Geochemical conditions of oil and gas potential of the South Caspian basin on the basis of pyrolytic studies of mud volcanoes

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Abstract. This paper provides the results of geochemical studies with products of mud volcanoes conducted for a purpose of evaluating the generative potential of the South-Caspian basin. The kerogen types have been identified for different stratigraphic intervals and stages of the organic matter (OM) thermal maturity have been determined. A correlation has been established between the generative potential and the basin deposition and subsidence rate.

There is no analog in the world to the South-Caspian oil and gas basin in terms of the number of mud volcanoes and their diversity. Over 400 mud-volcano buildups are concentrated there, which is a quarter of the world count. This region also displays active mud volcano behavior, which is accompanied by ejection of a large volume of rock fragments and blocks.

Each mud volcano may be treated as a natural well that delivers rock fragments to the surface from the entire feed channel. The region of the South-Caspian basin is built by a tremendous thickness (25 – 30 km) of Mesozoic-Cenozoic sediments and represents a unique opportunity for a depth study of Earth. The origin of mud volcanoes is often connected with oil and gas fields [1]. Large oil and gas-condensate fields have been discovered in other mud volcano areas (Lokbatan, Garadag, Neftyanye Kamni [«Oil Rocks»], Mishovdag, etc.).

For a purpose of evaluating the generative potential of the Mesozoic-Cenozoic complex in the South-Caspian depression, in the geochemical laboratory studies have been conducted of 69 rock samples from 22 mud volcanoes. The volcanoes are located on the Absheron Peninsula, in the Shamakhy-Gobustan area, Lower Kura area, as well as the Caucasus Major (Fig.1). Also, micro-oil samples from mud volcanoes Lokbatan, Chapylmysh and Gushchu have been studied.

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The samples were studied using pyrolysis with Rock-Eval equipment. This enabled the determination of a spectrum of parameters describing qualitative and quantitative features of the rock OM. The parameters included: total organic carbon (TOC), realized ($S_1$) and residual rock generative potential ($S_2$), oxygen and hydrogen indices (OI and HI), temperature of maximum hydrocarbon yield at pyrolysis ($T_{\text{max}}$), productivity index (PI), etc.

Genetic and catagenetic characteristics of the organic matter are illustrated by various correlation diagrams for such pyrolytic parameters as HI, OI, S$_1$+S$_2$, $T^\circ_{\text{max}}$, TOC, etc. One such diagram is a correlation diagram of the hydrogen index (HI) vs. $T^\circ_{\text{max}}$. This diagram is in essence a modified Van-Krevelen diagram. It provides the opportunity to identify kerogen fields of different OM types as well as following their catagenetic evolution.

The modified Van-Krevelen diagram (Fig. 2a) enabled a classification of the kerogen type in samples:

- **The Pliocene and Miocene** sediments are dominated by type III kerogen (*mostly mud volcanoes of the Absheron Peninsula*);
- **The Oligocene and Eocene** sediments are dominated by type II and III kerogen (*mostly mud volcanoes of the Shamakhy-Godustan area*); in several Oligocene samples type I kerogen was discovered;
- **The Jurassic** sediments are dominated by type III kerogen (*mostly mud volcanoes of the Caucasus Major*);
- **In the Cretaceous** sediments the OM is represented by type IV kerogen and is positioned in the non-generative area (*mostly mud volcanoes of the Caucasus Major*).

Low oxygen index values (less than 30 mg CO$_2$/g of TOC) in most samples indicates the low extent of oxidation.

A dual diagram of HI and $T_{\text{max}}$ (Fig. 2b) shows that the samples capable of generating hydrocarbons have $T_{\text{max}}$ 435-468°C.
According to J. Espitalier and K. Peters [2-4], reservoirs containing liquid oil or high concentrations of mobile bitumoid have anomalously low pyrolysis temperatures $T_{\text{max}}$.

In the correlation diagram $T_{\text{max}}$ vs. PI (Fig. 3a) the points belonging to samples of different age and stage of OM thermal maturity (regarding the capability for oil and gas generation), are distributed by their stratigraphic association:

- The Pliocene sediments in the 436-444°C area – early maturity stage;
- The Miocene sediments in the 440-458°C area – between the peak of oil generation and the late maturity stage;

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**Fig. 2.** Modified Van-Krevelen diagrams: hydrogen index HI vs. oxygen index OI (a) hydrogen index HI vs. maximum pyrolysis temperature $T_{\text{max}}$ (b).
The Oligocene sediments in the 416-438°C area – the early maturity stage;
The Eocene sediments in the 432-440°C area – the early maturity stage;
The Cretaceous sediments in the 434-443°C area – the early maturity stage;
The Jurassic sediments around 410-445°C – between immature and the early maturation stage.

Fig. 3. Correlation $T_{\text{max}}$ vs. PI (a) and $(S1 + S2)$ vs. TOC (b).

Overall, low $T_{\text{max}}$ values emphasized the migration nature of the bitumoid [5-8]. At temperatures that low, the extent of OM catagenetic maturity is quite low [9-13]. Despite an insignificant OM maturity extent, it is possible that hydrocarbon generation is already occurring. It is supported by the elevated content of $S_1$ in the samples. For mature samples of the Miocene sediments in the value range of the pyrolytic parameter $T_{\text{max}} = 440-458^\circ\text{C}$, the OM catagenetic permutation corresponds with the middle and completing stage of the «oil window» MK2-MK3. This is also supported by an increase of the productivity index up to 0.44.
The correlation diagram of the total (oil and kerogen) potential ($S_1+S_2$) vs. TOC (Fig.3b) shows wide variability. These stratigraphic associations are identified:

- **The Pliocene sediments** with very high and outstanding generative potential;
- **The Miocene and Oligocene** with satisfactory to very high generative potential;
- **The Eocene sediments** with mostly satisfactory generative potential;
- **The Cretaceous sediments** with low generative properties (both according to $S_1+S_2$ and $C_{org}$);
- **The Jurassic sediments** with widely variable generative properties between satisfactory to very high.

### Conclusions

A pyrolytic study of 69 rock samples from 22 mud volcano ejecta in the Apsheron Peninsula, which describe the entire stratigraphic section of the South-Caspian Basin, suggested the following conclusions:

- The South-Caspian basin is a polyfocal basin. Within it are identified several stratigraphically separated autonomous generation foci: Aalenian-Bajocian (Middle Jurassic), Valanginian (Lower Cretaceous), Laleogene-Lower Miocene (mostly Oligocene-Lowe Miocene, i.e., Maykopian), Diatomaceous (Middle-Upper Miocene) and Kalin (lower part of the Lower Pliocene, i.e., Productive Series PT).
- Kerogen types in various stratigraphic intervals were established, organic matter thermal maturity stages were determined and the source rock generative potential was correlated with the total organic carbon content.

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