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NEW THOUGHTS ON THE PROSPECTS OF PETROLEUM POTENTIAL IN THE EGER RIFT (CZECH REPUBLIC)

ROZWAŻANIA O NOWYCH MOŻLIWOŚCIACH PRZEMYSŁU NAFTOWEGO NA OBSZARZE ROWU TEKTONICZNEGO W OKOLICY MIASTA EGER (CZECHY)

The present paper highlights the problem related to the source of hydrocarbons in the Eger Rift in Czech Republic. The authors discuss the existence of polygenetic deep sources of hydrocarbons. The investigations are based on direct indicators of Polycyclic Aromatic Hydrocarbons (abbr. PAHs). Among the diverse components of PAHs has been recognized typomorphic oil association – videlicet: phenanthrene, chrysene, pyrene and benzo(a)pyrene. On the basis of new geochemical, geological and mathematical data the oil and gas potential of Eger Rift is also discussed.

Keywords: rift structures, polycyclic aromatic hydrocarbons, correlation analysis, sources of hydrocarbons

W pracy omówiono problemy związane z obecnością źródeł węglowodorów na obszarze rowu tektonicznego w okolicy miasta Eger (Czechy). Autorzy dyskutują o możliwej obecności w regionie głębokich złożach węglowodorów. Analizy prowadzone są w oparciu o bezpośrednie wskaźniki obecności policyklicznych węglowodorów aromatycznych (PAH). Spośród węglowodorów wyodrębniono typomorficzne produkty ropopochodne: fenantren, chrysen, piren oraz benzoalfapireny. Na podstawie nowo uzyskanych wyników badań geochemicznych, geologicznych oraz w oparciu o dane matematyczne analizowano potencjalne zasoby gazu i ropy naftowego na obszarze rowu tektonicznego w okolicy miasta Eger.

Słowa kluczowe: rów tektoniczny, policykliczne węglowodory aromatyczne

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1. Introduction

The Eger Rift is a key site that has attracted the international geoscience's community for many decades.

It is believed that rifts penetrate to great depths of the Earth and are a channel for the flow of a mixture of hydrogen, carbon and other fluids. Fluids (CO, CH_4, H_2S, H_2, $C_7H_5(NO_2)_3$, HCl, HF) carry tremendous energy and can generate oil and gas fields. Noted that a large and giant oil and gas fields connected with rift structure. A consistent conclusion can be made, on the basis of the presence of the rift structure, which is the first most important positive for prospects of presence of oil and gas.

1.1. Deep Sources of Hydrocarbons

The existence of deep hydrocarbons as sources for the formation of oil and gas us a very important issue that is discussed continuously. The existence of deep-seated sources of oil and gas is based on several facts: fluxes of hydrocarbons on the surface of the ocean floor, hydrocarbons in the mantle derivatives, obtaining hydrocarbons in the experiments corresponding to the deep zones of the Earth, etc. Thus, inside the Pacific Ocean Rift hydrothermal field as well as an emanation of methane and its homologues discovered. Also, gaseous methane homologues were found in thermal springs of Kamchatka, Yellowstone Park and elsewhere. Within oceanic rifts the flow of methane is 1.6×108 cubic meters per year. Many mantle rocks contain methane. Should also be noted that methane and its homologues discovered in the inclusions of diamonds (Beskrovniy, 1985). The conducted experiments with inorganic substances such as iron oxide, calcium carbonate and hydrogen at high temperature 1500 K and high pressures up to 5 GP showed the synthesis of hydrocarbons. Such conditions reply Earth's upper mantle (Kucherov, 2008). Possible to assume that the mantle around the globe under these conditions contains hydrocarbons.

It is believed that the rift structures penetrate into to the depths of the Earth. In rifts of: Dead Sea, Iceland, Pacific and Indian Ocean rifts, evidence of migration of hydrocarbons had been discovered by using Polycyclic Aromatic Hydrocarbons (Galant et al., 2007). The mass transfer involved a large number of components: gaseous, solid, etc. It is natural to assume that the portable components have been formed by different geological processes and at different depths. In our case, the object of mass transfer is the basalt rock, which is taken out on the surface of Eger Rift the PAHs.

1.2. Polycyclic Aromatic Hydrocarbons

The alkyl-substituted homologues of naphtalene, benzofluorene, phenanthene, chrysene, pyrene, and benzo(a)pyrene and pther PAHs widely occur in the oils and sedimentary rocks of oil-bearing regions as well as unsubstituted PAHs. The PAHs series of oils consist mainly of alkylated naphtalenes, phenanthrenes, chrysenes, benzofluorenes, benzo(a)pyrenes with minor unsubstituted PAHs which as a rule are not detected by the used method. The composition of PAHs in oil from various oil and gas-bearing basins studied is similar. Significant amounts of different PAHs occur in sedimentary rocks within the oil deposit aureoles.

The PAHs consist of alkylated naphtalenes, phenantrenes, chrysenes, benzofluorenes, benzo(a) perylenes as well as unalkylated hydrocarbons: naphtalenes, benzo(ghi)perylenes and others.

Name of PAHs associations	**Typomorphic PAHs for the group**
Recent sediments	perylene
Hydrothermal	pyrene, coronene
Volcanic	biphenyl, fluorene
Petroleum	chrysene and benzo(a)pyrene

The issue of the deep sources of oil and gas reserves is complex and much debated. Polycyclic Aromatic Hydrocarbons are important parts of carbonaceous substances and can be used as geochemical markers of hydrocarbon migration from the depth of the Earth's Crust. One of the main sources of natural PAHs is synthesis of simple component (methane, ethane, etc.) to the PAHs in the Earth's Crust and Mantle. Consequently, existents PA refers to the movement along with the fluids from deep sources. As indicators of migrations, the relationship between components of PAHs can serve for revealing oil/gas deep sources.

The small oil and gas deposits in the Czech Republic are located mainly in south Moravia. Their exploration started in the early years of 20th century. The first commercial oil extraction opened in 1919. To 2005 340,600 m³ crude of oil and 98.75 million m³ of natural gas was extracted. Of special interest is the Eger Rift, which is characterized by the presence of favourable geological conditions for oil and gas bearing.

2. Overview of geology of the Eger Rift

The Eger Rift (Fig. 1), located in the north-western part of the Bohemian massif, is the easternmost outcrop of the Varisc, an orogenic belt in the Alpine foreland in Europe. The rift is

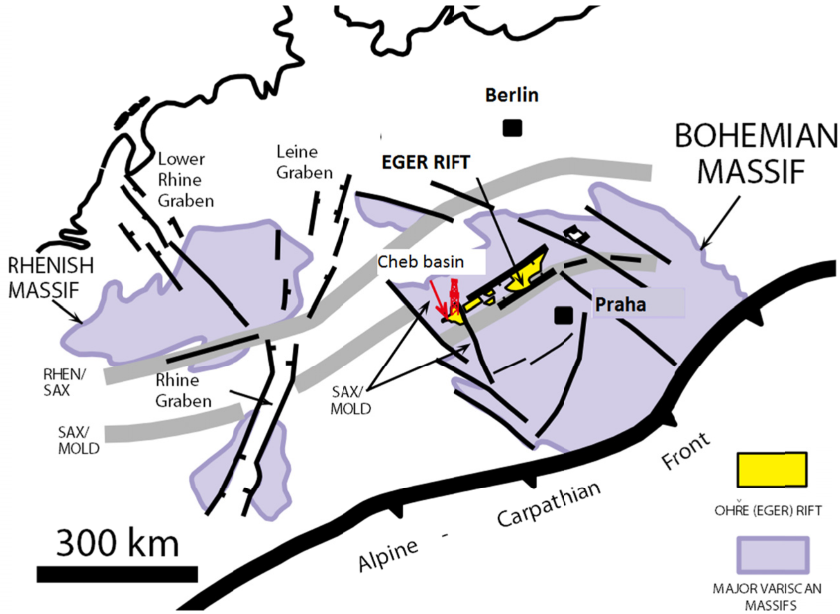

Fig. 1. The Eger Rift as part of the European Cenozoic Rift System (*Source:* Špičák et al., 2005)

the result of young, deep-seated geodynamic processes manifested by episodic Cenozoic volcanism (the youngest at 0,2-0,5 Ma), repeated earthquake swarms, numerous mineral springs, CO2 emissions with high he content, and abundant mofette. The crust-mantle boundary (27 km) and lithosphere-asthenosphere boundary (80-90 km) are shallow compared to the conditions below the Bohemian massif. Also, surface heat flow (60-80 $mW.m^{-2}$) within the rift zone is higher than within the massif (Špičák et al., 2005; Janočko et al., 2005).

Although sharing many common features with other dominant structures (e.g., the Rhine graben and the Bresse-Rhone grabens) of the European Cenozoic Rift System, i.e. anomalous upper-mantle structure, thinned crust, abundant intra-plate basaltic volcanism carrying lower-crustal and mantle xenoliths to the surface, moderate seismicity, mantle-derived fluids approaching the surface, typical graben morphology, and graben-related sedimentary basins, the western part of the Eger Rift stands out because of a number of unique signatures highlighting the recent dynamics. This system of graben structures and volcanic fields spreads over a distance of about 1000 km, including the French Massif Central, the Upper Rhine Graben, the Eifel, the North Hessian Depression, the Vogelsberg, the Ohře (Eger) Rift and the Pannonian Basin (Babuška & Plomerová, 2010).

3. Method and factual material

A geochemical survey was initiated in order to find out perspective sites in Eger rift (Fig. 2). Samples of 13 rocks were collected from quarry and outcrops of Eger Rift (Tab. 1).

All of the volcanic rocks samples in Eger Rift were from two sites W and E. Among them were: igneous rocks presented by 6 samples of basalt and 5 samples of granite. To study the

TABLE 1

Samples of rocks from quarry and outcrops of Eger Rift

	Site	Samples	Place	Rocks	Situation
Eger Rift	W	1	Uhostanny	Basalt	Quarry
Eger Rift	W	2	Uhostanny	Basalt	Quarry
Eger Rift	W	3	Ostrov	Basalt	Outcrops
Eger Rift	W	4	Jachymov	Gneiss (Phylitte)	Outcrops
Eger Rift	W	5A	Oberwiesenthal	Granite (Muscovite-Biotite)	Outcrops
Eger Rift	W	5B	Oberwiesenthal	Granite (Grey)	Outcrops
Eger Rift	W	6	Medenec	Basalt	Outcrops
Eger Rift	E	7	Most	Basalt	Outcrops
Eger Rift	E	8	Vlastislav	Basalt	Outcrops
Eger Rift	E	9	Bilinka	Mergel	Outcrops
Eger Rift	E	10	Kuba	Rhyolite	Quarry
The Bohemian massif	The crystalline Bohemian basement	11	Mezirici	Syenite	Outcrops
The Bohemian massif	The crystalline Bohemian basement	12	Mikulov	Limestone	Outcrops

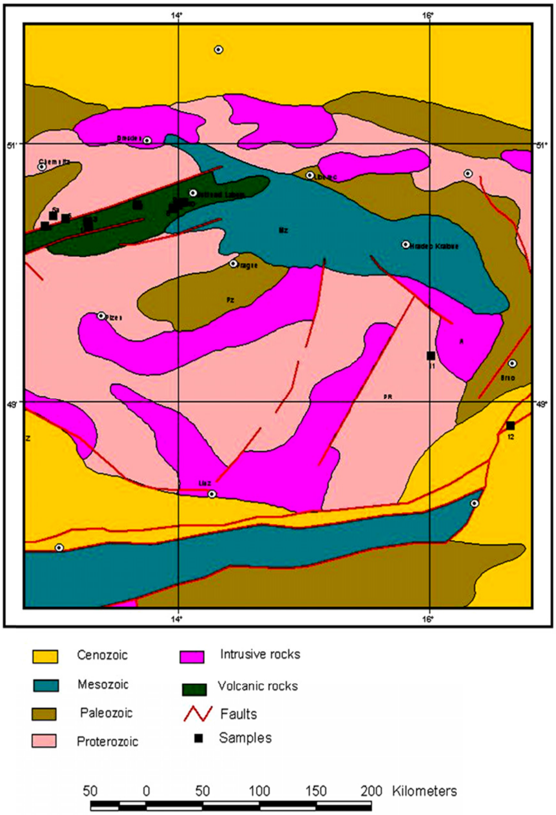

Fig. 2. Map of sampling from quarry and outcrops of Eger Rift (*Source:* Pikovsky et al., 1991)

PAHs content in sediment deposits several rock samples were selected from crystalline fundament Bohemian variscan massifs. Sample locations and some preliminary characteristics are summarized in Table 1.

4. Analytical procedure

PAHs were identified by low-temperature spektrofluorometry (Shpol'sky spectroscopy) on experimental Laboratory spectrofluorometric installation (resolution 0.1 nm) in frozen n-hexane matrix at 77K (Shpol'sky spectroscopy) providing both high selectivity and sensitivity. Each sample of the rocks were air dried and completely crushed to <0.25 mm. PAHs were extracted from sediments and water by continuous shaking with chloroform at room temperature. Identification of PAHs was achieved by reference of fluorescence, phosphorescence and excitation spectra and data bank spectra. A foolproof identification in complex organic mixtures was conducted by Spectrum fractionation method. Development and application of Shpol'sky spectroscopy for research in the field of PAH geochemistry made these investigations in the last three decades very popular all over the world (Gennadiev & Pikovsky, 1996).

The analyses of individual PAHs and some homolog series were performed in the Laboratory of Biospheres Carbonaceous Substances (Faculty of Geography, Moscow State University) by the Shpol'sky spectroscopy method that provides both high selectivity and sensitivity (Geptner et al., 2006). Shpol'sky spectroscopy determined the 10 components of PAHs in basaltic rocks.

5. Correlation Analyses

In geological studies, the specificity lies in the impossibility of direct observation of the past and the present deep processes (Shishljannikova, 2006). Mathematical methods allow a certain probability to fill this gap for assessing the possible nature of PAHs and their source. Correlation analysis was used to identify the strength, direction and form relations of association of PAHs in the basalts of Eger Rift. In order to determine the presence of relations between gases in basalt rocks coefficient correlation was used. Treatments were made according to the Component-Component scheme.

In order to determine the statistical significance of the relationship between the gas components the coefficient of correlation was calculated and analyzed. Pearson's coefficient of linear correlation reflects a measure of the linear relationship between two variables to measure the strength of association. The correlation coefficient is positive, with an increase when X is an increase in Y (directly proportional relation), negative for contrary communication. The general formula for calculating the correlation coefficient (r_{xy}) is:

$$r_{xy} = \frac{n\sum(x_i \cdot y_i) - \sum x_i \cdot \sum y_i}{\sqrt{\left(n\sum x_i^2 - \left(\sum x_i\right)^2\right)\cdot\left(n\sum y_i^2 - \left(\sum y_i\right)^2\right)}}$$

where x_i and y_i compare quantitative traits, n — the number of compared cases.

The obtained correlation coefficient was tested for meaningful connections between the gas components using the "Table of critical values of Pearson" as a two-tailed test. Value 0,05 and lower estimated as significantly related, and more 0,05 are not significantly related.

6. Results and discussion

All 13 samples contain PAHs. It is valuable to note, that in sedimentary samples 9 marl and 12 limestone there are only naphthalene and naphthalene and homologous. An average content of components for all samples is done in Fig. 3.

In all samples collected in Eger rift 4 components: naphthalene, naphthalene and homologous, benzo(ghi)perylene and pyrene predominate and constitute (62%).

The total PAH content is given in circular diagram. Content and PAHs composition are given in the Tables 2-4.

In the Eger rift, the result of PAH analysis in rocks demonstrates the following definite relationship between the components (Tab. 5).

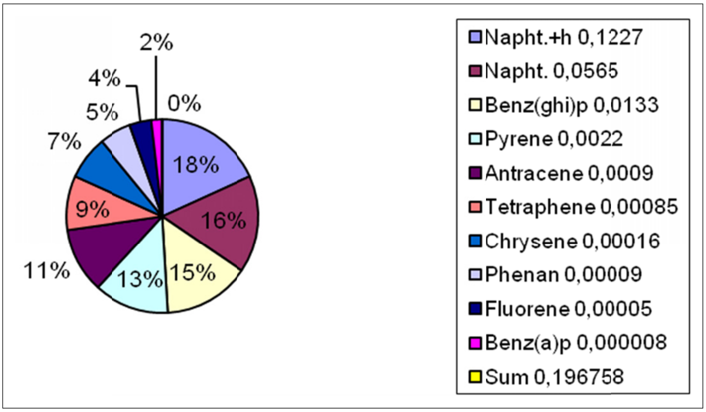

Fig. 3. PAH (average/all samples, mg.kg^{-1}) in Eger Rift (Czech Republic)

TABLE 2

Polycyclic aromatic hydrocarbons content in the eastern part of Eger Rift

Type of rocks	**Basalt**	**Basalt**	**Basalt**	**Gneiss (Fillit)**	**Granite (White-Black)**	**Granite (Grey)**	**Basalt**
Samples	1	2	3	4	5A	5B	6
Place	Uhostanny	Uhostanny	Ostrov	Jahimov	Ober-wiesenthal	Ober-wiesenthal	Medenec
Naphtalene	0	461	0	4	0	0	2
Naphtalene and homologous	15	705	5	8	11	7	3
Phenanthrene	trace	0	1	0	0	0	trace
Chrysene	0	0	1	0	0	0	0
Pyrene	0	0	2	23	1	0	Trace
Antracene	0	0	1	0	0	0	Trace
Benz(a)pyrene	0	0	0	0	0	0	Trace
Fluorene	0	0	0	1	0	0	0
Tetraphene	0	0	0	0	0	0	0
Benz(ghi)perylene	0	0	0	0	0	0	0
Sum PAH ng/g	15	705	11	32	12	7	3

TABLE 3

Polycyclic aromatic hydrocarbons content in the western part of Eger Rift

Type of rocks	**Basalt**	**Basalt**	**Mergel**	**Riolit**
1	**2**	**3**	**4**	**5**
Samples	7	8	9	10
Place	Most	Vlastislav	Bilinka	Kuba
Naphtalene	0	2	3	2
Naphtalene and homologous	0	5	5	3
Phenanthrene	0	0	0	0

1	2	3	4	5
Chrysene	0	0	0	0
Pyrene	0	0	0	0
Antracene	10	0	0	0
Benz(a)pyrene	0	0	0	0
Fluorene	0	0	0	0
Tetraphene	10	0	0	0
Benz(ghi)perylene	159	0	0	0
Sum PAH ng/g	179	6	5	3

TABLE 4

Polycyclic aromatic hydrocarbons content in the crystalline Bohemian basement of Eger Rift

Type of rocks	Granite (Sienit)	Limestone
Samples	11	12
Place	Mezirici	Mikulov
Naphtalene	204	0
Naphtalene and homologous	685	19
Phenanthrene	0	0
Chrysene	0	0
Pyrene	0	0
Antracene	0	0
Benz(a)pyrene	0	0
Fluorene	0	0
Tetraphene	0	0
Benz(ghi)perylene	0	0
Sum PAH ng/g	685	19

TABLE 5

Significant relations between components

Component	Components with significant relations	Numbers of relations
Naphtalene	Naphtalene and homologous	1
Naphtalene and homologous	Naphtalene	1
Phenanthrene*	Chrysene	1
Chrysene*	Phenanthrene	1
Pyrene*	Fluorene	1
Antracene	Tetraphene, benzo(ghi)perylene	2
Benzo(a)pyrene*		0
Fluorene	Pyrene	1
Tetraphene	Benzo(ghi)perylene, antracene	2
Benzo(ghi)perylene	Tetraphene, antracene	2

* Components of Petroleum Association

A result of research showed the following. Thus, out of 45 possible relationships between the components of PAHs, there are only six significant relations (13%). Of the 10 components of the PAHs, only 3 components of antracene, tetraphene and benzo(ghi)perylene have 2 connections. It is important to note that the oil components have the least amount of relations or no relations at all.

In the rock samples of Eger rift the results of conducted analysis manifested the following certain relationship between the components of PAH and melting temperature. In Figure 4 the components are distributed consistently according to their molecular weight. It is noteworthy that the correlation between close in the mass of the components does not exist. And there is a correlation over two grades. Correlation exists between the following components: fluorene-pyrene, phenanthrene- chrysene, antracene-benzo(a)pyren.

In the rocks of Eger rift the results of conducted analysis show the following definite relationship between the components of PAH and melting temperature. In Figure 5 the components are distributed consistently according to their melting point. It is noteworthy that the correlation

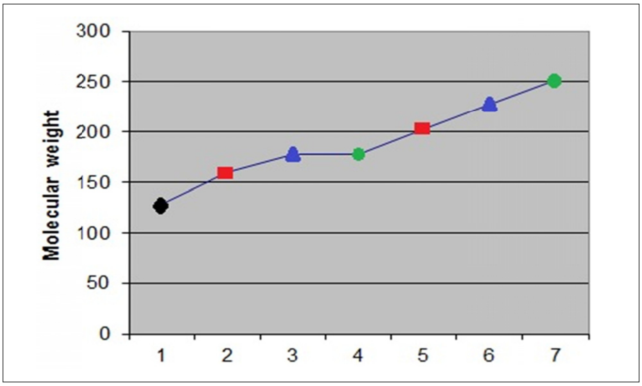

Fig. 4. Distribution of PAHs according molecular weight (1 – naphtalen, 2 – fluorene, 3 – phenanthrene, 4 – antracene, 5 – pyrene, 6 – chrysene, 7 – benzo(a)pyren. The same colored shapes are the components between which there is a connection)

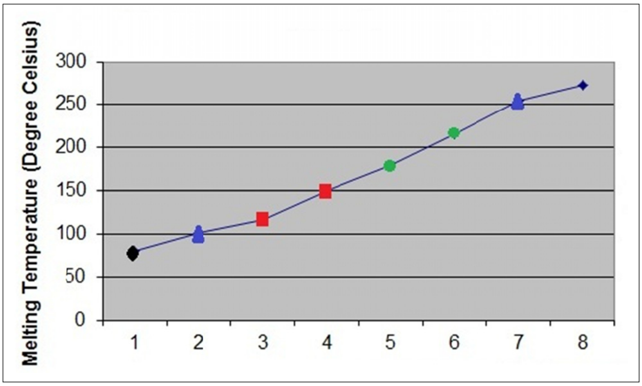

Fig. 5. Distribution of PAHs according of the melting temperature (1 – naphtalene, 2 – phenanthrene, 3 – fluorene, 4 – pyrene, 5 – benzo(a)pyren, 6 – antracene, 7 – chrysene). The same colored shapes are the components between which there is a connection

exists between close to the melting temperature of the components, except for phenanthrene and chrysene. Despite the presence of correlation between these components, the difference between the melting points is large. Correlation exists between the following components: fluorene-pyrene, phenanthrene-chrysene, antracene- benzo(a)pyren.

The authors propose the following scheme for the relationship between: components of PAH and molecular weight, components of PAH and melting temperature, components of PAH (Fig. 6).

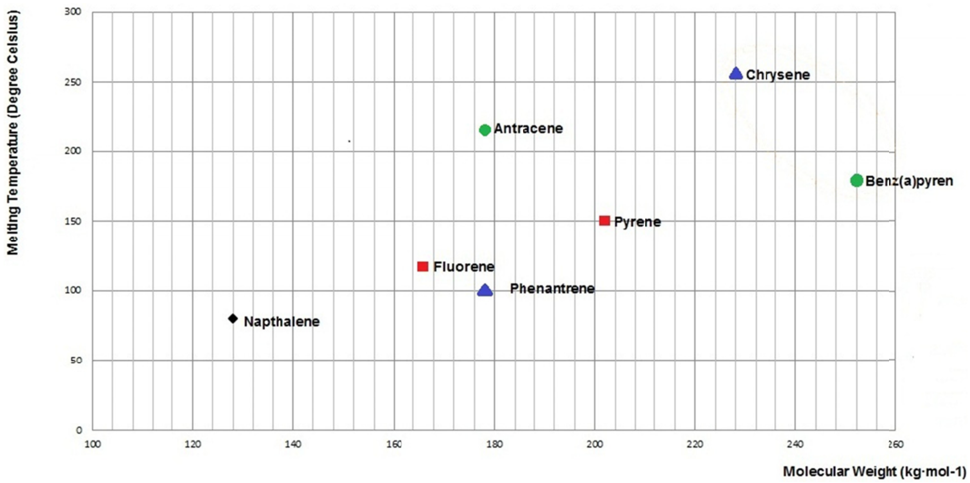

Fig. 6. Relationship between melting temperature and molecular weight of association of PAHs

When considering the figure 6 we observe the following phenomena:

- There is a petroleum association of PAHs between the components of which there is a correlation: between typomorphic PAHs associations chrysene and benzo(a)pyren.
- Other components of the petroleum association of Polycyclic Aromatic Hydrocarbons have no correlation.
- There is a petroleum association of PAHs, as well as hydrothermal and volcanic between the components of which there is a correlation: between fluorene and pyrene (occur in sedimentary rocks within the oil depositaureoles).
- Is Magmatic Association of PAHs between the components of which there is a correlation: between typomorphic PAHs associations fluorene (volcanic) and pyrene (hydrothermal).
- The presence of relations is possibly broken under the influence of migration of deep gases which leads to a situation not applicable to the relations between the components.

7. Conclusions

Reviewing the above, we can assume:

1. Direct positive correlation significant relationship exists only between certain components.
   - The existence of a correlation between oil components reflects a single source of their origin.

- Absence of correlation between oil components reflects the existence of different sources of their origin.
- The presence of correlation between oil, volcanic and hydrothermal associations reflects their inorganic origin.

2. Source of components may be a middle mantle (C-fluid structure) and upper mantle (H-fluid structure). Previously been calculated as the following geological and geochemical data about the prospects of oil and gas Eger Rift:
   - **geological data**: (Tyracek et al. 1990, www.enviweb.cz) 1 – rift structure with presence of migmatites, 2 – seismic active area, 3 – new tectonic movements, 4 – crystal rocks – analogy of collectors the Oilgasbearing basins of Moravia.
   - **geochemical data**: 5 – existing and diverse composition of PAHs, 6 – presence the components resembling on compositions of Moravia oil, 7 – existing of typomorphic oil association – the components characteristically for oil, videlicet: phenanthrene, chrysene, pyrene, benzo(a)pyrene.
   - **mathematical processing the data**: 8 – the correlation coefficients suggest the presence of the deep and various sources of hydrocarbons.

Our investigations are based on direct indicators of PAHs. They can serve as indicators of migrations widely distributed in rocks of oil/gas bearing territory. 13 rock samples have been collected. All 13 samples contain PAHs. Among the components of PAHs existing of typomorphic oil association – videlicet: phenanthrene, chrysene, pyrene and benzo(a)pyrene.

Previous studies have shown favourable geological and geochemical parameters of petroleum potential in the Eger Rift. The present study aims at finding relationships between PAHs.

Result of PAHs correlation analysis of rocks demonstrated the significant relationships between the following components: naphthalene and naphthalene + homologous, phenanthrene and chrysene, pyrene and fluorene, antracene and tetraphene, antracene and benzo(ghi)perylene, tetraphene and benzo(ghi)perylene.

Existing typomorphic oil associations – the components characteristical for oil, videlicet: phenanthrene, chrysene, pyrene, benzo(a)pyrene and the absence of correlation between the components of the oil association may be indicative of different independent sources of hydrocarbons at depths of Eger Rift. The composition and features of relationship of PAH associations may reflect time of hydrocarbon generation, and physic-chemical aspects of rocks, which include hydrocarbons from gas emanations of deep source.

Correlation analysis revealed the existence of significant relationships between the following components: naphthalene and naphthalene + homologous, phenanthrene and chrysene, pyrene and fluorene, antracene and tetraphene, antracene and benzo(ghi)perylene, tetraphene and benzo(ghi)perylene.

Existing typomorphic oil associations – the components characteristically for oil, videlicet: phenanthrene, chrysene, pyrene, benzo(a)pyrene and the absence of correlation between the components of the oil association may be indicative of different independent sources of hydrocarbons in depths of Eger Rift.

So, at the Eger Rift basalt influence brought up to the surface mostly hydrocarbons: naphtalene, naphtalene and homologous, benzo(ghi)perylene, and pyrene. And also there is no correlation between the type of rocks and their enrichment with PAH components. Thus, together with previous geological, geochemical data and mathematical processing of the data: the correlation coefficients suggest the presence of the deep and various sources of hydrocarbons. In addition, geological, geochemical and data on the correlation coefficients can serve as a basis for constructing theoretical models of oil and gas generation.

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