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DISTRIBUTION OF METALS IN PETROLEUM ASPHALTENES AND BITUMOIDS FROM RESERVOIR AND BASEMENT ROCK OF THE ROMASHKINO FIELD, RUSSIA

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Abstract

Specific features of the distribution of trace elements in petroleum asphaltenes and bitumoids from the sedimentary rock of different ages and the crystalline basement of the Romashkino field (Tatarstan, Russia) are determined. The effects of major natural processes and technology such as initial organic matter, migration and distribution of trace elements in fluids and rock, long-term waterflooding and transport of trace elements from the deep formations on the trace element composition of petroleum are estimated. Natural correlations between the hydrocarbon and trace element compositions in petroleum are shown to be distorted by the joint impact of such factors.

Introduction

Exploration for oil and gas requires more sophisticated tools, in particular in the zones with complex geology and at deep horizons which include crystalline basement. Recent data on the possibility of formation and accumulation of hydrocarbons at deep horizons [1] need to be taken into account in the geological models of petroleum basins and in the scientifically based reservoir management. In Tatarstan, successful development of natural resources greatly depends on the comprehensive understanding of oil and gas deposits and the advancements in science and technology. The process of petroleum formation is a complex phenomenon due to an impact of many factors. Trace elements and hydrocarbon composition provide some important information about the formation conditions of a petroleum deposit [2-8]. Most of the trace elements are concentrated in the resin-asphaltene components of petroleum. In this regard, the study of trace element composition in asphaltenes is of the particular interest in geochemistry. Asphaltenes are the petroleum fraction which is the most sensitive to natural processes and technology [9-11].

Theory and/or Method

Petroleum asphaltenes, bitumen and bitumoids from the deposits of different ages in the Berezovskaya (Ber), Abdrakhmanovskaya (Abd), Minibaevskaya (Min), Almetyevskaya (Alm) and North-Almetyevskaya (N-Alm) areas of the giant Romashkino field are the subject of the study. Trace element composition of asphaltenes is determined by the Emission Spectral Analysis with a DFS-458 diffraction spectrograph and the NCAY No 246-C method. The method implies burning a 25 mg sample in an AC arc in the crater of the carbon electrode. Spectra of volatile elements are obtained at the current of 8A. Spectra of refractory elements are fixed at the current of 18A by complete evaporation of the sample. Emission spectra are recorded on photographic plates (PPS-03) and a treated microphotometer (MF-2). The quantitative content of microelements is determined by the sample weight (wt.%).

Results and Discussion

The study shows that the specific distribution of the metals in the studied fluids indicates the prevalence in their composition elements of the fourth period, mainly the family of Fe and Cu. In the investigated range of petroleum elements, the concentration of the elements in the iron family changes as V> Fe> Ni> Ti> Mn> Cr while the concentration of the elements in the copper family changes as Zn> Cu> As> Ga> Ge. Petroleum asphaltenes are enriched with V, Ni, B and Fe. The amount of these trace elements decreases in petroleum in deeper horizons, from the Lower Carboniferous (C_1) to the Middle Devonian (D_2) formations. Organic extract from basement rock (BROE) has a relatively low amount of V but an enhanced amount of Ni, Co, Cu, Mn, Ti and Zn which might migrate to the upper horizons (Figure 1).

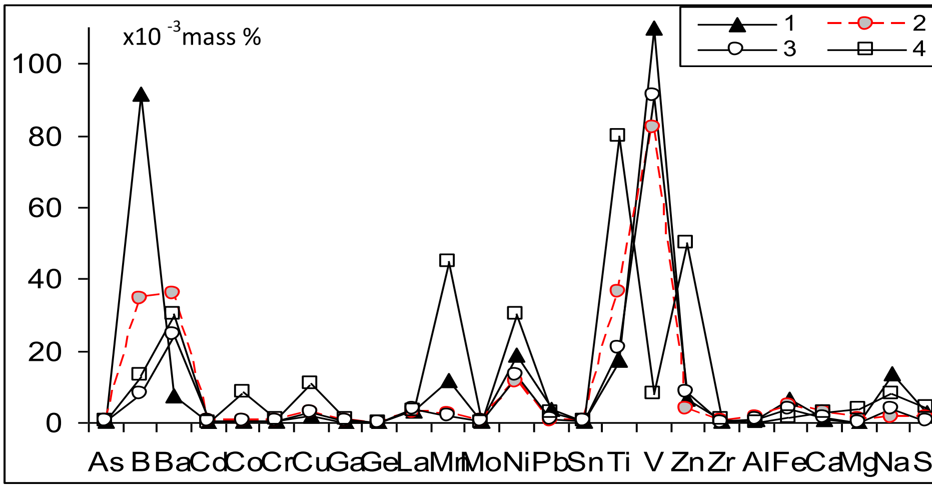

Figure 1. Distribution of the average amount of trace elements in petroleum asphaltenes and bitumoids from crystalline basement: 1 - C_1-D_3 dm; 2 - D_3 psh; 3 - D_2 gv; 4 - BROE

Asphaltenes have an increased amount of different elements. In a number of petroleum samples, the amount of B, Ni, and V is increased and the amount of Cu, Fe, Ti, Zn, Ba, Cd, Co, Cr, Mo and Pb is also increased. Sorption of metals from formation water and sedimentary rock by the petroleum fraction with the high molecular weight and some secondary processes can be reasons for that. These elements are also able to migrate and get accumulated in the petroleum [3, 6, 7]. Petroleum becomes enriched with V, Ni, Co, Mn, Cd and other trace elements due to the accumulation of such elements in resin-asphaltene compounds, chemical oxidation and an sulphurization of petroleum [2, 9, 10].

Distribution of trace elements in petroleum asphaltenes from different areas and different stratigraphic zones has been analyzed. In the Upper Devonian formation, the highest amount of trace elements is found in petroleum. In the Middle Devonian formation, petroleum is also enriched with trace metals. Bitumen is characterized by a different distribution of trace elements than petroleum. Thus, the Upper Devonian bitumen in the Abd rea is enriched with Ni and V. The Middle Devonian bitumen in the Abd area is enriched with B, Cu, Mn and Fe. Average amount of trace elements is related not only to the age of the deposit but also to the distribution of fluids on the area. The Domanik formation in the Ber area (well 21549) is characterized by the increased concentration of metals in petroleum asphaltenes. Petroleum asphaltenes with the increased concentration of metals are also typical for wells of abnormally high productivity located in the Pashiysky formation of the Abd area (wells 719, 9161, 13813) and the Min area (wells 9505, 3162). The abnormal concentration of trace elements in petroleum from those formations can not be explained by sorption of marine water with Clarke concentrations of metals at the initial stages of diagenesis of organic matter and formation water. There could be an additional source of elements associated with metal transportation from deep horizons. For the Abd area, specific features of petroleum asphaltenes and bitumoids of extracted from producing formations of different age are shown. Thus, in the Pashiysky formation, values of La/Ge, La/Ga, Co/Cu, Ni/Cu, Ni/Pb and B/Ni are higher in bitumoids extracted from rock compared to petroleum while values of Zn/Co, V/Ni, V/Cu and Fe/Cu are higher in petroleum. In bitumoids from the Givetian rock, one can see a decrease in values of La/Ge, La/Ga and Co/Cu and a slight increase in values of Zn/Co and V/Cu. Value of V/Ni is higher in the Givetian petroleum compared to the bitumoids from the Givetian rock. Redistribution of trace elements in the studied fluids might be attributed to the migration phenomena in the Pashiysky and Giventian sedimenary deposits.

Zones of the oil-water contact are known to be characterized by the high content of Fe, higher values of V/Ni and leaching of Zn from oil due to oil-water interactions which leads a decrease in value of Zn/Co [4, 8]. Petroleum samples from the Abd area can divided into two groups according to the amount of Zn. The first group is characterized by a relatively high content of Zn ($3.0*10^{-3}$-$8.5*10^{-3}$ wt.%). The second group has less Zn. No similar trends are found for Ti and La. No leaching of Zn and simultaneous enrichment of petroleum with V are found.

"Mantle elements" which could be transported from the Earth's mantle to petroleum deposits though fractures in the Earth's crust, are found in petroleum in Russia. Such elements are La, Hg, Sn, Li, B and others [1, 11]. In our study, Bo is found to be a predominant element in the Lower Carboniferous and Upper Devonian deposits. That is likely related to the transfer of Bo from rock to petroleum.

A biomarker study has been conducted on a series of fluid samples from the Pashiysky-Kynovskih and Givetian reservoir rock, including “abnormal” (very high productivity) wells and bitumoids extracted from the basement rock [1, 11]. The study shows that petroleum from the Pashiysky-Konovskih and Givetian deposits are of a different genetic type, i.e. of different sources. Interestingly, petroleum samples from each deposit also have different biomarkers which might be attributed to a possible inflow of hydrocarbons of other genetic type to the reservoirs. Genetic similarity of the Givetian petroleum and petroleum from the abnormal wells located in the Abd and Alm areas with bitumoids from basement rocks is found. A connection between those petroleum deposits and faults in the crystalline basement is established. No clear connection between abnormal wells and lateral geological structures is found.

Compared to petroleum samples from “normal” (typical/average productivity) wells, petroleum samples from abnormal wells located in the Pashiysky-Kynovskih deposits have lower values of B/Ni, Ni/Pb, Fe/Cu. This is due to a high concentration of trace elements (Ni, Li, Cu) which predominate in the basement rock (Table 1). Tatarstan is known to have petroleum enriched with V [6]. Values of V/Ni in asphaltenes indicate genetically similar petroleum in producing horizons (petroleum is genetically related to sapropel organic matter and reduction conditions in sediments). Hydrocarbon extract and organic matter extracted from the basement rock have a lower value of V/Ni compared to the petroleum from sedimentary rocks.

Bitumoid samples from the basement rock is found to have a high correlation parameter (>0.80) between trace elements which might be related to processes taking place in the Earth's depth: Ni and Ge, Ga, Zn, Co; Cd and Cu; Zr and Al; Zr and Na, etc. These relationships almost lose their significance in the HBA rocks of sedimentary cover and noticeably weaken in petroleum. Unlike basement rock, petroleum is characterized by correlations of B and Pb, Mn and Ti, Ni and V. Values of La/G and La/Ge are in line with distribution of trace elements in bitumoids and bitumen samples from crystalline basement and petroleum. That might be related to fluid migration and some secondary processes taking place in sedimentary deposits.

Table 1. Average values of geochemical parameters

Subject	La/Ge	La/Ga	Zn/Co	V/Ni	V/Cu	Ni/Cu	Co/Cu	B/Ni	Ni/Pb	Fe/Cu
Abnormal wells	9.67	7.55	6.82	2.74	31.8	12.6	5.50	0.420	1.88	21.2
Normal wells	9.78	8.04	5.60	2.43	32.8	15.1	6.18	1.17	2.53	44.2
Bitumoids	21.5	11.2	20.6	4.77	9.41	1.70	0.260	3.20	7.22	3.78
BROE	31.0	27.5	109.0	1.71	0.170	0.480	0.410	129.0	1.93	84.0

Factor analysis has been used in the study (Table 2). Five main factors controlling distribution of trace elements in petroleum of the Romashkino field are found [11, 12]. The most significant is Factor 1. It has a 20.5% load on V/Ni and V/Cu and is considered to be genetic. The factor is associated with the amount of "biogenic" elements in petroleum and is related to the type of the initial organic matter. Factor 2, with a 17.9% load on Ni/Cu and Ni/Pb, is likely related to the migration processes. Factor 3, with a 10.1% load on B/Ni, is thought to be related to the transport of trace elements between produced petroleum and bitumen species left in the reservoir rock. As a result, asphaltenes can be enriched with Bo and Ni. Factor 4, with a 14.5% load on Co/Cu. Value of Co/Cu increases from condensate fields to oil fields. This parameter can be used to differentiate hydrocarbon deposits and to trace hydrocarbon migration due to waterflooding. Factor 5 (12.7%) has the highest weight on the value of La/Ge and can be considered an indicator of the transportation of microelements from the Earth's depth to the sedimentary deposits.

Table 2. Factor analysis data for trace metals of petroleum asphaltenes

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
La/Ge	0.07	0.11	0.02	0.11	0.89
La/Ga	0.46	-0.49	0.05	-0.08	0.63
Zn/Co	0.02	-0.10	0.01	-0.20	0.16
V/Ni	0.95	-0.17	0.01	-0.03	0.11
V/Cu	0.92	0.26	0.02	0.21	0.08
Ni/Cu	0.20	0.72	0.02	0.58	0.09
Co/Cu	0.05	0.12	0.05	0.97	0.05
Zn/Cu	0.13	-0.05	0.03	0.21	0.12
B/Ni	-0.01	-0.07	-0.99	-0.05	-0.03
Ni/Pb	-0.03	0.93	0.08	0.04	-0.02
Factor weight, %	20.5	17.9	10.1	14.5	12.7

Summary

The study provides new knowledge about complex physical and chemical processes affecting formation of trace element composition of petroleum asphaltenes, bitumen and bitumoids in the giant Romashkino oil field. Accumulation of trace elements in asphaltenes and secondary processes are found to be two main factors affecting distribution and amount of trace elements in petroleum and rock.

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