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# Variation of i-butane/n-butane ratio in oils of the Romashkino oil field for the period of 1982–2000: Probable influence of the global seismicity on the fluid migration

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### Abstract

Changes in oil composition in the course of the development depend on numerous factors including both technogenic and natural ones. Physicochemical compositional analysis of 2456 oil samples collected in the Romashkino field in 1982–2000 from two productive strata (Devonian and Carboniferous reservoirs) has indicated statistically significant variations in the i-butane to n-butane content ratio (i-b/n-b). This ratio is characterized not only by a trend of steady growth but also by a significant variation with a period of ~4.5 years. The i-b/n-b ratio variations are well correlated ( $R^2$ =0.61) between these two reservoirs (Devonian and Carboniferous) occurring at different depths. However, the average i-b/n-b ratios recorded in these reservoirs are essentially different (~0.44 and ~0.55, respectively). A possible relationship is discussed between the i-b/n-b ratio variations and those in global seismicity.

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Keywords: Romashkino oil field; Oil composition; Oil migration; Global seismicity

## 1. Introduction

The study of physicochemical, compositional, and time-dependent changes in oils of fields under development is an exceptionally challenging and multifaceted problem. From a practical point of view, this analysis allows the prediction of oil properties for the nearest future (Pedersen et al., 1989), and its scientific application permits the acquisition of explicit data on the migration of hydrocarbons through thick and permeable beds. These specific, natural experiments cannot be carried out in laboratory conditions. The longer this natural experiment proceeds (i.e. oil field development time), the larger the volume of rocks that becomes involved in it, and the greater the amounts of fluid undergoing migration. The development of the oil field and its depletion are naturally expected to be accompanied by the regular increase in density and viscosity as well as by the decrease in the gas content of oil. Variations in physicochemical properties of oil can also occur through the action of numerous other factors. An oil field is a complex formation consisting of a number of relatively isolated portions. For this reason, some deviations from the natural general trend are observed in the course of the development, depending on the applied production methods. Variations in oil properties can also

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be associated both with the involvement of various portions of the deposit in the development and with the hydrocarbon crossflow between strata. Natural causes of the recorded variations in oil properties can include the natural formation, re-formation and collapse of oil pools due to present-day tectonic movements and deep fluid dynamics (Hunt, 1979). Moreover, the dramatic impact on the reservoir from intensive production can change tectonic stress at great depths and the natural fluid dynamic processes. On the other hand, natural seismic events can stimulate oil migration (Beresnev and Johnson, 1994). As the oil migrates, its composition fractionates and changes. It is suggested that some fine variations in oil composition can provide information on the processes occurring in natural oil reservoirs.

This paper presents preliminary results from the analysis of the i-b/n-b ratio variations in oils of the giant Romashkino oil field, and discusses some possible mechanisms that may cause these variations.

## 2. Geology

The giant Romashkino oil field ( $54^{\circ}50'$ N;  $52^{\circ}30'$ E) is confined to the upper portion of the Tatarstan Arch's southern dome, which is a large, isometric, plateau-like high with the dimensions of around  $100 \times 100$  km. This is a typical multilayer platform-type oil field. Its production targets are represented by the Devonian terrigenous rocks occurring at a depth of 1730-1850 m and the Carboniferous terrigenous-carbonate rocks occurring at a depth of 820-1150 m. Oils of these two reservoirs are substantially different in physicochemical properties (Muslimov, 2003). This oil field was put on stream in the late 1940s and is still being developed.

## 3. Methodology

Since the early 1950s, the main characteristics of oil in place have been determined in laboratory conditions in the course of the development of this field. Special standards were adopted to govern the measuring methods and define the types of measured characteristics (Pedersen et al., 1989). These characteristics included density, viscosity, gas content, and composition of some gaseous and fluid components (Jaubert et al., 2002). A total of several tens of thousands of oil samples have been analyzed. However, as the physicochemical measuring methods improved, the correlation between new and old measurements has become more difficult.

In this work the authors used the data on the butane and isobutane volume contents of the oil-in-place samples collected during the period from 1982 to 2000 when these components were measured using an unchanging technique and a single type of equipment (Muslimov, 2003). Moreover, only samples from the central portion of the Romashkino field were selected.

The authors have studied the i-butane to n-butane ratio for the following reasons. Firstly, use of this ratio precludes numerous procedure errors occurring in the course of measuring the absolute value of these oil components in laboratory conditions. This ratio reflects the balance between two groups of petroleum hydrocarbons that are most similar in their physical and chemical properties (Petrov, 1984). It is obvious that the narrower the fraction used for measuring such ratios, the more limited is the effect produced by vaporization, dissolution and sorption both in natural conditions and in the course of collecting the samples and their analysis in laboratory conditions. Secondly, the high information value of this ratio is illustrated by the profound attention given by various researchers to its changeability related to the hydrocarbon origins, tectonic regimes, occurrence depths, rock types, and temperature and pressure gradients (Eremenko and Chilingar, 1996). The use of this ratio also avoids the use of total gas content variations, minimizing the total data variance, and simplifying the interpretation of acquired data.

Fig. 1 shows time behavior of the i-b/n-b ratio for the Devonian and Carboniferous reservoirs of the Romash-kino oil field.

### 4. Results and discussion

Although n-butane and i-butane have many similar fundamental properties, they differ in free energy. Although the number of carbons is equal in both types, the free energy of n-hydrocarbons is lower than that of their isomers (Petrov, 1984). As a result, in closed systems with low pressures and temperatures, the i-b/n-b content ratio decreases in the course of time. However, the reaction can only be triggered by energy exceeding the isomer kinetic stability energy. In the case of biochemical or catalytic processes occurring in open systems, the opposite trend is observed (Petrov, 1984). The formation of isobutane can also prevail in the thermal catalysis of paraffin oil (Cubitt and England, 1995).

Experimental data on the butane ratios in natural oils are very inconsistent. It is noted that "young" light oil from the present-day rifting zones has a significantly higher concentration of n-butane than of i-butane (Eremenko and Chilingar, 1996). In contrast to the above, most oils from the ancient platforms are characterized by a higher isobutane content. The isobutane content is also recorded to increase in the upward

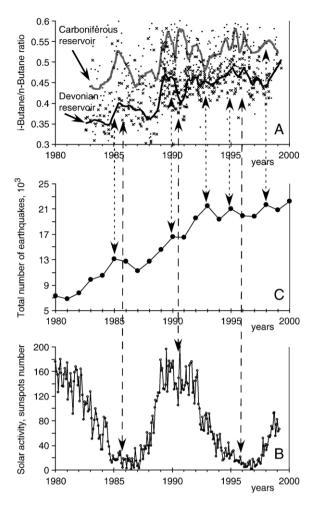


Fig. 1. (A) i-butane and n-butane ratio (i-b/n-b) variations; (B) correlation with solar activity; and (C) total number of earthquakes. Good correlations between the indicated parameters are shown by arrows.

direction throughout the geological section (Cubitt and England, 1995).

The obtained data have permitted the following basic observations (Fig. 1):

- 1. The i-b/n-b ratio variations are well correlated  $(R^2=0.61)$  between these two reservoirs (Devonian and Carboniferous) occurring at different depths. The i-b/n-b ratio in oils from the upper strata (~0.55 in the Carboniferous) is higher than that recorded in deeper oils (~0.45 in the Devonian).
- 2. The i-b/n-b ratio steadily and rapidly increases with time in both oil types at a rate of ~0.01 i-b/n-b units per year. Noteworthily, the rate of increase is slightly more rapid in the deeper Devonian reservoir.
- 3. The period of i-b/n-b ratio variations is  $\sim$ 4.5 years with no significant differences recorded between

oscillation phases for the oils from different reservoirs.

- 4. A distinct correlation observed between the i-b/n-b ratio variations and those of solar activity (ftp://ftp. ngdc.noaa.gov/STP/SOLAR\_DATA/) is characterized by the following: all three solar activity extrema (both maximum and minima) coincide with the i-b/ n-b ratio maxima. Good correlation between these parameters is probably due to the relationship between solar activity and global seismicity (Nurgaliyev, 1991; Shaltout et al., 1999).
- 5. Variations in the total number of earthquakes (http:// neic.usgs.gov/neis/cqlists/) are well correlated with those in the i-n/b-n ratio. Peaks in the total number of earthquakes generally coincide with i-n/b-n ratio peaks. It should be noted that the total number of earthquakes is generally defined by the number of earthquakes with magnitude M<4, which actually reflect general seismicity of the Earth.

It is concluded that an increase in the i-n/b-n ratio reflects the natural aging process in oils of the fields under development. This process can originate both from thermal catalysis in the lower sedimentary cover rocks and from the bioconversion of oil. It can also be supposed that an increase in the i-b/n-b ratio during the periods of higher seismicity is caused by the inflow of hydrocarbon gases from the zones affected by the processes of biological degradation and thermal catalysis of paraffin oil, i.e. oil generating zones that are not actually involved in the development. Noticeably, these processes run essentially in a synchronous manner in both the Devonian and Carboniferous reservoirs.

Although some of these arguments are disputable, the described research trend (i.e. the monitoring of oil composition in fields under development) is very promising for both practical purposes and solving fundamental problems of petroleum geology. The authors believe that the main potential of this technique lies in the intensive use of hydrocarbon isotope geochemistry methods in the study of both deep and near-surface biogenic and thermochemical processes that are accompanied by the fractionation of carbon and hydrogen isotopes.

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