)O pressure change after 2 h 853 K: 6.5 – 8.9 GPa</td>
</tr>
<tr>
<td>#4</td>
<td>CaCO(_3) + SiO(_2) (4:1) and H(_2)O pressure change after 2 h 853 K: 6.5 – 8.9 GPa</td>
</tr>
</tbody>
</table>

Table 3
Serpentine and fayalite were natural samples. Samples #1 - #3 were heated for 2 hours at a starting pressure of 5-6 GPa and then the pressure increased after cooling to 7 – 9 GPa. The fact of pressure change should be a consequence of the reaction proceeding and the positive difference of molar volumes between the final products of the reaction and the initial reactants, but it is impossible to exclude the possibility of pressure increasing as a result of cell parts heating and stress relaxation because the method of heating as well as temperature measurements were not described. Decreasing of the intensity of 1112 cm\(^{-1}\) \(\text{CO}_3^{2-}\) signal and intensity growth of C-H stretching vibration at 2950 cm\(^{-1}\) confirms the fact of carbonate reduction to methane.

The “gas bubbles” formation mentioned by (Scott et al. 2004) and (Chen et al. 2008) can be interpreted as follows. All gaseous components that can be formed from elements, available in the above mentioned experiments, are: hydrocarbons, \(\text{H}_2\), \(\text{CO}\), \(\text{CO}_2\), \(\text{H}_2\text{O}\) and \(\text{O}_2\).

Analysis of critical parameters (Table 4) of main mantle gases shows that, at a pressure above 1 GPa these compounds can be fluid or solid, so the observed phenomenon of bubble appearance should be interpreted in terms of fluid-fluid and fluid-solid interactions: for example, as a result of the formation of hydrogen and its isolation from hydrocarbons on gradient cooling.

### Table 4 Critical parameters of important mantle gases

<table>
<thead>
<tr>
<th>Compound</th>
<th>(T_{\text{crit}}), K</th>
<th>(P_{\text{crit}}), MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen ((\text{H}_2))</td>
<td>33.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Methane ((\text{CH}_4))</td>
<td>190.4</td>
<td>4.60</td>
</tr>
<tr>
<td>Ethane ((\text{C}_2\text{H}_6))</td>
<td>305.3</td>
<td>4.87</td>
</tr>
<tr>
<td>Propane ((\text{C}_3\text{H}_8))</td>
<td>369.8</td>
<td>4.25</td>
</tr>
<tr>
<td>N-butane ((\text{C}<em>4\text{H}</em>{10}))</td>
<td>425.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Water ((\text{H}_2\text{O}))</td>
<td>647.0</td>
<td>22.06</td>
</tr>
<tr>
<td>Oxygen ((\text{O}_2))</td>
<td>154.55</td>
<td>5.043</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>304.19</td>
<td>7.38</td>
</tr>
<tr>
<td>(\text{CO})</td>
<td>132.35</td>
<td>3.50</td>
</tr>
</tbody>
</table>

In 2009, (A. Sharma et al. 2009) published the experimental results of hydrocarbon synthesis under extreme conditions from a water gas shift (WGS) reaction (2.3) perspective.

\[
\text{HCOOH} = \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \quad (2.3)
\]

**water gas shift reaction**
They used the diamond anvil cell method with resistive heating to reach temperatures of up to 1200 K and laser heating (Nd:YAG 1060 nm) for temperatures up to 1700 K at a pressure range of 1-5 GPa. Raman spectroscopy, by means of 632, 540, 514.5 and 488 nm lasers, was used for the analysis as well as standard optical observation. Temperature was measured by nichrome thermocouples with a ±5 K accuracy. Pressure was measured by the ruby technique or by shifts of species in the cell at high pressures, and the authors have estimated its accuracy to be ±0.5 GPa. The treatment time was not less than half an hour. A summary of the experimental results is presented in Table 5.

**Table 5 (A. Sharma et al. 2009) Summary of the experimental results**

<table>
<thead>
<tr>
<th>Run number</th>
<th>Starting material</th>
<th>Reactor</th>
<th>Conditions (T, P)</th>
<th>CH4</th>
<th>CO2</th>
<th>CO</th>
<th>H2</th>
<th>H2O</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pure formic acid</td>
<td>Au lined</td>
<td>330°C, 1.2 GPa</td>
<td>n/d</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>n/d</td>
</tr>
<tr>
<td>2</td>
<td>pure formic acid</td>
<td>Au lined</td>
<td>550°C, 5.5 GPa</td>
<td>n/d</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>n/d</td>
</tr>
<tr>
<td>3</td>
<td>pure formic acid</td>
<td>stainless steel</td>
<td>250°C, 1.0 GPa</td>
<td>m</td>
<td>w</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>Fe–carbonate, Fe(CO)2</td>
</tr>
<tr>
<td>4</td>
<td>puriformic acid</td>
<td>Au lined</td>
<td>440°C, 1.5 GPa</td>
<td>m</td>
<td>w</td>
<td>s</td>
<td>m</td>
<td>m</td>
<td>Fe–carbonate, Fe(CO)2</td>
</tr>
<tr>
<td>5</td>
<td>pure formic acid</td>
<td>Fe3O4</td>
<td>560°C, 3.5 GPa</td>
<td>s</td>
<td>m</td>
<td>s</td>
<td>w</td>
<td>s</td>
<td>Fe–carbonate, FeCO3</td>
</tr>
<tr>
<td>6</td>
<td>CO2, H2O, Fe3O4, FeO</td>
<td>Au lined</td>
<td>360°C, 2.5 GPa</td>
<td>m</td>
<td>m/w</td>
<td>s</td>
<td>m</td>
<td>m</td>
<td>CO2, Fe–carbonate, CO, H2, no detectable C–H</td>
</tr>
<tr>
<td>7</td>
<td>graphite–formic acid</td>
<td>Au lined</td>
<td>350°C, 4.5 GPa</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>m</td>
<td>m</td>
<td>graphite</td>
</tr>
<tr>
<td>8</td>
<td>graphite–formic acid</td>
<td>Cu–Be</td>
<td>420°C, 4.0 GPa</td>
<td>s</td>
<td>s</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>graphite</td>
</tr>
<tr>
<td>9</td>
<td>graphite–formic acid</td>
<td>Au lined</td>
<td>550°C, 4.5 GPa</td>
<td>s</td>
<td>s</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>C–H, more than methane</td>
</tr>
<tr>
<td>10</td>
<td>graphite–H2</td>
<td>Au lined</td>
<td>&gt;1500°C, 5.5 GPa</td>
<td>s</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
<td>graphite</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>graphite–H2</td>
<td>rhenium</td>
<td>&gt;1500°C, 5.0 GPa</td>
<td>s</td>
<td>n/d</td>
<td>n/d</td>
<td>n/d</td>
<td>graphite</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>FeO–CaCO3–H2O</td>
<td>Au lined</td>
<td>550°C, 7.0 GPa</td>
<td>m</td>
<td>w</td>
<td>s</td>
<td>m</td>
<td>s</td>
<td>Fe–carbonate, Fe2O–carbonate</td>
</tr>
<tr>
<td>13</td>
<td>FeO–CaCO3–H2O</td>
<td>stainless steel</td>
<td>520°C, 6 GPa</td>
<td>m</td>
<td>m</td>
<td>m</td>
<td>s</td>
<td>Fe–carbonate, FeCa–carbonate</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>FeO–CaCO3–H2O</td>
<td>Au lined</td>
<td>350°C, 4.0 GPa</td>
<td>n/d</td>
<td>s</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>Fe–carbonate, Fe–oxides</td>
</tr>
<tr>
<td>15</td>
<td>FeO–CaCO3–H2O</td>
<td>Au lined</td>
<td>620°C, 6.5 GPa</td>
<td>w</td>
<td>s</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>Fe–carbonate, magnoite</td>
</tr>
</tbody>
</table>

* s, strong; m, moderate; w, weak; vw, very weak; n/d, not detected.

Most of the experiments were initiated at pressures of around 1.0 GPa. However, at high temperatures, higher pressures were typically achieved and, in some cases, also manually adjusted to maintain conditions within an estimated geothermal gradient.

The authors have reported that Raman signals, corresponding to pure formic acid, disappeared after heating up to 625 K at pressures higher than 0.5 GPa with the formation of a water-gas (CO, CO2, H2O, H2) mixture (2.3). The stoichiometry of the mixture remained constant after heating-cooling cycles with gold liner (material that divides sample from metal gasket), that presumed the equilibrium character of the water-gas mixture. Liner change from a gold to a steel gasket has led to methane signal observation together with iron carbonate and iron carbonyl species at temperature of 525 K and at pressure of 1.0 GPa due to gasket oxidation processes. In the experiments with pure formic acid, heating of up to 600 K at a pressure of 1.2 GPa and up to 825 K at 5.5 GPa with gold-liner, no hydrocarbon formation was observed. Strong Raman signals of methane were received in the experiments where pure formic acid was heated with presence of Fe/FeO or graphite in the temperature interval of 525-825 K at pressure range of 1-4.5 GPa (Table 5). The formation of methane in contact with iron was interpreted as some sort of catalysis through carbonyl species formation. The loading of formic acid with graphite and the heating of the system to a temperature of 625 – 825 K at a pressure range 3.5 – 5 GPa (see Table 5) also led to methane formation. Some new peaks near methane were observed and interpreted by the authors as other hydrocarbons, e.g. ethane, formation. To investigate the possibility of the direct hydrogenation of graphite, the authors heated hydrogen and graphite up to 1500 K. The formation of several signals in the 3000 cm⁻¹ region was observed. These could be the features of the hydrocarbons. The sharp
individual structure of the signals (see Figure 2-4) can be a sign of clathrate formation. Changing the heating method the authors have explained as anticipation of a “sluggish” reaction character. This change does not allow us to compare the results of the new set of experiments with the previous set, where the authors used resistive heating.

![Figure 2-4 Raman spectra of graphite – H₂ mixture after exposition – to 1773 K at 5 GPa.](image)

**Figure 2-4** Raman spectra of graphite – H₂ mixture after exposition – to 1773 K at 5 GPa.

**Conclusion.**

The synthesis of hydrocarbons under mantle thermobaric conditions from minerals was confirmed by (Kutcherov et al. 2002) in Russia using a big volume CONAC cell; by (Chen et al. 2008; Weng et al. 1999) in China using a diamond anvil cell; and by (Scott et al. 2004; A. Sharma et al. 2009) in the USA using DAC.

The temperature and pressure range of the hydrocarbon synthesis is sufficiently wide. According to experiments with resistive heating (A. Sharma et al. 2009), the lowest fixed temperature for methane high-pressure synthesis from mantle modeling compounds CaCO₃-FeO-H₂O is 825 K (at 7 GPa). Formation of methane was observed already at 633 K from formic acid, FeO, Fe nanoparticles and water at a pressure of 2.5 GPa.

The highest temperature for a fully hydrostatic experiment was 1473 K at 5 GPa (Kutcherov et al. 2002). In most of the experiments methane was the only hydrocarbon to form from mantle compounds due to the small reaction volume. Alkynes, alkenes and alkanes up to C6 were observed in products only in (Kutcherov et al. 2002). Until the present, the only thing that can be clearly stated is that it is possible to synthesize hydrocarbons from the inorganic material under upper mantle conditions. Thus, the next step should be an investigation of influence of different factors (the oxidation state of carbon and hydrogen donor, pressure and temperature) on the quantity and the composition of the final hydrocarbon mixture.

Another interesting field of study that may clarify the question about the mechanism of hydrocarbon synthesis is investigation of individual hydrocarbons.
3. METHANE TRANSFORMATION AT HIGH PRESSURES AND TEMPERATURES

Thermal transformations of hydrocarbons at atmospheric pressure attracted proper attention, producing a base for the petrochemical industry. At high pressures, they have also been investigated, especially unsaturated hydrocarbons (Schettino et al. 2005), but less widely. Mostly because of the experimental complexity, systematic and sufficiently precise work has been carried out only in the last decade. The number of works about methane transformations under hydrostatic conditions is rather small, and there are no reviews on this topic. Due to the complex and the usually custom-made character of the experimental setups, and analytical problems (most often because of the absence of reference spectral information at high pressure), it is hard to find regularities or comparability in the works of different authors. In this part of the introduction, the available information about methane transformation at high pressure and high temperature is considered to pick out critical problems that are necessary to study in the first place.

The transformation of methane at high temperatures has been a matter of interest mostly for the chemical vapor deposition process for diamond growing and carbon films making. (Akatsuuka et al. 1988; Matsumoto et al. 1987; Matsumoto et al. 1982), but the effect of very high pressure – more than 1 GPa did not attract attention until recently. (Culler and Schiferl 1993) reported about the high pressure high temperature methane dissociation (3.1) for the first time.

\[ \text{CH}_4 \rightarrow \text{C}_{\text{soot}} \]  \hspace{1cm} (3.1)

The pressure in the Merill-Basset diamond anvil cell (DAC) was up to 13 GPa and the temperature was up to 915 K. The determination of pressure was realized by the ruby \( R_1 \) luminescence method. A vacuum oven with water cooling was used for heating. Temperature was measured as an average value of three W-Re thermocouples and error was assumed to be the maximum difference between the thermocouples values. The gasket material was a molybdenum -13 wt% rhenium alloy. An analysis of the reaction products was carried out using Raman spectrometry. After heating the DAC in the oven, the authors observed a weak Raman signal of 1619 cm\(^{-1}\) which was interpreted as a signal of soot-like material. Due to the different thermal expansion coefficients of the cell components and ruby signal broadening, the authors estimated the pressure region for the transformation as 2.5 – 5 GPa. At these pressures, the temperature of methane dissociation was estimated as 912±7 K. The time of the methane to soot transformation was estimated to be less than a minute. The soot-like material was formed at a laser intensity of 80 mW (21836 cm\(^{-1}\) laser). Increasing of the laser intensity up to 200 mW (20492.2 cm\(^{-1}\) laser) accelerated the soot formation, that suggests the photochemical character of the observed reaction. The p-T parameters of this reaction without laser influence could be different. The authors have drawn a conclusion about soot formation on the basis of the following factors: visual observation, a weak Raman signal of 1619 cm\(^{-1}\) and its pressure dependence. At a pressure of 10-13 GPa and temperature of 948 K, the authors observed that clear hard solid material was formed during 40 mW 20492 cm\(^{-1}\) laser exposition. This material looked like a diamond film that was confirmed by the experiment with \(^{13}\)CD\(_4\).
Methane signals observation in icy planet spectra and the theoretical calculations of (Ancilotto et al. 1997) motivated (Benedetti et al. 1999) to investigate methane transformation at very high thermobaric conditions. Besides Raman spectrometry and laser heating in diamond anvil cells, the authors have used infrared spectrometry and the X-ray diffraction method with synchrotron radiation. In the experiments, an infrared 1064 nm Nd:YAG laser was used for laser heating, and rhenium was the gasket material. In some experiments, platinum couplers were placed inside the sample for better IR-radiation absorption. Temperature measurement was carried out by fitting a Planck-function for “grey body”. Pressure was determined by a ruby technique (Mao et al. 1986). Raman analysis was carried out only at an ambient temperature after the heating experiment. No thermoresistive diamond covers were used. The duration of the experiment was $10^2-10^3$ seconds. After heating up to 2000-3000 K at a pressure range of 10-50 GPa, opaque and transparent products were formed. Raman analysis after quenching has shown that the opaque compounds were diamonds. Transparent products have escaped from the cell during quenching (i.e. opening at an ambient temperature), becoming a vapor. Hydrogen was not detected, but the authors have interpreted the increase of the crystal cell parameter of rhenium gasket in contact with methane as evidence of rhenium hydrides formation, though no reference information was presented. At the same time, the authors proposed that a gasket material did not influence methane transformation.

(Benedetti et al. 1999) have reported about hydrocarbons with double and triple bonds formation (Figure 3-1), but have not referred to any literature data on the spectral characteristics of hydrocarbons at high pressure, excluding methane. Peaks identification were carried out only on the frequency values at normal pressure (0.1 MPa).

![Figure 3-1](Benedetti et al. 1999) After heating to 2000-3000 K at 19 GPa. (A) Opaque reaction region. (B) The transparent reaction region. (C) Unreacted area of the sample with no transformations.

The formation of unsaturated compounds in the declared thermobaric range of 2000-3000 K and 10-50 GPa is unlikely due to the polymerization reactions of ethene (Chelazzi et al. 2004; Chelazzi et al. 2005) and acetylene (Aoki et al. 1989; Aoki et al. 1987; Sakashita et al. 1996).
The strong 1600 cm$^{-1}$ peak in (Figure 3-1) could be identified as graphite (Goncharov 1990; Hanfland et al. 1989) (Figure 3-2), in-plane interlayer mode vibration. A second order peak of graphite should be seen at 2750 cm$^{-1}$ but this spectral range is not presented in this paper.

**Figure 3-2** (Goncharov 1990) Graphite Raman spectrum, 1600 cm$^{-1}$ range.

The experimental thermobaric conditions mentioned in the paper (10-50 GPa, 2000-3000 K) correspond to the region of equilibrium diamond formation (Figure 3-3).

**Figure 3-3** Phase diagram of individual carbon (Bundy et al. 1996). Grey region indicates experimental conditions in (Benedetti et al. 1999)
Taking into consideration kinetic, surface or catalytic factors other forms of carbon could be also synthesized. Formation of opaque material was observed only in the laser heating point where the temperature was higher than 2000 K. Transparent products were located around the heating point, where temperature was less than 2000 K due to the usual temperature gradients in the DAC experiment.

(Zerr et al. 2006) have investigated diamond formation during the hydrocarbons dissociation process. Methane (CH₄), ethane (C₂H₆), octane (C₈H₁₈), decane (C₁₀H₂₂), octadecane (C₁₈H₃₈), and nonadecane (C₁₉H₄₀) had been chosen as the initial reactants. Experiments were made in the temperature interval of 2500 – 7300 K and at a pressure range of 4 – 25 GPa. In laser heating experiments in the diamond anvil cell with rhenium gaskets, different coupler materials (Al₂O₃, SiC, MgO) were used. An experiment without a coupler was carried out using a 1060 nm CO₂-laser. Temperature measurement was made by fitting the Planck-function for a “grey body” with a wavelength-independent emissivity to the measured thermal radiation spectrum. The diameter of the heated area varied between 50 and 100 μm, depending on the sample material. The thermal radiation of the heated sample was measured at the centre of the hot spot from areas of about 3 μm in diameter. The authors described, that due to the absence of a thermally insulating pressure medium, significant axial temperature gradients in the heated volume have taken place. These gradients were the reason of the systematic error in temperature determination. Model calculations of the temperature distribution in the laser-heated DAC have shown that, in this case, the sample temperatures vary, from almost room temperature on the diamond anvil surface to a peak temperature in the centre of the heated sample volume (Bodea and Jeanloz 1989). This peak temperature could be 18% higher than the measured average temperature (Manga and Jeanloz 1996).

The Raman spectra were registered at intervals of 300-1200 cm⁻¹ and 2800-4500 cm⁻¹ using Ar-laser radiation. The authors have found that at temperatures higher than 2300 K and at pressures higher than 13 GPa methane at least partly dissociated to atomic carbon and hydrogen. The signals of the stretching vibrations and rotations of hydrogen were found to be around 4200 cm⁻¹ and in the interval of 300-1300 cm⁻¹ correspondingly. A complex signal, found around 4200 cm⁻¹ corresponds to the methane-hydrogen compounds formation (Somayazulu et al. 1996). After heating methane up to 3000 K at 23.1 GPa without a coupler, hydrogen signals were observed with high fluorescence due to the probable ultradispersive diamonds formation.

Measurements of the Raman spectra were made both in the heat point and in the cold sample zones. Using different coupler materials (Figure 3-4) the authors have observed a set of Raman signals in the cold sample zones. Only hydrogen was identified. Nevertheless, the data presented in the paper is enough in order to make an analysis of all of the Raman signals received. On the basis of experimental results published in (Kolesnikov et al. 2009) Raman characteristic of ethane, propane and n-butane could be recognized (Figure 3-5).
**Figure 3-4** Raman spectra of methane transformation products from (Zerr et al. 2006). (A) CH$_4$ heated without absorber at 23.1 GPa; (B) CH$_4$ heated in contact with Al$_2$O$_3$ at 17.9 GPa; (C) CH$_4$ heated in contact with SiC at 13.2 GPa; (D and E) CH$_4$ heated in contact with MgO at 14.1 and 15.3 GPa, respectively.

**Figure 3-5** Pressure dependencies of the Raman bands of decomposition products obtained after heating of methane and ethane in work (Zerr et al. 2006). The dependencies are shown for the Raman bands observed in the low frequency range (300–1200 cm$^{-1}$) and in the range of the hydrogen vibron bands (4000–4500 cm$^{-1}$). Solid circles, CH$_4$ heated without absorber; solid squares, CH$_4$ heated in contact with Al$_2$O$_3$; solid diamonds, CH$_4$ heated in contact with SiC; triangles, CH$_4$ heated in contact with MgO; open diamonds, C$_2$H$_6$ heated without an absorber. The arrows indicate the pressures at which the samples were heated.
At a pressure of 4 GPa, frequency of 1010 cm\(^{-1}\) corresponds to ethane, 894 cm\(^{-1}\) - to propane and 864 cm\(^{-1}\) - to n-butane (Kolesnikov et al. 2009). As it is possible to see from (Figure 3-5), the formation of hydrocarbons takes place in the pressure range from 4 GPa to 17.9 GPa with Al\(_2\)O\(_3\), SiC and MgO couplers at a temperature of less than 2300 K. After heating up to 6400 K at 13.2 GPa, a non-evaporating liquid was found on the diamonds' surface. As reported in the paper, Raman analysis of liquid has failed, probably because of its low quantity. The conditions of the dissociation of ethane to diamond and hydrogen are 3000 K and 13 GPa. After heating up to 6800 K at 21.8 GPa, the liquid was found on the diamond's surface again. The formation of hydrocarbons were not observed. Octane, decane, octadecane and nonadecane became diamonds without any coupler at 3000 K and in the pressure range from 10 to 20 GPa. In the Raman spectra, neither hydrogen nor hydrocarbons were found.

Methane transformations under the thermobaric conditions of Uranus and Neptune interiors (1100-3000 K and 10.4 - 81.4 GPa) were investigated by (Hirai et al. 2008). Methane was loaded in the diamond anvil cell and heated from both sides by a Nd:YAG laser or only from one side by a CO\(_2\) – laser. Temperature measurement was carried out by fitting a Planck-function. Pressure was measured by the ruby technique (Mao et al. 1978; Piermarini and Block 1975). The time of the heating was in the interval from 10 seconds to 15 minutes. To be able to reach a higher temperature, a platinum ring was used or a platinum powder was placed in the sample. Raman analysis and X-ray diffraction were employed both before and after the heating experiment. By varying the laser intensity, the authors have defined four temperature intervals: lower 1100 K, 1100-2200, 2200-3000, higher 3000 K. If the temperature was below 1100 K at pressures of 10, 20, 35, 52 и 81 GPa, the sample of methane was stable. In the temperature interval of 1100-2200 K fluid formation was observed. After the sample cooling, X-ray and Raman spectra showed its amorphous character, proving high temperature fluid-solid phase transition. It suggests that the melting temperature of methane at pressures higher than 10 GPa was higher than 1100 K.

In the temperature interval of 1100-2200 K at pressures of 13, 14 and 33 GPa, a Raman signal in the interval of 1000 -1150 cm\(^{-1}\) was found (Figure 3-6). The authors have identified this Raman signal as an ethane one. Ethane intensity rising after heating to 1800 K was interpreted as a greater ethane yield.

**Figure 3-6** (Hirai et al. 2008) Observation of ethane signals formation (arrows) after methane heating to 1100-2200 K at 13, 14 and 33 GPa.
In the temperature interval of 2200-3000 K in a pressure range of 10.4 – 81.4 GPa, a black product formation was observed. After the sample cooling, an X-ray analysis of these products was made. X-ray diffraction spectra have shown a set of broad low intensity lines. These lines did not correspond either to methane, ethane, the hydrides of iron or platinum. Without X-ray data, it is possible to guess that these signals could refer to carbon. In the opened cell, Raman vibration modes in the interval from 2750 to 3000 cm\(^{-1}\) were observed. To explain this fact, the authors have suggested the formation of a C-H compound, which did not evaporate at ambient pressure and temperature, e.g. polyethylene or polyacetylene.

The sample which was investigated at the temperature interval of 1100-2200 K was heated once more up to a temperature of 3000 K at 16.8 GPa. Black product formation was observed. X-ray analysis has shown the presence of diamonds in these products.

To examine the effect of heating time on the process of methane transformation, the authors have heated the samples in the temperature intervals of 1100-2200 K and 2200-3000 K for 10 s and for 15 min. The pressure range was not mentioned. The products of reaction in both cases were the same: ethane at 1100-2200 K, and black substance at 2200-3000 K.

The influence of cooling speed on the products’ composition was also investigated. In the first case, the products obtained at high pressure and high temperature, were cooled down to ambient temperature for milliseconds. In the second case, the temperature was gradually decreased over 10 minutes. No quality changes in the composition of the products of reaction were observed, which is an argument for the instant character of the chemical transformation.

Conclusion

Most of the experimental results dealing with the study of methane under pressure higher than 1 GPa could not be accepted as reliable data. There are the following problems: spectral identification of transformation products was not performed unambiguously; the role of different materials in contact with methane as well as the role of the hydrogen during the reactions was unclear; transformation pathways were not well established; thermodynamic conditions of the upper mantle were not modelled.
4. EXPERIMENTAL PART 1. INVESTIGATION OF ABIOTIC HYDROCARBON SYNTHESIS UNDER THE EARTH’S UPPER MANTLE CONDITIONS

To investigate regularities of the hydrocarbons synthesis under upper mantle conditions, two large-volume techniques were used.

The experiments were carried out in a CONAC high-pressure chamber (Institute for High Pressure Physics RAS, Troitsk, Russia) (Figure 4-1).

![CONAC high pressure chamber scheme](image1)

**Figure 4-1** CONAC high pressure chamber scheme: 1 – container, 2 – tube heater, 3 – metal current distributor, 4 – meal disk, 5 – heat-insulated tube, 6 – inner isolation tube, 7,8 – heat-insulated disk, 9 – experimental ampule.

and in a split-sphere multianvil device Figure 4-2.

![Pressless split-sphere multianvil device (BARS)](image2)

**Figure 4-2** Pressless split-sphere multianvil device (BARS), Trofimuk United Institute of Geology, Geophysics and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia.

The high-pressure equipment and experimental procedures were described in detail previously (Chepurov et al. 1997; Kutcherov et al. 2002; Nikolaev and Shalimov 1984; Nikolaev and Shalimov 1999).

Pressure in the BARS apparatus was determined before the sample heating by measuring environmental stress, calibrated on Bi and PbSe. The temperature was measured by the thermocouple PtRh6/PtRh30, calibrated on melting of Au, Ag in the cell at high pressure.
The pressure in the CONAC chamber was estimated using calibration curves, which were preliminarily constructed by studying the phase transitions in reference substances (Bi, Tl, PbTe). The reproducibility of the calibration curves was within 2%. Heating was performed by passing an alternating electric current through a graphite heater. The temperature was measured with a chromel/alumel thermocouple. Programmable temperature control allowed experimenters to maintain the temperature with an accuracy of 5 K throughout the experiment. The temperature gradient in a sample did not exceed 10 K at 1500 K.

The reaction cells in all experiments were platinum ampoules 0.6 cm$^3$ (Chepurov et al. 1997; Kutcherov et al. 2002). The method for filling the ampoules with the initial substances ruled out the presence of air, biogenic compounds or hydrocarbons in the sample, and ensured gas tightness at all the stages of the experiment. The size of the particles of the solid components was 10–50 μm.

The experimental procedures in both setups were similar. A filled ampoule was placed in a high-pressure chamber, compressed to the target value of pressure and then heated to the target value of temperature. After a certain exposure time that was the same in all the experiments, the ampoule was cooled, the pressure was reduced to a normal value, and the ampoule was removed from the chamber. The time of cooling to ambient temperature in the experiments varied from several seconds (quenching) to 4 hours. Then, the ampoule was opened in a chromatographic system, and qualitative and quantitative compositions were determined at 120–700°C for substances that are gaseous or liquid under normal conditions: hydrocarbons, CO$_2$, CO, and N$_2$. The rest of the material in the ampoule was subjected to X-ray diffraction analysis.

Results and discussions

The main chromatographic data and values of the important parameters are shown in the (Table 6) for four successful high-pressure experiments.

The first fact, which can be derived from the presented data, is confirmation of complex hydrocarbons synthesis from inorganic compounds under upper mantle conditions. Though such information was reported earlier by (Chekaluk et al. 1969; Kutcherov et al. 2002), quantity of positive results is still too low to become an “obvious fact”.

To investigate possible isotopic effects, two similar experiments were carried out, but in the experiment A normal water reacted with calcium carbonate and iron, and in the experiment B – deuterated water was used.

The chromatographic data for the experiments A and B (Table 6) shows the formation of a complex hydrocarbon system and the absence of a significant effect of deuterated water on the composition and quantity of the hydrocarbon part of the products.
Table 6 Summary of experimental results of high-pressure high-temperature hydrocarbon synthesis at 5 GPa, 1500 K. Temperature of ampoule unsealing 120 °C.

<table>
<thead>
<tr>
<th>Experiment, reagents, cooling rate</th>
<th>Concentration, mol.%</th>
<th>CH₄, μmol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>N₂</td>
</tr>
<tr>
<td>Toroidal high-pressure apparatus (CONAC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experiment A quenching CaCO₃+Fe+H₂O</td>
<td>0.0</td>
<td>tr.</td>
</tr>
<tr>
<td>experiment B quenching CaCO₃+Fe+D₂O</td>
<td>0.0</td>
<td>tr.</td>
</tr>
<tr>
<td>Split-sphere high-pressure device (BARS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experiment C quenching C+Fe+H₂O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>experiment D 4 h. cooling C+Fe+H₂O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Severo-Stavropolskoe gas field</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>Vuctyl'skoe gas field</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

The product mixture was heated in the unsealing device at different temperatures. Results of the chromatographic analysis for the experiments A and B are presented in the Table 7. One can see that the greatest volume (>90%) of hydrocarbons was extracted from the system at 120°C. At the same time, the quantity of hydrocarbons does not decrease linearly with temperature but has a peak at 500 °C. The quantity of carbon monoxides and dioxides is negligible up to 700°C. This can be explained by destruction of residual calcium carbonate or oxidation of carbonaceous substances.

Figure 4-3 shows the X-ray diffraction pattern for experiment A. The clear cut Ca(OH)₂ lines in the absence of CaCO₃ lines in the X-ray diffraction pattern prove that hydrocarbons in the experiments form by the reactions:

Experiment A:
\[ n\text{CaCO}_3 + (3n+1)\text{Fe} + (2n+1)\text{H}_2\text{O} \rightarrow n\text{Ca(OH)}_2 + (3n+1)\text{FeO} + \text{C}_n\text{H}_{2n+2}, \]  \hspace{1cm} (4.1)

Experiment B:
\[ n\text{CaCO}_3 + (3n+1)\text{Fe} + (2n+1)\text{D}_2\text{O} \rightarrow n\text{Ca(OD)}_2 + (3n+1)\text{FeO} + \text{C}_n\text{D}_{2n+2}, \]  \hspace{1cm} (4.2)
Table 7 Composition of products, received in high-pressure high-temperature hydrocarbon synthesis, as dependence from temperature during opening procedure

<table>
<thead>
<tr>
<th>T, °C</th>
<th>CH₄</th>
<th>C₂H₆/C₂H₄</th>
<th>C₃H₆/C₃H</th>
<th>C₄H₁₀/C₄H₈</th>
<th>H₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>CO₂</th>
<th>CO</th>
<th>N₂</th>
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<tr>
<td></td>
<td></td>
<td>Concentration, mg/kg</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>120</td>
<td>310</td>
<td>210</td>
<td>30</td>
<td>4</td>
<td>60</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0,6</td>
<td>0</td>
<td>0</td>
<td>0,0</td>
<td>0,0</td>
<td>0,0</td>
<td>4200</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0,0</td>
<td>0,0</td>
<td>2</td>
<td>8100</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
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<td>1</td>
<td>0,8</td>
<td>1</td>
<td>40</td>
<td>40</td>
<td>4000</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>20</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>40</td>
<td>40</td>
<td>4800</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>10</td>
<td>1</td>
<td>0,4</td>
<td>tr.</td>
<td>40</td>
<td>40</td>
<td>44000</td>
<td>7</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>7</td>
<td>1,4</td>
<td>0,8</td>
<td>0,9</td>
<td>50</td>
<td>50</td>
<td>4000</td>
<td>140</td>
<td>100</td>
<td>0</td>
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<tr>
<td></td>
<td></td>
<td>Experiment A (CaCO₃ + Fe + H₂O, quenching)</td>
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<td></td>
<td></td>
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<tr>
<td>120</td>
<td>240</td>
<td>160</td>
<td>30</td>
<td>4</td>
<td>80</td>
<td>80</td>
<td>34600</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0,0</td>
<td>0,0</td>
<td>0,0</td>
<td>4000</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>4</td>
<td>0,5</td>
<td>0</td>
<td>0,0</td>
<td>0,0</td>
<td>30</td>
<td>3400</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>3</td>
<td>0</td>
<td>0,4</td>
<td>0,5</td>
<td>60</td>
<td>60</td>
<td>4900</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>500</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1800</td>
<td>1800</td>
<td>43000</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>600</td>
<td>8</td>
<td>1</td>
<td>0,9</td>
<td>1</td>
<td>5400</td>
<td>5400</td>
<td>4000</td>
<td>8</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>700</td>
<td>6</td>
<td>0</td>
<td>tr.</td>
<td>0,0</td>
<td>1600</td>
<td>1600</td>
<td>4600</td>
<td>20</td>
<td>110</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experiment B (CaCO₃ + Fe + D₂O, quenching)</td>
<td></td>
<td></td>
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</tbody>
</table>

Figure 4-3 X-ray diffraction pattern of the products of the experiment A.

The factual absence of CO and CO₂ in the reaction products (Table 6) implies the instability of compounds with a C=O bond at the experimental temperature and pressure values, at least, in the fluid that should contain these gases. The absence of nitrogen in the reaction products suggests the gas tightness of the ampoule at all the stages of the experiments.

While the carbon donor in the experiments A and B was CaCO₃, the carbon donor in the experiments C and D was graphite (Table 6). The other reactants were H₂O and Fe(0). The experiments were carried out in sealed platinum ampoules 5 mm in diameter at two
different cooling rates. Ampoule in the experiment C was cooled down with the rate of 500°C/sec. In the experiment D constant cooling lasted for 4 hours.

The chromatographic data (Table 6) suggests that the experiments at temperatures and pressures close to those in the mantle resulted in synthesis of hydrocarbon mixtures similar in composition to natural gas. If the carbon donor was CaCO$_3$ (experiments A and B), the methane concentration in the produced mixture was the same as that in “fat” (rich in heavy hydrocarbons) natural gas (as in the Vuktyl’skoe gas field). If the carbon donor was individual carbon (experiments C and D), the hydrocarbon composition corresponded to “dry” (methane-rich) natural gas (as in the Severo-Stavropol’skoe gas field).

Rapid cooling (quenching) fixes CH$_4$ and C$_2$H$_6$/C$_2$H$_4$ in the reaction products (the gas chromatographic analysis procedure we used was incapable of separating saturated and unsaturated hydrocarbons). After cooling for 4 hours (experiment D), the amount of CH$_4$ and C$_2$H$_6$/C$_2$H$_4$ in the reaction products increased by a factor of tens, and heavier hydrocarbons up to C$_4$H$_{10}$/C$_4$H$_8$ were detected. Thus, the time of cooling of the fluid, forming at high pressure (e.g., in the course of its jet migration to the surface), has a significant effect on the final composition of the fluid. A decrease in the rate of cooling of the initial fluid results in the synthesis of heavier saturated hydrocarbons.

The X-ray diffraction pattern in the experiment D (Figure 4-4b) contained no reflections of FeO at 2θ = 36°, 42°, and 61°, which were clearly seen in experiment C (Figure 4-4a). This suggests complete oxidation of iron to Fe$_3$O$_4$, which gives rise to weak reflections in X-ray diffraction patterns. The oxidant in this case should be water.

Then, at the first stage, in case of quenching (experiment C), the reaction is the following (4.3):

$$H_2O + Fe \rightarrow FeO + H_2$$

and in case of slow cooling (experiment D), the reaction is (4.4)

$$4H_2O + 3Fe \rightarrow Fe_3O_4 + 4H_2$$
At the second stage, in both cases, hydrocarbons can be assumed to form from carbon and hydrogen by the reactions (4.5) and (4.6).

\[
\begin{align*}
\text{(4.5)} & \quad nC + (n+1)H_2 = C_nH_{2n+2} \\
\text{(4.6)} & \quad nC + nH_2 = C_nH_{2n}
\end{align*}
\]

Cooling shifted the equilibrium of the reaction between Fe(0) and water toward the formation of hydrogen and stronger iron oxidation. The fact that the reaction (4.4) involves more hydrogen than the reaction (4.3) does, results in an increase in the amounts of hydrocarbons in the reactions (4.5) and (4.6).

However, although the influence of the quenching time is obvious, the full explanation of this effect requires further investigation.
5. EXPERIMENTAL PART 2. INVESTIGATION OF METHANE AND ETHANE TRANSFORMATION UNDER THE EARTH’S UPPER MANTLE CONDITIONS

To understand the mechanism of hydrocarbon synthesis in the Earth's upper mantle it is important to investigate the properties of basic hydrocarbons in the pressure range of 2-5 GPa and in the temperature interval of 1000-2000 K. These thermobaric conditions correspond those at the depths of 50-200 km, where synthesis of hydrocarbons is the most probable. We chose hydrocarbons that dominated in the products of hydrocarbon synthesis from inorganic compounds: methane and ethane (Table 6). The method of diamond anvil cells was chosen because of the possibility to work with gases in a simple way and to observe chemical processes in-situ. This method has a lot of custom-made operations that may influence the final result so the next chapter will be devoted for accurate description of the experimental procedure.

5.1. Experimental Method

5.1.1. Reagents Quality

Methane – 99,9995% Airgas Inc.,
Ethane – 99,99% Airgas Inc.,
Propane – 99,97% Aldrich,
Al₂O₃ – powder 0.05 μm, Allied High Tech Products, Inc.,
Ir – foil 25 μm, Aldrich,
Re – plates 250 μm, 99,98%, Aldrich,
W - plates 250 μm, 99,9%, Aldrich,
B – amorphous submicron, Aldrich,
Au – 99,9% wire 200 μm, Alfa Aesar,
Fe₃O₄ – monocrystal, spectral pure.
5.1.2. Equipment

Figure 5-1 Optical scheme used for Raman measuring and IR-heating.

For continuous wave (CW) laser heating the Raman system (Deemyad and Silvera 2008; Goncharov and Crowhurst 2005; Goncharov and Crowhurst 2006) was used and modified in the process of work (experiments #5 - #11 in Table 8) to include a double-sided heating option, to use an Ytterbium fiber laser, to provide a flat-top laser heating spot, and to measure spectra-radiometric temperature in the near IR spectral range.

For excitation of Raman scattering a Coherent 300 mW Ar+-laser 458 nm or 488 nm was used. Heating of the samples was provided by 60 W 1053 nm Nd:YLF (Neodymium-doped yttrium lithium fluoride) for experiments 1-4 (Table 8), 1075 nm Ytterbium Fiber laser for experiments #5 - #11. The radiation of the Raman excitation laser entered into an optical system with a beamsplitter – Kaiser Optics laser band-pass filter. The scattered/emitted sample radiation was analyzed by a single-stage grating spectrograph Jobin-Yvon HR460. A schematic of the system is shown in (Figure 5-1).

Similar to the optical arrangement described in (Goncharov and Crowhurst 2005; Goncharov and Crowhurst 2006), an unpolarized output beam of the fiber laser was split into two beams with orthogonal polarizations using a polarizing beam-splitter cube. Other two polarizing beam-splitter cubes were used to inject these two heating laser radiation beams into the Raman/radiometry system from both sample sides. These polarizing cubes reflected virtually 100% of the p-polarized IR laser radiation (1075 nm) and transmitted very well in the visible spectral range (e.g., there were no ripples characteristic for dichroic beamsplitters).

The laser heating power could be controlled independently at each sample side by rotating a \( \lambda/2 \) waveplate (which rotate the polarization plane). The net laser output power could
also be controlled by changing the laser diode current; this does not change the mode state and quality.

A Mitutoyo near IR 20X and 10X long-working distance objective lenses were employed for the sample visualization, focusing the fiber laser in the sample, collection of radiation spectra in the visible (all from both sides), collection of Raman and near IR radiation spectra (from one side) in the axial geometry.

A separate beam expander (acting as a contractor) was used in combination with a 20X Mitutoyo lens to match the IR fiber laser beam diameter and the entrance pupil of the lens and also to move the position of the focused laser spot in depth with respect to the focal plane of the lens.

A π-Shaper® was positioned in the fiber laser beam approximately 1000 mm upstream from the lens to provide a flat-top beam intensity profile of approximately 12 μm diameter in the focal plane of the 20X lens.

For radiometric temperature measurements in the near IR range we set up a dedicated system that consisted of a 300 mm focal length spectrograph equipped with 150 groove/mm grating and an InGaAs nitrogen cooled array detector. The spectra were recorded at 1400-1600 nm. The typical accumulation time was 0.1 s.

Figure 5-2 Scheme of standard diamond anvil cell. Gasket (Re / W / Au ), II – diamonds of symmetric cell, III – laser Nd:YLF 1053 nm / Yb-fiber 1075 nm laser for IR-heating, IV – Raman laser Ar⁺ 458 nm/488 nm, V – ruby (Al₂O₃ + Cr³⁺), VI – copuler (Ir/B/Fe₃O₄), VII – reagent – methane/ethane.

Figure 5-3 Microphotograph of the inner side of the diamond anvil cell with ruby and coupler.
5.1.3. Diamond Anvil Cell Loading Procedure

Gasket preparation

Rhenium or tungsten plates 10*10*0.25 mm were cleaned in an acetone ultrasonic bath. After air flushing, a gasket was pre-indentated, by cleaned and centered diamonds, to 0.04 – 0.05 mm thickness. In most cases for stable positioning of the coupler an additional cavity was made by an 90 μm copper wire in an electric arc microdrilling machine. The final thickness of the gasket in the additionally indented cavity was about 35 μm. A Nd:YAG laser or electric arc microdrilling machine was used to make a 100 μm circle hole in the gasket cavity.

When using a gold liner, a hole in the gasket cavity was drilled to 250 μm. A thin piece 200 μm in diameter was placed in the gasket and pressed between working diamonds hugging the gasket and preventing contact between sample and gasket material.

Coupler Preparation

Methane is a week absorber of IR-radiation of available wavelengths 1062 and 1075 nm. To have a good absorption process there is a need for an opaque and inert material like iridium or platinum. When transition metal presence is undesirable, pressed amorphous boron was placed in the sample.

In experiments with iridium coupler, foil of this material was cut by the Nd:YAG laser on squares 50*50 μm with 1÷4 10 μm holes. In the case of the samples with double cavity, the size of a coupler was chosen to be rigidly placed in the second cavity, usually 100*80 μm. There were 4÷8 inner holes of 10 μm diameter in this case.

Iridium couplers in experiments from 5.1 were washed in diluted nitric acid and then in distilled water to remove metal oxides that could be formed after laser cutting, but afterwards it became clear that this last procedure was not crucial.

Powder of amorphous boron was pressed by working diamonds and the received plates were positioned on the edge of second cavity.

Thermoresistive Coating

Starting from the 5.1 experiment, thermoresistive coating on diamonds was employed to reduce thermal gradients in the sample and to avoid ultra-dispersive diamonds formations in the experiments with ethane. Alumina powder was pressed between the working diamonds to cover one of the diamonds. Another one was covered by pressing with a steel gasket positioned on a tungsten carbide seat.

Sample Loading

For successful loading and prevention of over-pressurising, preliminary calibration was made. The essence of this procedure was in the choice of the starting and finishing point for screws. The finishing point was chosen on the fringe formation on alumina coating. For experiments without alumina, a special calibration procedure was not carried out, nor was preliminary vacuum drying. For the last procedure the open DAC was placed in the
vacuum chamber for two hours at ambient temperature and pressure of several millitorr. Absence of moisture was controlled by optical microscopy and Raman spectroscopy.

**Gas Loading**

Only methane was loaded by this method because of its high saturation vapour pressure. DAC was placed in gas loading chamber, that was flushed with methane 3 times during pressurizing to 0.1 GPa and release. DAC was closed at the pressure of 0.2 GPa with following control of success, pressure measuring and its correction.

**Cryogenic Loading**

After flushing in cryogenic chamber DAC was filled by liquid ethane or propane, cooled by liquid nitrogen. The next procedures were similar to gas loading procedure.

**5.1.4. Scheme of a Spectral Experiment**

Standard experimental procedure consisted in registering of Raman spectra before heating at purposed pressure with diffraction greed 300 lines/mm in full range of vibration frequencies 0-4500 cm\(^{-1}\). Narrow ranges were recorded with 1500 lines/mm.

During stepwise sample heating by increasing of intensity of IR laser radiation, spectra were gathered in 0-4500 cm\(^{-1}\) spectral range with accumulation times 1-30 sec. Spectrum in 20000 cm\(^{-1}\) region was used for temperature determination by Planck function approximation. Duration of heating varied between 30 s to 15 minutes in different experiments. Laser heating point could also be changed in one heating or between heating steps.

After heating IR-laser was switched off temperature in the sample was almost instantly became equal to room temperature and detailed spectral analysis was carried out. Crucial points that always attracted attention were: gasket region, heating point, several points from heating centre to edge of gasket, back of heating point in case of two-side heating experiments. Then second step of heating, pressure change or quenching was carried out. Pressure was controlled before and after heating experiment and difference rarely exceeded 0.5 GPa.

**5.1.5. Pressure Measuring Method**

Pressure was determined at room temperature using a conventional ruby manometer (Mao et al. 1978; Piermarini and Block 1975), before and after laser heating.

This method included measuring of the wavelength position of a ruby fluorescence radiation and comparison with namely known shift of pressure-dependent shift to longer wavelength of the R\(_1\) and R\(_2\) ruby emission lines.

These spectral lines have a number of necessary characteristics: narrowness, high quantum yield and strong pressure dependence shift. All these features are shown in
The resolution of the R1 and R2 lines is an indication of the quasi-hydrostatic character of the environment.

The linear calibration of the ruby fluorescence emission is reliable up to 30 GPa for a quasi-hydrostatic environment.

![Figure 5-4](image_url) Ruby fluorescence spectrum at 7.7 GPa (upper). ((Schettino et al. 2005) The empirical dependence of R1 line shift with pressure (Mao et al. 1978).)

The precision of the pressure measurements by ruby techniques was ±0.5% above 20 GPa under hydrostatic conditions (Schettino et al. 2005).

The empirical equation that links the pressure and the ruby wavelength is

\[
P = \frac{A}{B} \left[ \left( \frac{\Delta \lambda}{\lambda_0} + 1 \right)^B - 1 \right]
\]

(5.1)

where \( P \) is expressed in gigapascals, \( A \) and \( B \) – empirical parameters with values (Mao et al. 1986) 1904 GPa and 7.665. \( \lambda_0 \) is the wavelength (expressed in nanometres) of the R1 ruby fluorescence line at ambient pressure and at the reference temperature, usually the room one. \( \Delta \lambda = \lambda - \lambda_0 \) is the R1 signal shift with pressure.

For the part of the experiments with propane pressure in the cell was calculated from diamond first order Raman signals due to their known shift with pressure (Akahama and Kawamura 2004; Occelli et al. 2003)

5.1.6. Temperature Measuring

The temperature was measured by collecting the thermal radiation of the heated sample and its fitting it with the Planck equation for the black-body emission (Boehler and Chopelas 1991a; Heinz et al. 1991):

\[
I(\lambda) = \frac{\varepsilon c_1 \lambda^{-5}}{e^{c_2/\lambda T} - 1}
\]

(5.2)

where \( I(\lambda) \) is the measured intensity, \( \varepsilon \) is the emissivity, and \( c_1=3.67\times10^{19} \) and \( c_2=1.4388\times10^7 \), \( T=2684 \). Emissivity is taken as 1, but it is in fact corrected by fitting of empirical parameters, namely \( c_1 \).

In the in-situ experiment pieces of diamond \(^{13}\)C were pressed in the iridium coupler Figure 5-5.
5.2. Modelling of Reductive-oxidative Conditions that Correspond to Earth’s Upper Mantle

In the case of DAC with laser heating, the using of a real buffer has strong drawbacks. The small laser heating point even after a defocusing procedure and large temperature gradients prevented uniformed values of oxygen fugacity throughout the reaction volume. The low number of investigated samples (in comparison with experiments with pure samples) led to low intensities of spectral signals.

To overcome these disadvantages it was decided to use one compound from the buffer. It should contain iron because almost all buffer reactions are based on iron oxidation state change. Reaction properties of hydrocarbons with oxygen or iron-containing compounds are not known in the thermobaric region of interest, so it was necessary to consider as reactions of iron oxidation so reactions of iron reduction. Magnetite Fe₃O₄ was chosen because it is a sufficiently oxidized form of iron to represent oxidative mantle conditions. It contains Fe(II) and Fe(III) simultaneously, it easily absorbs IR laser radiation so it can be employed as coupler.

After experiments where methane was laser heated in contact with the magnetite coupler it was found that Fe₃O₄ reduced to Fe (0) (see corresponding chapter 5.5.3) in the heating point, starting at temperatures from approximately 1000 K. At the same time existence of Fe₃O₄ was observed in points that were not directly exposed to IR laser radiation. Simultaneous existence of buffer components in the sample after the finishing of the experiment allowed us to say that oxygen fugacity in methane environment was closed to the above mentioned iron-magnetite buffer (1.7) value.

Though debatable, discussed method of modelling the redox conditions can be proposed to use when buffer mixtures are undesirable.
<table>
<thead>
<tr>
<th>№</th>
<th>Reagent</th>
<th>Gasket</th>
<th>Coupler</th>
<th>Diamond coating</th>
<th>P, GPa</th>
<th>T max, K</th>
<th>Products/commentaries</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>CH₄</td>
<td>W</td>
<td>Ir</td>
<td>No</td>
<td>2.54</td>
<td>1800</td>
<td>C₂H₆, C₃H₈ , (CH₄)ₙ(H₂)ₘ, C, H₂</td>
</tr>
<tr>
<td>1.2</td>
<td>CH₄</td>
<td>W</td>
<td>Ir</td>
<td>No</td>
<td>3.54</td>
<td>2000</td>
<td>Increasing intensity of C₂H₆, C₃H₈</td>
</tr>
<tr>
<td>1.3</td>
<td>CH₄</td>
<td>W</td>
<td>Ir</td>
<td>No</td>
<td>5.02</td>
<td>2000</td>
<td>Increasing intensity C₂H₆, C₃H₈</td>
</tr>
<tr>
<td>1.4</td>
<td>CH₄</td>
<td>W</td>
<td>Ir</td>
<td>No</td>
<td>6.64</td>
<td>2000</td>
<td>1.4 + C₄H₁₀</td>
</tr>
<tr>
<td>2.1</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>1.97</td>
<td>900, 1500</td>
<td>C₂H₆, C₃H₈, C, H₂/in situ</td>
</tr>
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<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>2.71</td>
<td>900, 1500</td>
<td>2.1 + C₄H₁₀</td>
</tr>
<tr>
<td>2.3</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
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<td>&gt;1000</td>
<td>C₂H₆, H₂, C</td>
</tr>
<tr>
<td>2.4</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>14.11</td>
<td>&gt;1000</td>
<td>H₂, (CH₄)ₙ(H₂)ₘ, increasing C₂H₆</td>
</tr>
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<td>2.5</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>12.4</td>
<td>11.4</td>
<td>Dependence of all products wavelengths from pressure</td>
</tr>
<tr>
<td>2.6</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>9.4</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>CH₄</td>
<td>Au</td>
<td>B</td>
<td>No</td>
<td>1.95</td>
<td>&lt;1000</td>
<td>C₂H₆/In situ</td>
</tr>
<tr>
<td>3.2</td>
<td>CH₄</td>
<td>Au</td>
<td>B</td>
<td>No</td>
<td>1.95</td>
<td>1500</td>
<td>C, H₂, C₂H₆, C₃H₈, C₄H₁₀</td>
</tr>
<tr>
<td>3.3</td>
<td>CH₄</td>
<td>Au</td>
<td>B</td>
<td>No</td>
<td>4.04</td>
<td>2685</td>
<td>C, C₂H₆</td>
</tr>
<tr>
<td>4.1</td>
<td>C₂H₆</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>3.29</td>
<td>&lt;1000</td>
<td>C</td>
</tr>
<tr>
<td>4.2</td>
<td>C₂H₆</td>
<td>Re</td>
<td>Ir</td>
<td>No</td>
<td>3.29</td>
<td>&lt;1000</td>
<td>C₃H₈</td>
</tr>
<tr>
<td>5.1</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>Al₂O₃</td>
<td>3.36</td>
<td>&lt;1100</td>
<td>C, C₂H₆, C₃H₈</td>
</tr>
<tr>
<td>6.1</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>Al₂O₃</td>
<td>3.38</td>
<td>&lt;1000</td>
<td>C₂H₆, C₃H₈, C</td>
</tr>
<tr>
<td>6.2</td>
<td>CH₄</td>
<td>Re</td>
<td>Ir</td>
<td>Al₂O₃</td>
<td>3.38</td>
<td>700-1100</td>
<td>C₂H₆, C₃H₈, C, H₂</td>
</tr>
<tr>
<td>7.1</td>
<td>C₂H₆</td>
<td>Re</td>
<td>Ir</td>
<td>Al₂O₃</td>
<td>5.00</td>
<td>&gt;1000</td>
<td>C, CH₄, C₃H₈, C₄H₁₀</td>
</tr>
<tr>
<td>8.1</td>
<td>C₃H₈</td>
<td>Re</td>
<td>No</td>
<td>No</td>
<td>0.4-17.5</td>
<td>300</td>
<td>Dependence of propane wavelengths from pressure</td>
</tr>
<tr>
<td>9.1</td>
<td>CH₄</td>
<td>Re</td>
<td>Fe₃O₄</td>
<td>Al₂O₃</td>
<td>2.19</td>
<td>1500</td>
<td>C, C₂H₆, C₃H₈, C₄H₁₀, Fe, H₂O, H₂</td>
</tr>
</tbody>
</table>
* - Separate loading experiments have a different integer part of the number, while different heating or pressure changing experiments inside the one loading are reflected by change in the decimal part of the number in the chronological way.

**Table 9** Raman modes used in characterization of the chemical reaction products

<table>
<thead>
<tr>
<th>Product</th>
<th>Initial (=0 GPa) frequency</th>
<th>Approximate type of mode</th>
<th>Frequency in solid phase (5 GPa)</th>
<th>Pressure dependence (cm⁻¹/GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ (methane)</td>
<td>2917</td>
<td>Symmetric stretch, ν₁</td>
<td>2964</td>
<td>10.6</td>
<td>This work, (Hebert et al. 1987)</td>
</tr>
<tr>
<td></td>
<td>1534</td>
<td>Degenerate deformation, ν₃</td>
<td>1540</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>C₂H₆ (ethane)</td>
<td>1468</td>
<td>CH₃ degenerate deformation</td>
<td>1476</td>
<td>1.1</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>995</td>
<td>C-C stretch</td>
<td>1025</td>
<td>6.75</td>
<td></td>
</tr>
<tr>
<td>C₃H₈ (propane)</td>
<td>1451</td>
<td>CH₃ degenerate deformation</td>
<td>1456</td>
<td>1.3</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1054</td>
<td>C-C stretch</td>
<td>1079</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1152</td>
<td>CH₃ rocking</td>
<td>1164</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>869</td>
<td>C-C stretch</td>
<td>900</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>C₄H₁₀ (n-butane)</td>
<td>837</td>
<td>C-C stretch</td>
<td>867</td>
<td></td>
<td>Assumed to be similar to propane</td>
</tr>
<tr>
<td>H₂ (hydrogen)</td>
<td>354</td>
<td>S₀(0)</td>
<td>355</td>
<td>≈ 0</td>
<td>This work, (Zerr et al. 2006)</td>
</tr>
<tr>
<td></td>
<td>587</td>
<td>S₀(1)</td>
<td>600</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>814</td>
<td>S₀(2)</td>
<td>829</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
### 5.2.1. Determination of Methane Transformation Pathways

To find an answer to the question about methane reaction pathways at a pressure of 2-5 GPa in the temperature interval of 1000-1500 K, it was necessary to define thermobaric limits of methane stability. A second problem was the qualitative analysis of the transformation products.

One of the main drawbacks of the DAC laser heating method is considered to be high temperature gradients in the sample due to extremely high thermal conductivity of diamonds. Without thermo-resistive coating, the temperature on gasket surfaces (and on the diamonds) is close to ambient conditions when in the heating point it reaches 2500 K. In this case such gradients allowed us to observe products of transformation at different temperatures in one heating experiment.

In the experiment #1.1 (Table 8) methane was loaded in a diamond anvil cell with an iridium coupler. At 2.54 GPa, a maximum temperature in stationary heating point reached 1800 K, while the overall exposure time was 13 minutes.

After the heating laser was shutdown, Raman spectra were obtained for points of the sample at different distances from the heating point and the composition of the sample varied correspondingly (Figure 5-6).

In all heated areas the intensity of signals of stretching C-H vibrations decreased, though even at maximum temperature these signals remained as assign of incomplete conversion of methane. Due to non-characteristic properties of C-H stretching vibrations, existence of signals in 3000 cm\(^{-1}\) region could be interpreted as residual quantities of methane or formation of some new hydrocarbon compounds, but the first explanation seems to be more reasonable.

<table>
<thead>
<tr>
<th>Product</th>
<th>Initial (=0 GPa) frequency</th>
<th>Approximate type of mode</th>
<th>Frequency in solid phase (5 GPa)</th>
<th>Pressure dependence (cm(^{-1}/\text{GPa}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1035</td>
<td>S_0(3) Rotational transitions</td>
<td>1050</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4162</td>
<td>Q_1(1) Vibrational transition</td>
<td>4220</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1581</td>
<td>In-plane intralayer mode</td>
<td>1607</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2723</td>
<td>Second order</td>
<td>2790</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(graphitic carbon)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Hanfland et al. 1989)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(Goncharov 1990)</td>
</tr>
</tbody>
</table>
Figure 5-6 Spectra of transformation products at different distance from heating point at 2.54 GPa. (a) – heating point $T_{\text{max}}=1800$ K – graphite formation, (b) – $T_{\text{max}}\approx1400$ K – formation of graphite and methane-hydrogen clathrate, (c) – $T_{\text{max}}\approx900$ K – formation of ethane, propane and hydrogen.

Maximum temperature was in the heating point (Figure 5-6a) 1800 K. Temperatures in point (b) – 1400 K and (c) – 900 K were estimated during analysis of sample temperature gradient (Figure 5-7), when optical observation of methane melting line (Yagi and Suzuki 1990) was correlated with temperature in the heating point.

Figure 5-7 Observation of methane melting during heating at 2.54 GPa. Temperature at heating point is about 1000 K. Melting temperature of methane at this pressure is 345 K according to (Yagi and Suzuki 1990).

In the hottest point (Figure 5-6a) high fluorescence was observed. Similar events occurred in all methane samples heated to the temperatures of 1600-2500 K with no thermo resistive diamond coatings.
This phenomenon can be explained by formation of ultradisperse diamonds (Zerr et al. 2006). Absence of fluorescence in case of Al2O3 coating may be explained by the catalytic character of this material for ultradisperse diamonds conversion to graphite, soot or relatively big and not so fluorescent diamonds.

A broad peak 4300 cm\(^{-1}\) was found in the heating point (Figure 5-6a). This signal was also observed in several experiments without diamond coating, but not in experiments with Al2O3 on diamond surfaces. The frequency of this peak and the elemental composition of the sample allow us to speak about formation of some hydrogen compounds, probably methane-hydrogen clathrate (Somayazulu et al. 1996). Formation of graphite can be stated due to Raman peaks 1600 cm\(^{-1}\) and 2780 cm\(^{-1}\) (Goncharov 1990; Hanfland et al. 1989).

In a less heated zone with approximate temperature 1400 K, graphite formations were also fixed (Figure 5-6b). In point (Figure 5-6c) no signals of graphite were fixed. Instead, signs of molecular hydrogen were observed: low frequency rotons So(0) –So(3) and frequency of stretching vibration Q1(1) (S. K. Sharma et al. 1980).

Besides known signs of hydrogen in spectra from points with ~900 K temperature there was found clear peak of 1025 cm\(^{-1}\) (Figure 5-6c). It was interpreted as a C-C stretching vibration of ethane. That was further confirmed by carrying out a special loading experiment with pure ethane.

A maximum quantity of ethane was discovered in the coupler hole. On the (Figure 5-8a) besides ethane and hydrogen signals, one can see small peak at 892 cm\(^{-1}\), that corresponds to C-C stretching vibrations on the next alkane – propane. Formation of this hydrocarbon was confirmed in a special loading experiment with pure propane. It is necessary to note that spectral information about ethane and propane under high pressure was absent in the literature.
Figure 5-8 Raman spectra of methane sample after heating in 0-1750 cm\(^{-1}\): (a) - at 2.54 GPa (exp. #1.1) in the hole of the iridium coupler. Signals of ethane 1020 cm\(^{-1}\), propane and hydrogen 379, 600, 826, 1043 cm\(^{-1}\) are observed; (b) – at 3.54 GPa (exp.#1.2) increasing of relative ethane and propane signals.

On the basis of Raman spectra analysis, the following methane transformation pathways were proposed. At temperatures from 900 K to 1500 K the following dominated:

\[
\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{C}_4\text{H}_{10} + \text{H}_2 \tag{5.3}
\]

At temperatures higher than 1500 K dissociation of methane to atomic form of carbon is favored. Signals of soot and graphite can hardly be distinguished between from each other, but soot has to have a broader signal than graphite. Formation of diamonds can not be noted due to diamonds of the diamond anvil cell signals so we will consider the next pathway:

\[
\text{CH}_4 \rightarrow \text{H}_2 + \text{C} \tag{5.4}
\]

Signals of reaction products stay unchanged over a period of hours, but become less intensive after several days. Chemical composition of the system does not change with pressure in the investigated pressure range.

For an explanation of absence of the hydrogen signals at high temperatures (Figure 5-6 a and b), the hypothesis was of high hydrogen diffusion throughout the sample and gasket.
and high hydrogen absorption by the iridium coupler. This hypothesis was confirmed by experiments with an amorphous boron coupler and gold liner (see further).

After the first heating (exp. #1.1), pressure was increased up to 3.54 GPa and the sample was heated a second time (exp. #1.2). At this time, the maximum temperature reached 2000 K. The intensity of ethane and propane signals in the coupler hole increased. Ethane signals of C-H deformation vibrations at 1492 cm\(^{-1}\) became well distinguished (Figure 5-8b). The heating point was positioned on a distance similar to exp. #1.1, so the temperature in the coupler hole was definitely less then 2000 K and probably was in the 1000-1500 K temperature range.

A further increase of hydrocarbon signals was observed after heating to 2000 K at 6.64 GPa. A new signal, interpreted as n-butane C-C skeletal vibrations was found at 865 cm\(^{-1}\) (Figure 5-9)

![Raman spectrum of methane transformation products after heating under pressure of 6.64 GPa to T\(_{\text{max}}\) 2000 K. Note n-butane signals formation.](image)

Influence of temperature exposition time was investigated by (Hirai et al. 2008). There was observed no difference between products composition in the experiments where exposition time was changed from several seconds to 10 minutes. This regularity was confirmed in this work.
Therefore, for similar experiments where temperatures were equal or close (1800 K in #1.1 and 2000 K in #1.2 and #1.4) increase of intensity of product signals should be explained by the pressure effect.

5.2.2. In-situ Observation of Methane Transformation

The traditional method of coupler technique diamond anvil cell includes free positioning of coupler inside the sample. But when the sample becomes fluid, the non-fixed coupler freely swims, and that leads to unstable coupling and consequently to big temperature jumps. The coupler moving makes it difficult to correlate distance from heatpoint with the exposed temperature.

This drawback is crucial for in-situ Raman observation at high temperatures due to high fluorescence of iridium coupler at the moment of IR laser radiation. Separation of IR laser heating point from Raman laser registering point overcomes this drawback if the coupler is fixed (see experimental chapter for peculiarities).

Temperatures below 1500 K can hardly be measured with sufficient accuracy using visible pyrometry method. To receive Raman data from the sample and determine its temperature, pieces of diamond $^{13}$C were pressed in the coupler and temperature was measured by the Stokes-anti-Stokes method. A combination of fixed-coupler technique and Stokes-anti-Stokes temperature calculation method allowed us to observe methane transformation and measure temperature in-situ.

![Raman shift, cm$^{-1}$](image)

**Figure 5-10** In-situ transformations of methane during heating at 1.97 GPa and microphotography of the sample.
Observation of in-situ methane transformation was realized at 1.97 GPa. At 900 K a formation of ethane frequency was registered. At the same time no hydrogen signals were observed. That can be explained by relatively low hydrogen quantities formed in reaction of condensation (5.3) and its absorption of by the material of the coupler.

Besides sharp signals in the 1000 cm\(^{-1}\) region, ethane formation changes the shape of still dominant methane peak in 1500 cm\(^{-1}\) region.

The intensity of methane signals intensities significantly decreases when heating up to 1500 K. At the same time hydrocarbon signals of ethane and propane can be found as well as graphite and hydrogen ones (Figure 5-10). The appearance of hydrogen signals in this case in comparison with 900 K can be explained by longer methane conversion, especially in dissociation reaction. Reaching of hydrogen sorption limit of iridium can also take place.

One of the quite important facts observed in this experiment was the simultaneous presence of hydrogen, methane, ethane, propane and graphite during heating. That can happen only when equilibrium takes place.

Formation of a methane-clathrate compound was observed in this loading experiment after heating to 1000 K at 14.11 GPa.

5.2.3. Methane Transformations in Thermobaric and Redox Conditions of the Earth’s Upper Mantle

Using magnetite (Fe\(_3\)O\(_4\)) as a material for modelling mantle redox conditions was previously discussed in the experimental part.

Two experimental loading were taken (exp. series 9 and 10). Temperature regularities and chemical composition of final products are similar to those observed in experiments with pure methane with some exceptions. Again in the heating point, where temperature exceeded 1500 K, methane transformed to atomic carbon, likely in the form of soot (Figure 5-11). Interesting to note was the fact that on the backside of the coupler heatpoint carbon signals were much narrower and the intensity of a graphite second order signal was much higher than in the original heatpoint. That allows us to speak about dominant graphite formation on the backside of the coupler. Some amount of amorphous material can not be excluded. Differences between the one and the other side of the coupler may have also been caused by the influence of laser radiation during heating. This phenomenon plays an important role in the polymerization of unsaturated hydrocarbons under pressure (e.g. acetylene (Citroni et al. 2002; Citroni et al. 2003a; Citroni et al. 2003b) and butadiene (Schettino et al. 2005)).

Hydrocarbons from ethane to n-butane were found in a distance from the heating point and temperature influence seems to remain the same as in the case with pure methane transformations (5.5) and(5.6).

The difference was in the form of hydrogen that is oxidized to water by Fe\(_3\)O\(_4\) that in its turn reduces to atomic iron.
Figure 5-11 Transformations of methane in contact with magnetite at 4.01 GPa, $T_{\text{max}}=1500$ K (exp. 10.1) and microphotography of the systems with registration points.

Reduction of Fe$_3$O$_4$ to atomic iron was established by the disappearing of Fe$_3$O$_4$ Raman signals and X-ray synchrotron spectra (Figure 5-12 and Figure 5-13).

Figure 5-12 A fragment of an x-ray diffraction image of the quenched reaction products after laser heating of magnetite in methane using nano-alumina as a thermal insulator/spacer at 2.7 GPa and room temperature. X-ray wavelength was $\lambda=0.40747$. The spots marked correspond to single-crystal diffraction from materials crystallized after the heating.
Two ways of methane transformation at 2-5 GPa in contact with magnetite can be generalized in the following schemes, though the boundary between the two pathways is approximate:

at 1000-1500 K:

\[
\text{CH}_4 + \text{Fe}_3\text{O}_4 \rightarrow \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{C}_4\text{H}_{10} + \text{Fe} + \text{H}_2\text{O} \quad (5.5)
\]

higher than 1500 K

\[
\text{CH}_4 + \text{Fe}_3\text{O}_4 \rightarrow \text{C} + \text{Fe} + \text{H}_2\text{O} \quad (5.6)
\]

Stability of the hydrocarbons in contact with magnetite was relatively strong. Before 900 K, temperature transformations of methane were not observed at all. That was established in the experiment with the magnetite coupler, when the laser intensity was increased stepwise and slowly. A word needs to be mentioned here about coupling explosion phenomenon. After overcoming some heating laser intensity in the step by step mode, little rise of intensity value gave a jump in coupling and corresponding temperature.
We suppose that this behaviour was caused by formation of some material with coupling properties different to the properties of the coupler.

Unexpectedly, we did not observe formation of carbon oxides which would be usual for ambient conditions when a carbon compound is in contact with an oxidizer. Raman spectroscopy in combination with DAC is very sensitive to these compounds. Their signals do not overlap with hydrocarbons, so their absence in reaction products would have to be explained by their high thermodynamic potentials in comparison with a reduced form of carbon: hydrocarbons and atomic carbon (soot, graphite, diamonds).

5.2.4. Influence of the Nature of Contact Materials and Pressure

An iridium coupler was used in the most parts of the experiments. It was easy to prepare, it has a low fluorescence and absorbs radiation of the infrared laser well. However, the nature of the transition metal suggests the possibility of a catalytic effect of iridium on the conversion of methane, as well as hydrogen absorption that may change compounds’ equilibrium rates (if the system has an equilibrium character). Fe3O4, used as a coupler, reacts with methane in addition to containing another transition metal – iron.

To avoid contact of methane with transition metal surfaces we used an amorphous boron coupler and gold liner as a gasket.

Figure 5-14 Microphotography of methane loaded DAC with gold liner (yellow metal) and pressed amorphous boron coupler (black material inside rectangle hole in gold).

On the (Figure 5-15) one can see the spectrum of methane transformation products after heating up to 1500 K at 1.95 GPa. On the background of an increasing baseline, signals of hydrogen and graphite can be clearly seen.

In comparison with the experiments with rhenium and iridium (Figure 5-10) the relative quantity of observed hydrogen was much higher, at the same time signals of hydrocarbons could not be found.

An ethane peak was discovered in products at 4.01 GPa and at a temperature not higher than 1000 K (the analyzing point was far from the heating point of 2500 K exp. 3.3). On the (Figure 5-16) it is shown together with the results of other experiments with different contact surfaces and reference spectra of methane, ethane, propane and hydrogen.
In the experiment carried out with the magnetite coupler (Figure 5-16) hydrogen was almost absent due to conversion to water and the quantities of hydrocarbons were sufficiently high again. It is clear why if we take into account an idea about reversibility of observed processes. If we limit methane conversion only to ethane:

$$2\text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}_2$$  \hspace{1cm} (5.7)

according to Le Chatelier's principle, absorption of hydrogen by iridium or rhenium shifts the equilibrium to hydrocarbon formation. In the case of magnetite, chemical bonding of hydrogen to water plays the same role if we suggest oxidation of hydrogen as the next step after methane conversion:

$$4\text{H}_2 + \text{Fe}_3\text{O}_4 \rightarrow \text{Fe} + 4\text{H}_2\text{O}$$  \hspace{1cm} (5.8)

and the full path in one step will be seen as follows:

$$8\text{CH}_4 + \text{Fe}_3\text{O}_4 \rightarrow 4\text{C}_2\text{H}_6 + 3\text{Fe} + 4\text{H}_2\text{O}$$  \hspace{1cm} (5.9)

At the same time, the number of hydrocarbons and their relative quantities stay the same in all experiments. Methane does not fully transform, if the temperature does not significantly increase above 1500 K (definite borders need to be establish) and even in this case small peaks of C-H stretching bonds are always found.

Relative quantities of hydrocarbons remained the same in all the experiments. Methane dominates, ethane is second, propane is the third and quantities of n-butane are always very small.
(Zerr et al. 2006) published spectral information of methane transformation products with different contact surfaces up to 17.9 GPa but could not identify the compounds. Spectral information about ethane and propane received during this work let us do it and we can say that formation of hydrocarbons occurs and in cases of using Al₂O₃, MgO and SiC from 4 GPa to 17.9 GPa, at temperatures lower than 2300K.

![Figure 5-16 Integrating spectra of methane transformation products with different contact surfaces. Description of definite experiment can be found through the number in (Table 8). Note the wavelength shift with pressure and general regularity of hydrocarbon decreasing intensity with increasing of molecular mass.](image)

### 5.3. Ethane Transformations

Methane is a founder of the saturated hydrocarbons class, but its properties may significantly differ from heavier saturated hydrocarbons because of the absence of C-C
bonds in it. To investigate this, we carried out experiments with ethane as reagent, with an iridium coupler and rhenium gasket.

When we started to work with ethane, we found it to be very sensitive to IR-laser radiation. Even at very small laser intensities we observed extreme background increase that exceeded the sensitivity detector limit (intensity explosion). We observed the same picture working with propane, but not for methane, which allowed us to work with laser intensities enough to produce 2500 K.

(Zerr et al. 2006) during experiments with methane at 23.1 GPa with heating to above 2300 K observed fluorescence and attributed this fact to the formation of ultradispersive diamonds. We can take this explanation in our case as an hypothesis.

Using thermoresistive diamond coating with Al2O3 prevented intensity explosion in the further experiments with ethane, where it was heated up to 2000 K with an iridium coupler in a rhenium gasket, and products of its transformations were successfully analyzed.

In the heating point in the experiment where ethane was pressed to 5.00 GPa, temperature reached 2000 K. Like methane at temperatures higher than 1500 K, ethane dissociated to elemental carbon and we suppose it is an amorphous carbon in the form of soot (Figure 5-17) due to the broad character of the peak and the absence of signal at 2770 cm\(^{-1}\) that is related to graphite second order frequency.

![Figure 5-17 Raman spectra of the reaction products of laser heated ethane at 5.0 GPa up to 2000 K at various spatial positions with respect to the hotspot and own reference spectra of methane and propane.](image-url)
At a temperature lower than 2000 K, due to distance from the heating point, the picture of products composition was similar to that with methane transformation. On the (Figure 5-18 point 1) one can see signals of propane and n-butane besides ethane that did not fully converted. The difference from the methane transformation product composition lay in the absence of molecular hydrogen. Instead, we could define peaks of methane (Figure 5-17 point 1). Thus the following ethane transformation pathways may be considered:

- at temperature higher than 2000 K
  \[ C_2H_6 \rightarrow C + H_2 \] (5.10)

- at temperature below 2000 K but higher than 1000 K (due to invariance of ethane signals and lack of peaks that can be attributed ethane transformation products)
  \[ C_2H_6 \rightarrow CH_4 + CH_3 + CH_4 \] (5.11)

  that can be the combination of the following reactions:

\[
\begin{align*}
3C_2H_6 &\rightarrow 2C_3H_8 + H_2 \\
2C_2H_6 &\rightarrow C_4H_{10} + H_2 \\
2C_2H_6 + H_2 &\rightarrow 4CH_4
\end{align*}
\] (5.12)

A process of methane dissociation also takes place in a reversible regime if we correlate our data with (A. Sharma et al. 2009) who observed formation of methane at 1773 K and 5 GPa:

\[ C + H_2 \rightarrow CH_4 \] (5.13)
Existence of methane in the ethane transformation products lets us speak about equilibrium character of the hydrocarbons transformations in the thermobaric conditions 2-5 GPa and 1000-1500 K.

Observed methane transformation allows us to offer an hypothesis about the properties of potential migration channels and the roles of carbon and hydrogen. If an oxidized compound is present in the migration channel, e.g. Fe$_3$O$_4$, it can be deactivated by components of the deep fluid: hydrogen and hydrocarbons. Hydrogen in this case is oxidized to water.

Hydrocarbons with carbon form an equilibrium mixture, which depending on conditions will be enriched by carbon or hydrocarbons.

Fluid that consequently will migrate through this channel will go through an inactive reduced environment. Thus, a migration channel surface must have reduced character.

In nature something similar is observed in kimberlite pipes. Diamonds that cover their surfaces represents elemental form of carbon, like soot and graphite observed in this work, but stable in another thermobaric conditions. The temperature in the channel may be too high for hydrocarbons and dissociation in this case will take place. Formed carbon may become a reagent for the next fluid portions if the temperature will decrease for some reason.
CONCLUDING REMARKS AND FUTURE OUTLOOK

The most important results in my thesis are the following:

Using two different high pressure chambers, (BARS and CONAC), different carbon and hydrogen donors to produce conditions close to those in the Earth's mantle, hydrocarbon mixture has been obtained from inorganic compounds. And it was shown that this mixture had a similar composition as the hydrocarbon part of natural gas.

According to our suggested transformation pathway, hydrogen plays an important role in the process of hydrocarbon synthesis, being the intermediate compound between inorganic substances and hydrocarbons.

Two investigating factors influenced on hydrocarbon synthesis in a different way. The cooling rate did not effect the composition of the hydrocarbon mixture, but significantly increased absolute quantity of hydrocarbons in the case of a lower cooling rate.

The nature of the carbon donor has no essential effect on the route of formation of hydrocarbons but considerably changes the ratio between the components of the forming hydrocarbon mixture. The relative amounts of heavier hydrocarbons in the obtained mixture, if the carbon donor is CaCO$_3$, are much higher than those if the carbon donor is an individual carbon.

Thermodynamic stability of hydrocarbons under the pressure of 2-5 GPa and temperature of 1000-1500 K was confirmed by experiments with pure methane and ethane in laser heated diamond anvil cells.

A mixture of methane, ethane, propane and n-butane was formed both from methane and ethane at 2-5 GPa, when the temperature was in the range of 1000-1500 K. If the temperature was higher than 1500 K, the final products of the reaction were elemental carbon and hydrogen.

The similar character of the hydrocarbon mixture received from methane and ethane means an equilibrium regime of the observed processes.

Existence of a mantle oxidizer (Fe$_3$O$_4$) in contact with methane did not principally change the hydrocarbon transformation pathway but the quantity of formed ethane, propane and n-butane in this case was higher than in the experiment with inert environment. Materials that can absorb hydrogen from the product mixture (Ir, Re, W) also favour higher methane conversion.

Now we can say that formation of natural gas from inorganic compounds in the mantle conditions is a proven fact. Modelling of liquid oil synthesis can be considered as a next goal. Pressure and catalysis should be considered as favourable factors while the temperature should not exceed 1500 K.

Due to the thermodynamic stability of hydrocarbons in mantle conditions, it is possible to suggest that the nature of reagents should not strongly affect hydrocarbon formation. This suggestion should be checked in the next series of experiments.
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