Composition and distribution features of microelements in high-carbon Domanic rocks, extracts from rocks and asphaltenes

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Abstract. The article presents the results of comparative studies of the microelement composition of samples of high-carbon carbonate-siliceous rocks from the Semiluki-Mendym (Domanic) deposits of the Romashkino, Pervomaisky and Muslimovsky deposits, which differ in mineral composition, organic matter (OM) content and spatial location in the territory of Tatarstan. The OM content in the rocks varies from 4.19 to 11.73%. The mineral composition of the rocks is represented mainly by quartz and calcite, the content of which varies from 24 to 61% and from 17 to 54%, respectively. Using the method of mass-spectrometry with inductively coupled plasma in the composition of rocks, extracts from rocks, asphaltenes and carbencarboids isolated from them, the presence of three groups of microelements (ME): biogenic, radioactive and rare earths was established, and also the features of their composition and distribution in the studied objects, depending on the spatial location of the deposits and the material composition of the rocks.

1. Introduction

A decrease of the resources of traditional oil leads to the need to develop hard-to-recover hydrocarbon reserves, which include shale strata [1-5]. According to experts, the total reserves of oil shale in the world are about 650 trillion t, which is equivalent to about 26 trillion t of shale oil [2]. Shale strata are a special type of low-permeability reservoirs represented by siliceous-clayey-carbonate rocks, the individuality of which is determined by an additional set of geochemical criteria — the presence of kerogen and dispersed organic matter (OM), paleofacial conditions for its burial, and the degree of its catagenetic transformation [3]. These deposits are characterized by high metal content, which is due, according to some data, to the long contact of sediments with seawater - the sources of these elements, and intensive diagenesis, and to others - manifestations of volcanism and the participation of deep fluids in the formation of carbon-containing strata [4-6].

In Russia, the Bazhenov Formation and Domanic deposits of the Volga-Ural Province are the most promising for the production of shale oil, the main problem of the development of which is currently the search for technological solutions for converting oil resources into industrial reserves [2]. On the
territory of Tatarstan, the prospects for the development of oil shale formations can be associated, first of all, with the rocks of the Domanic formation of the Upper Devonian - with the Semiluki (Domanic) and Rechitsa (Mendym) horizons, as well as the Domanic formations of the central and side zones of the Kamsko-Kinelsky deflection system [6]. In this regard, in order to “formulate a systematic approach to the development of unconventional and hard-to-recover resources”, the Domanic research polygon was created in 2014, where pilot production of shale oil from poorly permeable domanic deposits of the Bavlinskoye field is currently underway [3]. Oil resources in dense low-permeable rocks of shale sediments by company "Tatneft" are estimated at 192 million tons [3], and, according to the company's chief geologist Khisamov R. S., for their effective development and creation of technologies for their production, an integrated approach is needed, including how laboratory study of core samples by specialized methods, as well as preliminary modeling of formation stimulation processes.

Domanic deposits are a promising source of shale oil production, as well as on industrial scale of a number of microelements: V, Ni, Co, Cu, etc., due to their high metal content. Studying the distribution of microelements in rocks allows us to obtain information on the genesis of hydrocarbons, as well as solve a number of environmental problems that arise in the process of developing domanic deposits [4].

The objective of the work is to study and identify the features of the microelement composition of high-carbon domanic rocks from coeval deposits from different territories of Tatarstan for the effective extraction of petroleum hydrocarbons from them.

2. Materials and Methods

The objects of the study were rock samples from Domanic deposits of three large fields of Tatarstan: Romashkino, Pervomaisky and Muslimovsky, differing in their spatial location on the territory of Tatarstan. The Romashkino field is located in the central part of Tatarstan and is timed to the top of the South Tatar Arch [6]. Within this field, rock samples were studied from the Semiluki-Mendym deposits from three areas: Sarmanovskaya area, an edge one in the north of the Romashkino field; Berezovskaya area, an edge one in the northwest of the field and Chishminskaya area, located in the northern part of the Romashkino oil field. The Muslimovsky field is located within the northeastern slope of the South Tatar Arch. The Pervomaisky field is located on the southeastern slope of the Northern Dome of the Tatar Arch, within the Pervomaisky Val [6]. All studied objects, in addition to the high depletion of traditional oil reserves, combine large proven reserves of Domanic deposits, rich in organic matter and promising to detect shale oil [6, 10-14].

Analysis of rock samples for the content of organic matter (OM) was performed using a STA 449 F1 Jupiter thermal analyzer (Netzsch, Germany) in the temperature range 40-1000°C. Measurement conditions: dynamic argon atmosphere, gas flow rate - 75 ml/min, heating rate - 10 deg/min.

The mineral composition of Domanic rocks was determined by X-ray diffraction analysis on an automatic powder diffractometer Shimadzy XRD-7000S.

Extraction of rock samples was carried out in a Soxhlet apparatus with a mixture of organic solvents: chloroform, toluene, isopropanol, taken in equal proportions. The obtained extracts were studied using a complex of physicochemical methods. The group composition of the extracts was determined by the SARA -analysis method and 4 fractions were isolated: saturated hydrocarbons, aromatic compounds, resins, and asphaltenes. Previously, asphaltenes were precipitated from extracts according to the standard method in a 40-fold amount of hexane [7].
The microelement composition of rock samples, extracts, and asphaltenes was studied on an iCAP Qc inductively coupled plasma mass spectrometer (ThermoFisher Scientific, Germany). The weighed portion of the test sample was 100 mg. Hermetically sealed Teflon autoclaves were placed in a Mars 6 microwave decomposition furnace (CEM Corporation, USA), in which the samples were heated to 210°C for 30 minutes and kept at this temperature for 30 minutes [5].

3. Results and Discussions

The characteristics of the material composition of the studied samples of Domanic high-carbon rocks taken from coeval deposits of the Romashkino, Muslimovsky, and Pervomaisky deposits are given in Table 1.

Table 1. Characterization of the mineral composition of Domanic rocks, its OM content and the group composition of the oil extracts

| No | Sampling depth, m | Mineral composition | OM, wt % | Extract yield wt % | *Group composition, wt % |
|----|------------------|---------------------|----------|--------------------|-------------------------|
|    |                  | Ca | SiO₂ |                | SHCs | ArH. | resins | Asph. | Carben-carboids |
| 1  | 1600.4           | 61 | 24   | 9.54            | 1.92 | 18.59 | 19.91  | 28.45 | 26.70           | 6.35 |
|    |                  |    |      |                |      |      |        |       |                |     |
| 2  | 1601.2-1607      | 24 | 54   | 8.15            | 2.56 | 27.55 | 29.48  | 33.14 | 9.83            | -    |
|    |                  |    |      |                |      |      |        |       |                |     |
|    | Muslimovskaya field | |     |                |      |      |        |       |                |     |
| 3  | 1621-1627        | 57 | 17   | 4.19            | 0.78 | 28.61 | 22.46  | 27.54 | 18.18           | 3.21 |
|    | Sarmanovskaya area | |     |                |      |      |        |       |                |     |
| 4  | 1718.5-1724.5    | 36 | 49   | 11.73           | 1.51 | 21.74 | 31.76  | 29.21 | 12.62           | 4.67 |
|    | Berezovskaya area | |     |                |      |      |        |       |                |     |
| 5  | 1891.7           | 37 | 53   | 6.27            | 2.40 | 22.10 | 23.57  | 30.94 | 23.39           | -    |
|    | Chishminskaya area | |     |                |      |      |        |       |                |     |

*(SHCs) saturated hydrocarbons, (ArH) aromatic compounds, (Asph.) asphaltenes.

The highest OM content in the rocks of the Berezovskaya area of the Romashkino field (11.73%), Muslimovsky (9.54%) and Pervomaisky (8.15%) fields, regardless of their location in this territory.
The yield of extracts from rocks varies over a fairly wide range - from 0.78 to 2.56 wt.%, which indicates a different content of free hydrocarbons in the rocks. In the group composition of the oil extracts, the differences are manifested in the content of saturated hydrocarbons and asphaltenes, the content of which varies from 9.83 to 26.70%. In extracts from rocks of the Muslimovsky field and the Sarmanovskaya and Berezovskaya areas of the Romashkino field, along with the fraction of ordinary asphaltenes, there is a fraction of insoluble carben-carboids [7-9]. These samples are characterized by a high kerogen content according to thermal analysis.

In rock samples, oil extracts from rocks and asphaltenes of the Romashkino, Pervomaisky and Muslimovsky fields, the presence of three ME groups was established: 1) biogenic (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Li, Cd, Sb, Ba, Mo, Ga, Ge, As, Se), 2) radioactive (Cs, Rb, Sr, Zr, Nb, Hf, U, W, Re, Tl, Pb, Bi, Th) and 3) - rare-earths (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Features of the ME distribution in each group of studied objects are shown in Fig. 1-3.

**Figure 1.** The distribution of ME in Domanic rocks and extracts: 1 - ( ) Muslimovsky field; 2 - ( ) Pervomaisky field; Romashkino field: 3 - ( ) Sarmanovskaya area, 4 - ( ) Berezovskaya area, 5 - ( ) Chishminskaya area.

**Biogenic ME.** Among the biogenic MEs in the rocks, elements of the iron and copper family prevail, the highest concentrations of which are Fe (4492-12143 ppm), V (198-2579 ppm), Ti (438-1358 ppm),
Zn (41-862 ppm), Ni (64-307 ppm), Cu (52-124 ppm). The dependence of the increase in the V content in the rocks with the increase in the OM content in them was revealed, which indicates the controlling role of organic material in its accumulation (Fig. 2).

An abnormally high content of Zn (2005 ppm) and V (1580 ppm) in comparison with all samples was recorded in the extract from the rock of the Muslimovsky field. By the high concentrations of Fe (12142 ppm) and Ti (1359ppm) are distinguished the rock of the Sarmanovskaya area of the Romashkino field, the content of which is ~ 2 times higher compared to other samples. In the rock of the Berezovskaya area of the Romashkino field the highest Ni concentrations (307 ppm).

In the extracts among biogenic MEs are high concentrations of V (927-3495 ppm) and Ni (137-310 ppm). An abnormally high Zn content (2005 ppm) was recorded in an extract from the rock of the Muslimovsky field. While the concentrations of Fe and Ti, which in the rocks reached 12143 and 1358 ppm, respectively, in the extracts did not exceed 24 and 5 ppm.

In asphaltenes among biogenic MEs (Fig. 3), as well as in extracts, are dominated by V and Ni. An abnormally high concentration of V was recorded in asphaltenes from the rock of the Muslimovsky field (7374.53). The concentration of V in other samples of asphaltenes varies from 3831.98 to 4668.54 ppm. The Ni content in the studied samples varies from 591.92 to 708.92 ppm, and the Fe content varies from 85.39 to 246.99 ppm. The highest values of the Zn content are observed in asphaltenes from the rock of the Muslimovsky field. In the asphaltenes of the Sarmanovskaya area of the Romashkino field, a high Ga content of 52.74 ppm is observed, the value of which for the remaining samples does not exceed 1.63 ppm.

The carben-carboides of the Muslimovsky field are characterized by abnormally high concentrations of V - 12460 ppm and Zn - 27618 ppm. A high concentration of V in carben-carboides from the rock of the Berezovskaya area of the Romashkino field is 5844 ppm. In the carben-carboides of the Muslimovsky field and the Berezovskaya area of the Romashkino field recorded high concentrations of Ni - 1359.64 and 1203.63 ppm and Fe - 928.37 and 773.94 ppm, respectively. The content of Cr and Mn in carben-carboides is 15-20 times higher than in asphaltenes.
Radioactive ME. Among radioactive MEs, the highest concentrations of Pb (12.06 ppm) and U (31.40 ppm) are observed in the rock of the Muslimovsky field, and Zr (58.40 ppm) and Sr (323.07 ppm) in the rocks of the Romashkino field. A characteristic feature of the rock of the Muslimovsky field is its high content of asphaltenes and carben-carboids. The highest Sr content in the rock of the Sarmanovskaya area of the Romashkino field may be due to the highest calcite content in the mineral composition of the rock. Thus, according to [5], phosphate in hydrothermal fluids can combine with Ca to form apatite, which may be the reason for the higher Sr content in the rock. In extracts, high concentrations of Pb (1.67 ppm) were recorded in the sample of the Muslimovsky field, and high concentrations of Sr 0.99 and 1.30 ppm in the Romashkino field. The concentration of radioactive ME: Cs, Rb, Nb, Hf, W, Re, Tl, Bi, Th, in the studied rock samples does not exceed 0.33 ppm.

In asphaltenes from radioactive MEs, Sr (0.19-1.20 ppm), Pb (0.31-1.03 ppm) and U (0.21-0.73 ppm) predominate. It has been established that in carben-carboids, from rocks of the Muslimovsky field, Berezovskaya and Sarmanovskaya areas of the Romashkino field, a number of elements - Rb, Sr, Tl, Pb, U, are present in high concentrations compared to their content in rocks and in asphaltenes. So, from radioactive elements, high concentrations of Sr (53.65 ppm) are in carben-carboids from the rock of the Berezovskaya area of the Romashkino field and Pb (94.75 ppm) and Tl (6.75 ppm) from the Muslimovsky field. The values of the index \[ \delta U = 2U/(U+Th/3) > 1 \], which is used as an indicator for
determining the redox conditions for the formation of shale rocks [5], indicates a reducing situation in the OM sedimentation basin of the studied rocks.

**Rare-earth elements (REE).** REEs in the studied rocks are represented by the range Ce < La < Nd < Gd < Pr < Dy < Sm < Yb < Er < Eu < Tb < Ho < Tm < Lu. The maximum concentration of ME of this group in the rocks is up to 38 ppm. REE concentrations in extracts and asphaltenes do not exceed 0.09 ppm. The highest concentrations are in ME: Y, La, Ce, and Nd.

### 4. Conclusion

As a result of the studies, it was shown that Domanic rocks selected from coeval deposits of the Romashkino, Muslimovsky, and Pervomaisky fields differ in mineral composition, OM content in them, yields and composition of oil extracts from the rocks, as well as in the composition and concentration of the distribution of microelements in them.

Differentiation of the studied rocks, extracts from rocks and asphaltenes was carried out according to three groups of ME: biogenic, radioactive and rare-earth, and the distinctive features of their distribution in each group of studied objects were revealed. It was established that biogenic (Fe, Ti, and V) microelements predominate in the rocks, and V, Ni and Zn prevail in extracts and asphaltenes. The dependence of the increase in the V content in the rocks with the increase in the OM content in them is established, which indicates the controlling role of organic material in its accumulation. Differences in the Domanic rocks of different deposits by the concentration of radioactive MEs in them are shown: the highest content of Pb and U in the rock of the Muslimovsky field, Zr and Sr in the rocks of the Romashkino field. The values of the index $\delta U = 2(U/(U+Th/3) > 1$ indicate a reducing situation in the sedimentation basin of OM of these rocks. High concentrations in oil extracts from Domanic rocks and in the composition of asphaltenes V and Ni and other metals allow us to consider these rocks as promising in terms of industrial metal mining.

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