

## Rare Earth Elements as Geochemical Criteria of the Oil-bearing Capacity of the Formations

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doi: <http://dx.doi.org/10.13005/bbra/1445>

(Received: 27 September 2014; accepted: 10 October 2014)

The REE studies in the formations of clastic and carbonate type with the presence of hydrocarbon oil and gas showed that components of bitumen and oil accordingly did not only have a significant impact on REE fractionation between the formations of oil and gas deposits, but also became the main differentiation cause (factor) in the behavior of the individual lanthanides being a part of REE of the formations' mineral and organic complexes. As exemplified by the study of the South Pyzhinskaya 1 parametric well's section (Western Siberia), the 12<sup>th</sup> Kokdumalak oil and gas deposits' well (Uzbekistan) and the Krapivinskoye oil and gas field (Western Siberia), there were shown the variations of the full REE composition spectra. There were specified the differences in the behavior of individual lanthanides in REE composition of formations and their factions - the acid extract (1.8% HCl), taken as a movable mineral complex (MMC), and the organic part of the alcohol-benzene mixture (OP ABM). Reasons for fractionation and differentiation in the lanthanide behavior are considered from the standpoint of the oil and gas hydrocarbons of petroleum fluids impact on the redox conditions of the environment, impact of their stabilizing properties on the lanthanide valence states and REE isomorphism. The results of the formation studies taken from the South Pyzhinskaya 1 well were compared with the changes in the isotopic composition of carbon and oxygen in the well section. There was provided a comparison of the ratios  $Ce^{4+}/Ce^{3+}$  in various samples of insoluble residue 1.8% HCl and OP ABM, as well as the ratio of  $Eu^{2+}/Eu^{3+}$  in oil from the zone of OM generation. As a result, there were revealed significant differences in the REE behavior within oil and gas deposits, enabling to interpret REE as geochemical criteria of the oil-bearing formations.

**Key words:** Formation fractions, Differentiation in the lanthanide behavior within the REE composition, variations of carbon and oxygen isotopic composition, the ratio of  $Ce^{4+}/Ce^{3+}$  and  $Eu^{2+}/Eu^{3+}$ , valence, isomorphism.

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From the standpoint of the oil formation and expansion<sup>1</sup>, the mechanism of oil and gas deposits conversion into reservoirs<sup>2-4</sup>, and concepts of oil and gas geology<sup>5</sup>, the condition for the oil and gas trap formation is the presence in sediment of, at least, several factors:

- a) Presence of the oil-source formation and generation of liquid oil and gas hydrocarbons from the buried organic matter (OM);
- b) Presence of the carrier bed, through which, due to overcoming the interstitial water boundary tension and migration, oil and gas fall within the shaped by geological and tectonic processes oil-bearing reservoir (field).

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For your information, oil is not produced in the reservoir formations. Such a statement is seen as an established fact by most followers of the organic theory of oil origin<sup>1</sup>.

REE reaction, due to its chemical properties in a row of La-Lu, owing to the “lanthanide contraction” effect and the ability of individual lanthanides to change valence and ionic radius in different redox conditions, allowed to record within the process of oil and gas formation, conversion and migration of oil and gas hydrocarbons the abnormal REE behavior on the background of their bulk earth distributions in the sedimentary cycle.

Initial information about the possibility of using REE in the practice of oil exploration is given in the works<sup>6-8</sup>. However, the use of instrumental neutron activation analysis method while determining the REE content did not make it possible to carry out detailed studies because of the difficulties in determining the full lanthanide spectrum in the REE composition. Over the past two decades, there were virtually no publications and information on the interrelationship between the REE and oil components of the formations. The works [9, 10, and others] occasionally getting

into print do not fully reflect the mechanism of abnormal manifestations of individual lanthanide, as there was not considered the REE exchange between mineral and organic complexes of formations. All this contributed to the development of oil and gas deposits research in the applied direction.

Therefore, there was made an attempt to analyze the REE behavior in the oil and gas bearing deposits, as well as in their host formations based on the balance of REE fractions of mineral and organic parts of formations in relation to the formation bank. For this purpose we used REE concentrations in the acid extract (1.8% HCl), the insoluble residue 1.8% HCl (IR) and the extract of alcohol-benzene mixture (ABM). There were given the variations and distributions of lanthanides in the formation bank and their fractions, as well as their behavior in a variety of geochemical conditions in the REE composition. There were observed lanthanide properties, capable of changing valence and ionic radius in the presence of oil and its high-molecular weight compounds (HMWC) - lubricants, resins and asphaltenes. There are provided the ratios of Ce<sup>4+</sup>/Ce<sup>3+</sup> and Eu<sup>2+</sup>/Eu<sup>3+</sup> calculated by analogy of their calculations in

**Table 1.** REE content in the formation bank of the “South Pyzhinskaya 1” parametric well samples, g/t

Element	Sample number				
	1	2	3	4	5
V	109.00	59.10	75.50	105.00	44.20
Ni	69.20	54.50	13.40	55.60	10.70
Sr	400.00	180.00	349.00	140.00	131.00
Y	23.60	17.90	22.10	25.40	12.50
La	42.00	22.50	26.00	26.50	24.70
Ce	81.50	47.80	48.50	57.50	54.00
Pr	9.37	5.16	5.95	6.87	6.24
Nd	34.80	20.40	26.90	26.70	21.00
Sm	6.73	3.68	5.55	7.00	3.50
Eu	1.50	0.90	1.38	1.44	0.82
Gd	6.57	4.24	5.52	6.13	3.62
Tb	0.83	0.61	0.80	0.85	0.53
Dy	4.47	3.45	4.47	5.00	2.57
Ho	0.89	0.62	0.73	0.98	0.56
Er	2.96	2.03	2.28	2.96	1.54
Tm	0.45	0.28	0.31	0.48	0.24
Yb	2.45	1.87	2.10	2.73	1.59
Lu	0.38	0.29	0.34	0.38	0.24
TR	218.5	131.73	152.93	170.92	133.65

the work<sup>11</sup> to explain the geochemical processes. In this work, all the spectra of REE composition are obtained by the normalized values to the chondrite carbonaceous (C1) according to the data of the work<sup>12</sup>.

The main purpose of this work is to identify the opportunities of rare earth elements, especially the individual lanthanides in various sedimentary formations of oil and gas deposits, as well as during the solution of the most relevant objectives in the practice of oil exploration. The not less important statement of the question is also the establishment of geochemical criteria for the formations' oil-bearing capacity, on the basis of unknown and anomalous factors within the behavior of rare earth elements in sedimentary processes.

#### Methodology of the analysis

REE contents within the formations and their concentrations in the fractions performed by the ICP MS method are specified in the Tables 1-4 (the analysis was performed by "Plasma", Ltd, Tomsk, accreditation certificate ROSS RU No 0001 516895 issued on May 21, 2008, valid until March 25, 2016). As a means of measurement there were used: inductively coupled mass spectrometer

ELAN, model DRC-e with the system of sample introduction in the form of solution using a peristaltic pump and an air sprayer, made in the USA, the company "Perkin Elmer Instruments LLS". Supplementary to the mass spectrometer, there was used a microwave decomposition system speedwave<sup>TM</sup> MWS-3, produced in Germany, the company "BERGHOF Products + Instruments GMBH".

#### Targets of research

As a research targets there was selected a section of the South – Pyzhinskaya 1 parametric well (West Siberia), Kokdumalak oil and gas field (Uzbekistan) and Krapivinskoe oil and gas field (southeastern part of Western Siberia). The research results are shown in Tables 1-9, and Figures 1-11.

#### Discussion of the results

Before proceeding to discuss the results, we consider some of the concepts in petroleum geology and geochemistry, according to the article applied. Oil and gas deposits, as it is well known<sup>1,5</sup>, are being formed during the sedimentary processes with the burial of organic matter with the subsequent kerogen generation to the oil and gas hydrocarbons over the geologic time period.

**Table 2.** REE concentrations in the acid extract (1.8% HCl) of the "South Pyzhinskaya 1" well formations, g/t

Element	Sample number				
	1	2	3	4	5
Mg	15 835.74	13 569.64	38 243.47	18 279.43	19 704.48
Ca	133 349.31	71 479.54	99 948.21	44 637.79	47 052.62
Sr	4 563.61	8 318.93	934.02	943.06	369.13
Y	142.91	45.32	48.27	66.12	69.96
La	172.60	40.64	25.61	33.30	52.65
Ce	429.71	117.60	64.02	98.80	156.08
Pr	64.13	15.50	7.89	12.32	18.88
Nd	280.65	64.14	36.17	60.14	90.06
Sm	58.25	16.61	9.21	21.53	22.77
Eu	12.70	5.29	2.46	5.16	5.23
Gd	62.89	20.82	12.52	28.01	28.73
Tb	7.45	2.78	1.91	3.53	3.53
Dy	35.56	10.90	10.22	16.82	17.42
Ho	5.30	2.05	1.69	2.72	2.69
Er	11.37	4.96	4.45	6.32	5.96
Tm	1.32	0.59	0.59	0.87	0.77
Yb	8.52	3.50	3.51	5.16	5.32
Lu	1.01	0.36	0.51	0.76	0.79
TR	1 294.38	351.05	229.03	361.55	480.84

Moreover, the proportion of organic matter comprises a small part of the formation mass and can range from 0.3-0.5% in the oil-source formations<sup>5</sup>, and reach more than 10% (!<sub>org</sub>) in the clay – siliceous formations of the Bazhenov Formation in Western Siberia<sup>10</sup>. Hence, it is obvious, that with allowances made for the low

clarkes of rare earth elements in nature and the lack of any significant fractionation of rare earth elements (REE) in sedimentary processes<sup>13</sup>, the thesis statement of geochemical criteria must be justified, at least, by the anomalous geochemical differences in sediment formations. To such factors there can be obviously related the anomalous REE

**Table 3.** REE content in the insoluble residue of acid extract (1.8% HCl) of the "South Pyzhinskaya 1" well formations

Element	Sample number				
	1	2	3	4	5
Sr	132	67.4	171	136	139
Y	61.5	24.5	62.5	28.5	20.8
La	214	47.53	232	36.8	69.6
Ce	473	108	508	84.1	160
Pr	49.2	11.2	52.0	9.24	15.7
Nd	178	40.5	195	33.3	56.2
Sm	28.9	6.88	32.5	6.10	8.79
Eu	2.62	1.26	2.95	1.28	1.30
Gd	29.1	7.64	30.8	7.99	9.30
Tb	3.54	1.06	3.91	1.09	1.13
Dy	14.6	4.95	14.5	5.54	4.72
Ho	2.53	0.96	2.22	1.18	0.83
Er	6.35	2.74	6.50	3.08	2.27
Tm	0.88	0.45	0.90	0.46	0.44
Yb	5.09	2.53	5.21	2.94	2.57
Lu	1.03	0.42	0.84	0.42	0.38
TR	1070.34	260.62	1149.83	222.02	354.03

**Table 4.** REE concentration in OP ABM and oil, South Pyzhinskaya 1 well

Element	Sample number			Oil
	1	4	5	
La	1.990	2.000	6.280	0.01300
Ce	6.250	4.070	17.600	0.02200
Pr	0.360	0.510	1.330	0.00380
Nd	1.660	2.020	5.340	0.01500
Sm	0.280	0.370	0.880	0.00320
Eu	0.091	0.110	0.130	0.00170
Gd	1.870	2.050	2.830	0.00380
Tb	0.350	0.430	1.930	0.00076
Dy	0.150	0.270	0.720	0.00250
Ho	0.036	0.042	0.110	0.00040
Er	0.150	0.110	0.550	0.00064
Tm	0.046	0.022	0.042	0.00019
Yb	0.120	0.190	0.410	0.00095
Lu	0.025	0.025	0.070	0.00042
TR	13.378	12.219	38.222	0.06836

concentrations within the boundaries of the oil-bearing deposits with respect to their host formations, or previously unknown behavior of individual lanthanide in the REE composition. It is established and known that such geochemical criteria are met by the hurricane accumulation of europium (Eu) on the boundaries of oil and gas deposits, as a consequence of the migration of europium in the form of  $\text{Eu}^{2+}$  with oil and gas hydrocarbons, as well as the  $\text{Sm}^{2+}$  and  $\text{Yb}^{2+}$  presence under the conditions of reducing environment and changes of the ionic radii, which contributes to capturing these lanthanides by oil components within the conditionally closed deposit system<sup>14</sup>. Out of all the specified lanthanides, the lowest redox potential belongs to europium (-0.55V), the largest – to samarium (-1.561V), ytterbium, accordingly, possesses (-1.518V) [14]. In the geochemistry of REE sedimentary processes,

it is established that the ratio of Eu/Sm usually corresponds to 1<sup>15</sup>, while in the organic complex of the oil-bearing formations, it can reach the above mentioned values by 1-2 orders and, in some cases, be approximately equal to (Eu/Sm = 130), and the relative maxima of europium are (Eu\* = 160). All the above specified data leaves no doubt that these

lanthanides are accumulated in the divalent form due to their complex formations with oil components<sup>14</sup>.

So, it is obvious that Eu<sup>2+</sup>, Sm<sup>2+</sup> and Yb<sup>2+</sup> can act as geochemical criteria of the oil-bearing sedimentary formations and will be needed in defining and clarifying the boundaries of oil-

**Table 5.** Change of the carbon and oxygen isotopic composition in the South Pyzhinskaya 1 well section\*

Sample number	Denomination	Sampling interval, m	$\delta^{13}\text{C}_{\text{org}}^{\circ}\%$	$\delta^{18}\text{C}_{\text{carb}}^{\circ}\%$	$\delta^{18}\text{O}_{\text{carb}}^{\circ}\%$
1	Bazhenov formation	2547.18-2548.01	-29.4-29.6	-10.7	13.1
		2551.5	-29.4-29.6	-1.0	22.3
2	Coal	2598.3-2610.3	-22.2-27.6	-7.3	16.1
		2780.1	-22.0	-5.1	20.0
3	Siltstone, sandstone, coal	2781.6	-24.1	not def.	not def.
4	Mudstone, siltstone, coal	2801.0-2809.0	-24.0-25.2	-5.5	21.1
	Mudstone, siltstone	2984.7-2989.0	-24.9-25.5	-5.0	15.9
	Mudstone	2993.2-2994	-32.4-32.9	-4.0	16.0-16.3
5	Sandstone with the HC layers	2999.0	-25.9	not def.	not def.
		3000.0-3004.0	-30.0	-0.6	19.3

\* According to the data of the Tomsk Branch of the Siberian Scientific and Research Institute of Geology, Geophysics and Mineral Resources (Tomsk).

**Table 6.** The balance of the REE composition in acid extract of the South Pyzhinskaya 1 well samples

Element	Sample number				
	1	2	3	4	5
Fractional yield *					
%	0.053	0.014	0.231	0.039	0.049
	Share to the formation bank, %				
Sr	60.460	64.700	61.800	26.470	13.910
Y	32.100	3.540	50.400	10.200	27.600
La	21.700	2.530	22.700	4.940	10.500
Sm	45.800	6.310	38.300	12.080	32.100
Eu	44.870	8.220	41.160	14.080	31.500
Yb	18.430	2.620	38.600	7.420	16.320
Ce	27.350	3.440	30.470	6.750	14.280
Pr	36.270	4.200	30.610	4.510	14.940
Nd	42.740	4.400	31.000	8.850	21.200
Gd	5.700	6.870	52.400	17.900	39.200
Tb	47.600	6.400	55.100	16.300	32.900
Dy	42.160	4.150	52.800	13.200	33.450
Ho	31.560	3.220	53.450	10.900	23.700
Er	20.400	2.340	45.000	8.400	19.100
Tm	15.500	2.950	43.900	7.100	15.800
Lu	14.100	1.740	34.600	7.860	16.200
La/Yb	1.180	0.960	0.600	0.660	0.640
Eu/Sm	0.980	1.300	1.070	1.160	0.980
TR	31.400	3.720	34.580	8.410	17.800

**Table 7.** Change of the carbon isotopic composition and the ratio of REE in OP ABM and oil from the OM generation zone

Sample number	Formation name	Sampling interval	$\delta^{13}\text{C}_{\text{org}}, \%$	$\text{Ce}^{4+} / \text{Ce}^{3+}$	$\text{Ce}^{4+} / \text{Ce}^{3+}$	$\text{Eu}^{2+} / \text{Eu}^{3+}$
				1.8% HCl	OP ABM	OP ABM*
1	Bazhenov formation	2547.18-2548.01	-29.4-29.6	2.63	4.32	-0.71
		2551.5	-29.4-29.6	not def.	not def.	not def.
2	Coal	2598.3-2610.3	-22.2-27.6	3.2	not def.	not def.
		2780.1	-22.0	not def.	not def.	not def.
3	Siltstone, sandstone, coal	2781.6	-24.1	2.82	not def.	not def.
4	Mudstone, siltstone, coal Mudstone from the RH generation zone	2801.0-2809.0	-24.0-25.2	3.3	2.24	-0.07
		2984.7-2989.0	-24.9-25.5	not def.	not def.	not def.
5	Sandstone with the HC layers	2993.2-2994	<b>-32.4-32.9</b>	not def.	not def.	not def.
		2999.0	-25.9	3.4	3.62	-0.77
6	Oil from the RH generation zone *	3000.0-3004.4	-30.0	not def.	not def.	not def.
		not def.	not def.	not def.	1.62	<b>8.3**</b>

Isotopic composition is taken in accordance with the data of the Tomsk Branch of the Siberian Scientific and Research Institute of Geology, Geophysics and Mineral Resources (Tomsk). \* Valence ratio of cerium and europium are given after their normalization to the chondrite carbonaceous C1 [8].

**Table 8.** The ratio of  $\text{Ce}^{4+}/\text{Ce}^{3+}$  in the formation fractions of the 12th Kokdumalak oil and gas field well according to the work [17]

Fraction	Ratio	Sample number					
		1	2	3	4	5	6
IR OP ABM	$\text{Ce}^{4+}/\text{Ce}^{3+}$	-0.2	0.013	0.85	-0.04	10.6	-0.5
OP ABM	$\text{Ce}^{4+}/\text{Ce}^{3+}$	0.36	0.39	0.23	0.41	0.4	0.59
IR OP ABM *	$\text{Ce}^{4+}/\text{Ce}^{3+}$	-0.75	-0.68	-0.51	-0.64	1.41	-0.82
OP ABM *	$\text{Ce}^{4+}/\text{Ce}^{3+}$	-0.61	-0.6	-0.58	-0.56	-0.56	-0.52

**Table 9.** Normalized values (C1) and the valence ratios of cerium, europium and terbium in the OPABM of the Kokdumalak oil and gas field (Uzbekistan). According to the work [17]

Element	Sample number					
	1	2	3	4	5	6
La	22.80	23.20	25.70	23.60	23.60	22.40
Ce	7.14	7.47	7.48	7.75	7.65	8.42
Pr	1.11	1.15	1.44	1.19	1.17	1.26
$\text{Ce}^{4+}/\text{Ce}^{3+}$	-0.40	-0.38	-0.44	-0.37	-0.38	-0.28
Sm	3.34	3.70	5.27	4.00	0.05	1.82
Eu	2.40	2.55	3.26	2.48	0.25	2.27
Gd	3.06	3.16	7.08	3.36	3.26	2.96
$\text{Eu}^{2+}/\text{Eu}^{3+}$	-0.25	-0.25	-0.47	-0.32	-0.90	-0.05
Gd	3.06	3.16	7.08	3.36	3.76	2.96
Tb	19.70	17.70	<b>72.60</b>	20.20	18.30	21.00
Dy	2.90	2.60	10.65	2.96	2.68	3.08
$\text{Tb}^{4+}/\text{Tb}^{3+}$	5.61	5.14	7.20	5.40	4.70	6.00

bearing formations in the section of exploratory drilling wells<sup>16</sup> and with a high probability in solving prognostic problems.

REE behavior in carbonate sediments is slightly different due to the presence of petroleum fluids in fractured reservoir systems and different redox conditions in the clastic complex formations, i.e., in the terrigenous sediments. Here, the geochemical criteria are represented by the lanthanides able to migrate and accumulate together with the petroleum fluids in the oxidized state due to their screening (stabilizing) by the oil and gas hydrocarbons<sup>17</sup> and (or) isomorphism. In the row of La - Lu capable of changing valence and ionic radius, are also possessed by: cerium, praseodymium and terbium, capable of participating in geochemical processes in the forms of  $Ce^{4+}$ ,  $Pr^{4+}$  and  $Tb^{4+}$ <sup>17</sup>, and terbium ( $Tb^{4+}$ ) additionally, with replacement of magnesium ( $Mg^{2+}$ ) during the process of heterovalent isomorphism, which is probably possible after solvation by organic acids of the oil and gas hydrocarbons and their (acids) deposition in the form of insoluble salts of calcium ( $Ca^{2+}$ ) and magnesium ( $Mg^{2+}$ )<sup>1,18</sup>.

For objective consideration of the approved task formulation, there were select several research targets. They reflect the differential behavior of the individual lanthanides as part of rare earth elements, which allows to regard their behavior as geochemical indicators in different lithological types of formations with the presence of petroleum fluid.

#### “South Pyzhinskaya 1”

The “South Pyzhinskaya 1” parametric well is located in the south-east of West Siberian, an oil and gas province on the right Ob riverside and exists in the transition zone of the Pyl-Karaminsk and Paiduginsk banks and the Ust-Tym depression. The well has been assigned the task of studying section in the deepest part of the depression and modeling a non-anticlinal trap in the zone of junction with the Pyl-Karaminsk megalithic bank.

According to the data of the Federal State Unitary Enterprise, Siberian Research Institute of Geology, Geophysics and Mineral Resources (Novosibirsk), during the process of the well drilling and exploration there were pulled out 2.4 m<sup>3</sup> of fluid, including 0.3 m<sup>3</sup> of oil, 13.0 m<sup>3</sup> of gas in

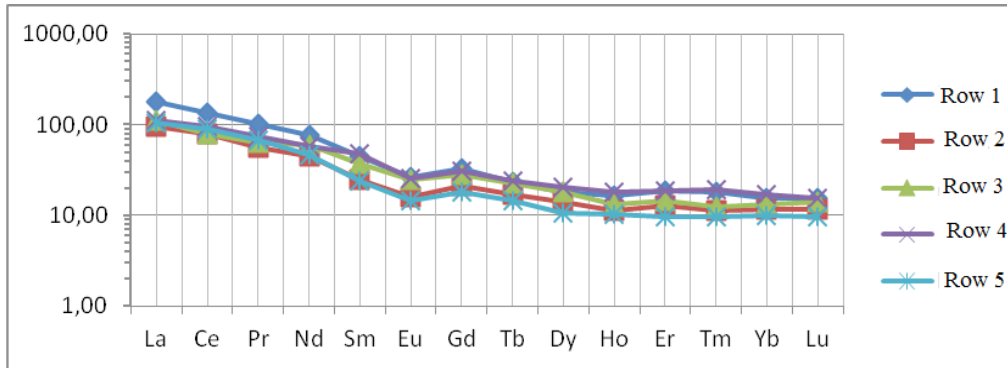
the interval of 2963-2970 m; in the interval of 2712-2723 m the was obtained a formation water flow of 11.51 m<sup>3</sup>/day.

In the previous works<sup>7,8</sup>, it was noted that in the clastic formations of oil and gas-bearing deposits of the West Siberian basin (for example, the study of oil and gas deposits in the south-eastern part), the REE in the mineral part vary within the range of 70%, and in the organic one they make up about 30%. There was marked the synchronicity in the Eu concentration changes and isotopic composition of carbon in sapropelites of the West Siberian plate<sup>8</sup>. At the same time, the synchronicity of these geochemical parameters was observed at all stages of the transformation of OM and varies from brown-coal to fat-gas one (B-BD-D-DG-G). It is noted that the maximum concentration of Eu (1.0 g/t and above) in the sapropelites of the West Siberian plate corresponds to the highest light value of the carbon isotopic composition (-31.0 ‰ or above) and is associated with the BD-D-DG stages and the interval of the main oil and gas formation phase (MOGFP)<sup>5</sup>.

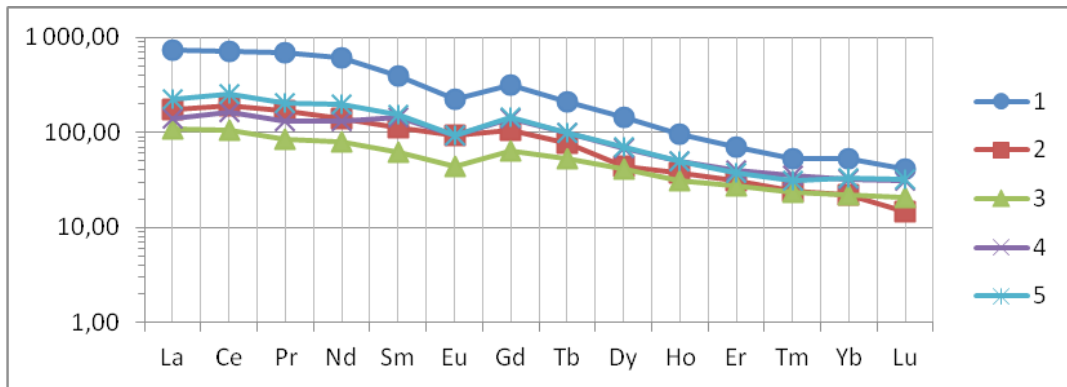
According to the Eu content in the bank (Table 1) and <sup>13</sup>S values in the BF, we can make a preliminary conclusion about the weak transformation of the OM (kerogen) buried in the BF, because the content of Eu in the organic part of the BF will be 0.3 g/t, which corresponds to the work<sup>8</sup> of the lignite stage of kerogen conversion. This corresponds to the change in the isotopic composition of carbon (-29.4 ‰), also indicating a weak transformation of organic matter buried in the BF. However, the BF REE distributions differ from other formation samples in the well section (see Fig. 1) and are reflected by a high content of light REE (La-Sm), which is typical for clay deposits of the black shale formations with organic matter content<sup>19, 20</sup>.

The Fig. 1 shows that weak REE fractionation in the formations of the studied section, and REE spectra slightly differ from the REE spectra of sedimentary rocks. Greater fractionation between the BF and the rest of the formations can be seen in REE concentrations in the acid extract (1.8% HCl) in Fig. 2.

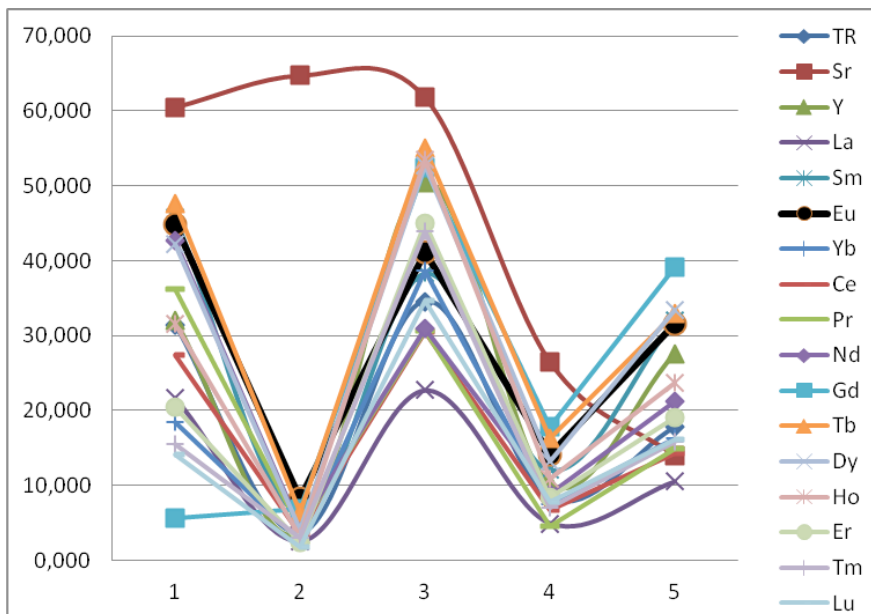
Interest of the 1.8% HCl fraction study is seen in the distribution of REE shares and other trace elements in relation to the carbon isotopic composition (Table 5, Table 6 and Fig. 3).



**Fig. 1.** Differences of the lanthanide distribution within the REE formation composition in the “South Pyzhinskaya 1” well section



**Fig. 2.** Lanthanides within the REE composition in acid extract of the “South Pyzhinskaya 1” samples

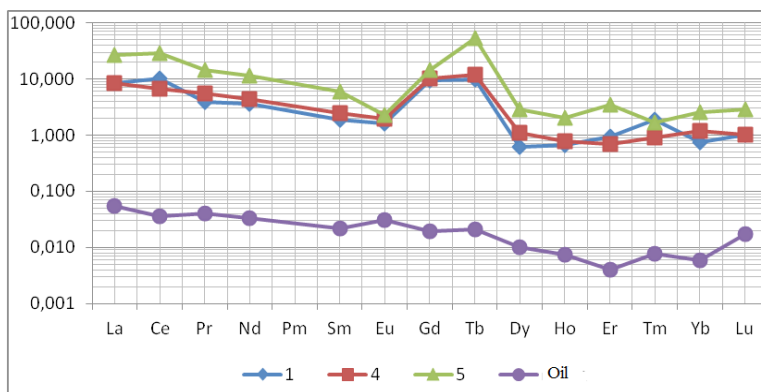


**Fig. 3.** Distribution of REE and Sr shares in the 1.8% HCl extract in the “South Pyzhinskaya 1” well section

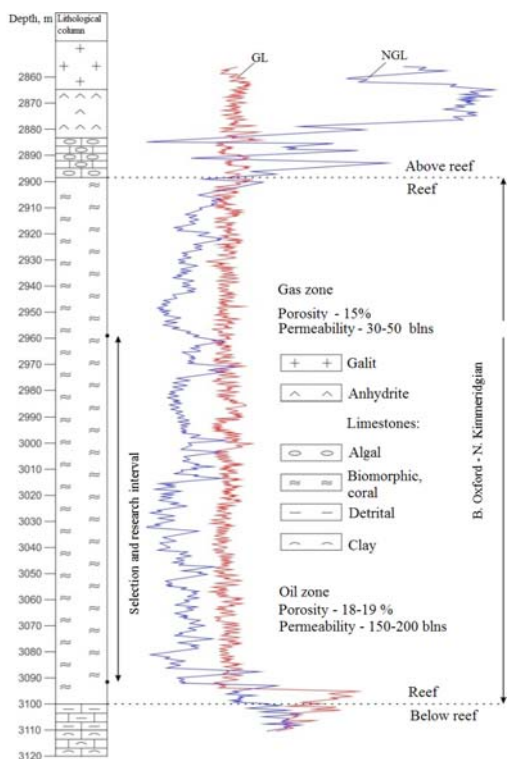


Table 6 and Figs. 3 demonstrate that the sample 3 vastly differs from all other samples. The REE share in fraction exceeds the REE share of other fractions almost by an order of magnitude, and the

fractional yield 1.8% HCl (23.1%) is much higher than the other fractions. The explanation for this phenomenon can be justified by the formation of carbonate cements during the epigenetic processes



**Fig. 4.** Variations in REE composition in OP ABM formations and differentiation in the behavior of Ce, Eu and Tb of OP ABM compared with the oil REE from the interval of 2963-2970 m



**Fig. 5.** Lithological and geophysical data of the 12<sup>th</sup> Kokdumalak field well. According to the data of the formation physics laboratory of the Institute of Geology and exploration of Oil and Gas Fields (Tashkent)

in the sedimentary cycle. This is evidenced by the sharp difference between REE concentrations in comparison with the sample 5, which is similar in lithology, as well as the resulting influx of formation water in the interval of 2712-2723 m. Based on the data of the work<sup>21</sup> on the change of the isotopic composition of carbon and oxygen in the oil-bearing sediments, it is possible to talk about the formation and deposition of secondary mineral in terrigenous formations. It is stated that in the sandstones of terrigenous formations, the carbonate cements are entirely secondary, due to the influence of katagenetic processes and typical feature of the oil and gas-bearing deposits in West Siberia.

Based on the data from the isotopic composition of carbon and oxygen (Table 5) in the interval of 2712-2780.6 m together with the data of REE in 1.8% HCl, it will be unjustified to state that the sample 3 presence in the bottom boundary area of the water-bearing formation. Our attention is drawn by the behavior of Sr in the well section: an abrupt drop in the sample 4 in the intended area of OM generation may be associated with catagenesis agents and the interaction of Sr<sup>2+</sup> and Eu<sup>2+</sup> with hydrocarbons of oil and gas<sup>8</sup>.

Thus, from the analysis of the fractions 1.8% HCl it becomes obvious that the further conclusion in the geochemical analysis of the studied section sediments will be connected with

the data on the isotopic composition of carbon in the zone of prospective generation of the oil and gas HC ( $\delta^{13}\text{C} = -32.9\text{‰}$ ) - form. 4 and form. 5, and the nature of the REE behavior in the extract of alcohol-benzene mixture.

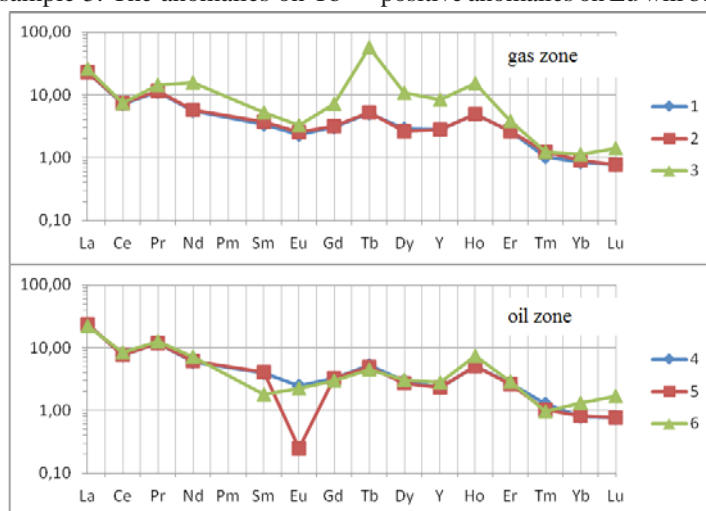
Fig. 4 demonstrates that there is a significant fractionation between the sample 4, sample 1 (BF) and sample 5, meanwhile the difference between the BF and the sample 4 is not observed.

In general, the REE composition in the samples is characterized by a slight excess on Ce, Eu deficiency and the anomalous behavior of Tb, especially in the sample 5. The anomalies on Tb

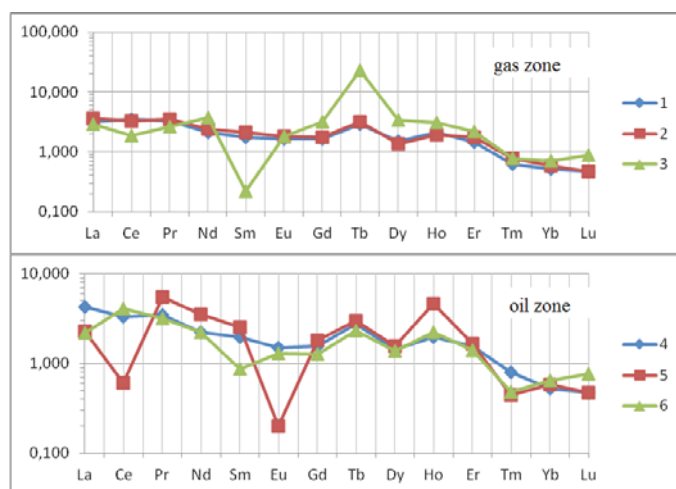
and the reasons for their occurrence in the oil and gas carbonate reef sediments are examined and determined by the influence of oil and gas hydrocarbon on the stabilization  $\text{Tb}^{4+}$  stabilization and its isomorphism<sup>18</sup>.

Significant REE fractionation in sandstones (sample 5) is in good agreement with epigenetic, chemical processes of formation and deposition of secondary carbonate cements<sup>21</sup>.

In our view, the change in the isotopic composition of carbon within the area of alleged generation ( $\delta^{13}\text{C} = -32.9\text{‰}$ ) and anomalies on Tb in the sample 5 without negative inversion on Ce and positive anomalies on Eu will be not quite complete



**Fig. 6.** Lanthanide and Y distribution in the REE composition of OPABM of the oil and gas areas taken from the work<sup>17</sup>.

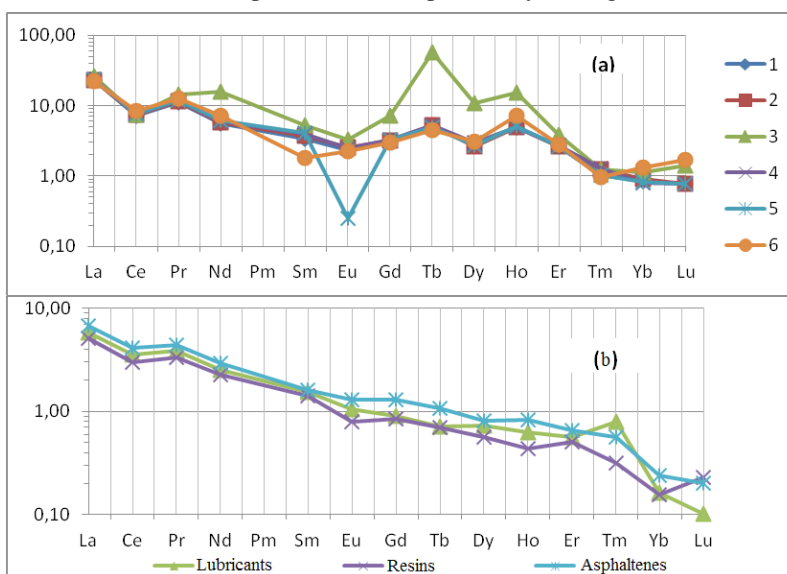


**Fig. 7.** Lanthanide distribution in the REE composition of insoluble residue in the oil and gas areas taken from the work<sup>17</sup>

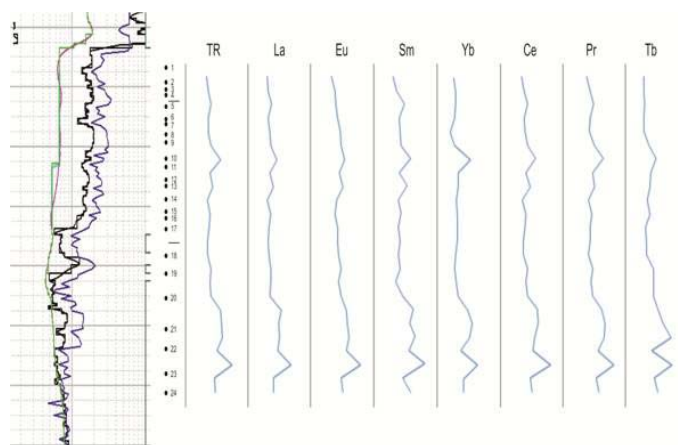
and sufficient for the assumption of existence of another (as opposed to the BF) oil generating bench (formation) in the well section. A confirmation of this assumption can be served by a fixation of changes in redox conditions and the anomalous behavior of Eu with the presence of oil and gas hydrocarbons<sup>7</sup>. Such a possibility is obtained on monitoring changes of  $Ce^{4+}/Ce^{3+}$  in fractions of 1.8% HCl, IS and OP ABM and directly of the oil itself in the ratio of  $Eu^{2+}/Eu^{3+}$  (Table 7) in the interval of 2963-2970 m according to the Table 4.

The Fig. 4 and Table 7 show that the “oil” sample is different from the BF samples 4 and 5.

Within the lanthanide spectrum as a part of the normalized REE values, in the “oil” sample there appears an inversion on Ce and a positive anomaly on Eu, which convincingly evidences the changes of redox conditions in this zone due to the presence of oil and gas hydrocarbons due to their generation out of the buried OM. This is clearly seen from the Table 7, where the values of  $Ce^{4+}/Ce^{3+}$  in the sample 4 (2.24) and of the oil (1.62) differ from the BF (4.32) in the OP BM. The value of  $Eu^{2+}/Eu^{3+}$  in the oil exceeding the same absolute value of the BF by more than 10 times once again confirms the possibility of a significant accumulation of  $Eu^{2+}$  in



**Fig. 8.** The contrast of REE distribution in the OP ABM (a) and petroleum fractions of the Kokdumalak oil and gas field (b)<sup>17</sup>.



**Fig. 9.** GIS and the distribution of individual lanthanides and TR in the formation bank of the Krapivinskoe field well (Western Siberia)

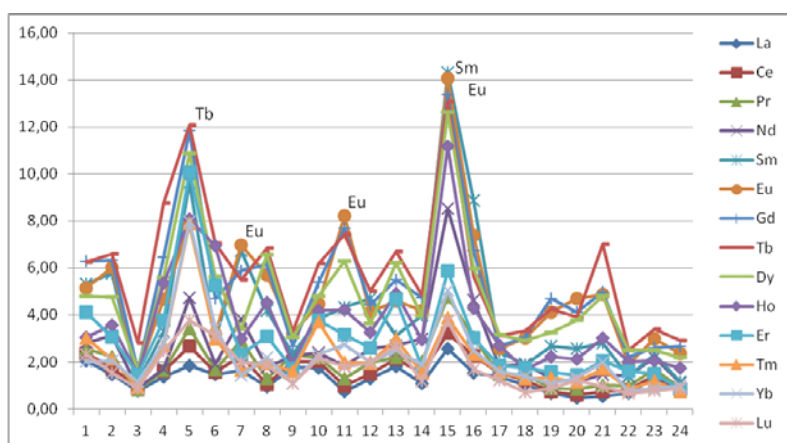
the HC of oil and gas, noted earlier on Eu\* and Eu/Sm-relations in sedimentary formations of the oil and gas-bearing deposits<sup>7</sup>.

Therefore, based on the data specified in Table 7, it can be reasonably assumed as for the presence in the well section of another oil generating formation different from the BF, and the sample 4 can be referred to the bitumen generation zone with their possible migration through the carrier bed (sample 5).

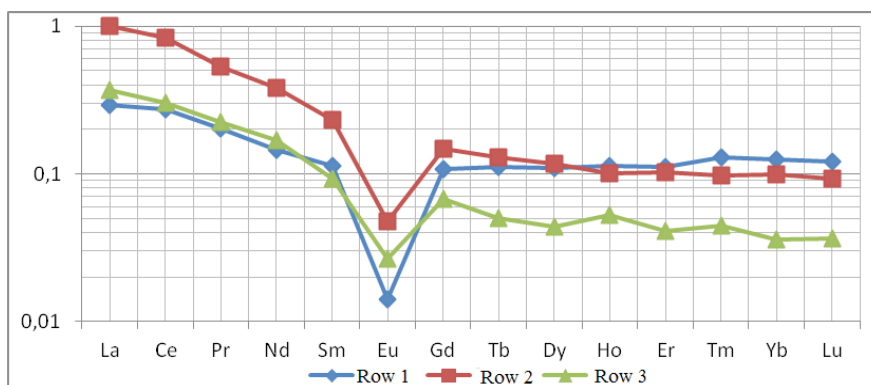
The absence of the oil and gas HC generation in the BF probably indicates the presence of the water bearing formation between the BF and mudstone sediments with OM, passed through a higher OM katagenesis stage ( $\delta^{13}\text{C} = -32.9\%$ ), than OM BM ( $\delta^{13}\text{C} = -29.4\%$ ).

Change of the temperature gradient<sup>1</sup> to the decrease direction is probably the main reason for absence of oil and gas HC generation from OM BM due to the presence of the water bearing formation, formed earlier during the epigenetic process of terrigenous formations of secondary deposits. It is marked by the influx of formation water in the range of 2712-2723 m in the well section and is also conditioned in the oil and gas geology upon the thesis statement about the formation of water-bearing and oil-bearing reservoirs in the terrigenous sedimentary formations prior to the oil entering the reservoir<sup>22</sup>.

Thus, a detailed geochemical analysis of the parametric well formations demonstrates the validity and feasibility during the works on



**Fig. 10.** The REE shares (%) in the acid extract of the Krapivinskoe oil and gas field to the formation bank. 1-24, sampling numbers from the upper part of the deposit to the bottom area. The samples for the studies are presented by the "TomskNIPIneft"



**Fig. 11.** Variations of the REE compositions in the extracts of alcohol-benzene mixture, where the Row 1 – samples 1-5; Row 2 – samples 6-15; Row 3 – Samples 16-24

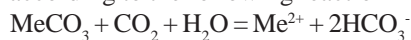
searching and estimating application of both geochemical methods on oil and gas – behavior of REE and isotopic composition of carbon and oxygen, reflecting catagenetic processes of organic matter<sup>14</sup>.

#### **Kokdumalak oil and gas field**

To observe the differences of the REE behavior in the clastic complex formations from the REE behavior in the carbonate sediments, there was selected a Kokdumalak oil and gas field well section. The 12<sup>th</sup> well size is represented by the biomorphic coral deposits (see Fig. 5). The aim of the section study was to detect the possibility of separating the oil-bearing and gas-bearing zones by geochemical method based on the geochemical behavior of REE, which was done and presented in the work<sup>18</sup>.

The most important conclusions made during the study of carbonate reef sediments in the work<sup>18</sup> and the present work are the following issues:

The difference of redox conditions in the formations with clastic complex and in the formations of carbonate deposits, which is fixated by a Ce deficit in the REE composition respectively to La and Pr, Eu deficit (negative anomalies) and positive anomalies on Tb and Ho in OPABM (see Fig. 6). The unusual behavior of individual lanthanides in REE composition allowed clarifying their indicator possibilities that appeared in carbonate sediments and are accompanied not only by abnormalities of Ce, Pr and Tb, but also by a manifestation of the Ho, Y, Nd and Tb isomorphism (Fig. 7). Abnormal manifestations of Nd and Tb are associated with the replacement of Ca, Mg, formed as a result of petroleum fluids solvation with organic acids and acid deposition in the form of insoluble calcium and magnesium salts within the carbonate medium<sup>1</sup>. In all probability, the formation of hydrocarbons took place according to the following reaction<sup>23</sup>



with replacement of  $\text{Me}^{2+}$  ( $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ ) by  $\text{Nd}^{3+}$  and  $\text{Tb}^{4+}$ , and, owing to the closeness of their ionic radii in the eightfold coordination<sup>24</sup>. In natural processes, it is likely to occur as follows:



And further, the ability to monitor the terbium and neodymium isomorphism, as a consequence of their accumulation in the organic component of

the formations, can be seen in the spectra of REE composition in Fig. 6, 7 and 8a. Hence we can assume about the increase of the isomorphous medium capacity with the influx of petroleum fluids into the reservoir with respect to rare earth elements.

Thus, from the previously identified studies<sup>8</sup> it follows that the rare-earth elements as geochemical criteria of the formation oil-bearing capacity in the terrigenous sedimentary formations, in contrast to the carbonate ones, in most cases, can be identified by the behavior of Ce and Eu. In turn, a manifestation of anomalies on Tb, and its presence in the lanthanide spectrum in the REE composition of OPABM terrigenous sediments<sup>7</sup>, now, obviously, can be associated with the formation and influence of the secondary carbonate cements. In calcareous deposits, where there is no insufficient reducing environment, these criteria may be formulated according to the behavior of Tb and Ho, together with Y, as well as the ratio of  $\text{Ce}^{4+}/\text{Ce}^{3+}$  (Table 8).

Table 8 clearly shows that the water-bearing area is located within the sample 5 displacing zone (10.6 and 1.41 values). The further attention is drawn by the sharply negative anomaly on Sm in both areas along with the negative anomalies on Ce and Eu (Fig. 7). The presence of such an effect as a result of the normalization of REE composition of the insoluble residue on C1 + NO, in all probability, is connected with the variable ability of dissolving the oil and gas hydrocarbons and bitumen formations in the water [1] and organic media, which is indirectly observed by comparing the OPABM spectra and the oil HMWC spectra – lubricants, resins, and asphaltenes obtained from the sum of the OPABM formations (Figure 8).

## **CONCLUSION**

Fractionation of REE and differentiation in the behavior of the individual lanthanides as a part of the formation REE fractions are somewhat different from the REE of terrigenous sediments. The distinctions of redox conditions in these sediments formed another indicator opportunities of REE and are associated with the behavior of Ce and Eu, and additionally with the oxidation of Ce, Pr, Tb and isomorphism of Nd, Tb, Ho and Y. The latter is well justified from the analysis of the Table

As it is seen from the Table 9, the calculated valence ratios of cerium and europium have slight negative values, which means the change of the redox conditions to the direction of weak oxidizing environment and their presence in a trivalent form. On the contrary, the valence ratios on terbium (Tb) are very different from cerium (Ce) and europium (Eu). According to the analysis of the chemical properties of lanthanide, given in the work<sup>17</sup>, the transition of  $Tb^{3+}$  into  $Tb^{4+}$  takes place in more severe conditions than for cerium and praseodymium, and, hence, such a transition in the expected geochemical conditions is unlikely. The phenomenon of terbium and paradox accumulation in its behavior in Fig. 4, 6, 7 and 8 indicates that this fact is preferably associated with the terbium ( $Tb^{4+}$ ) isomorphism as a result of substitution of magnesium ( $Mg^{2+}$ ) to the hydrogen carbonate, which has been possible only in the presence of oil and gas hydrocarbons and carbonate components of formations, which is quite natural for the absence of other physical and chemical processes. It is logical to associate terbium and neodymium isomorphism with replacement of magnesium and calcium as a result of subsequent solvation of oil and gas hydrocarbons by the organic acids and their depositing in the form of insoluble salts of  $Ca^{2+}$  and  $Mg^{2+}$  and the strong presence of these ions in the formation waters of oil and gas deposits. Studies of the Tyumen reservoir formation waters of Western Siberia showed that the concentrations of calcium, magnesium, strontium and yttrium at depths of about 3000 m ( $mg/dm^3$ ) correspond to the values for Ca – 425.0; Mg – 57.1; Sr – 72.3 and Y – 0.0015. Hence, it follows that the isovalent Ho and Y isomorphism cannot be explained in a similar manner due to the practical absence of Y in the formation waters. However, significant concentrations of Y were found both in the mobile mineral complex and in the organic phase of the carbonate deposit formations<sup>18</sup>. It can be assumed that the accumulation of Y occurred in petroleum hydrocarbons after their generation and migration, followed by reaction with the mineral moving formation part. The assumption of such version is justified by the proximity of the Ho and Y ionic radii<sup>11</sup>, which allows us to position Y in the REE composition near Ho (Fig. 6), and therefore refer both lanthanides to the position of the heavy REE.

The latter are known to have a high complexing properties with bicarbonates<sup>15</sup> and are probably also able to form complex compounds with the hydrocarbon oil part of the formation.

#### **The Krapivinskoe oil and gas field**

Installation of the most oil-saturated part of the reservoir is one of the most important problems of petroleum geology, necessary for the calculations of hydrocarbon reserves and optimum exploitation of the deposit. However, there also exist the problems necessary for clarifying and defining the most oil-saturated part of the field in real time during the exploitation of the oil and gas field. As it can be seen from the Fig. 9, it is difficult to fulfill these tasks in accordance with the GIS data and distribution of individual lanthanides, capable of changing the valence of lanthanum that possesses the largest ionic radius in the La - Lu and TR rows in accordance with the formation bank in the well section. Solution of this problem is shown in Figure 10 on the distribution of the REE share ratios of the mineral movable complex to the formation bank along the whole well section. Such changes in the REE distribution, as it is known, cannot take place without the presence and impact of petroleum fluids and oil and gas hydrocarbons<sup>7, 8</sup> and migration processes in the reservoir<sup>1-4</sup>. However, let us consider the obtained results of the well section studies. Figure 9 demonstrates that the initial capacity of the oil-saturated part, prior to the formation opening, can be assumed to be within the range of the studied sample selection<sup>1-24</sup>. The distribution of elements in the formation bank and TR along the well section may reduce the range of the initial oil saturation of the reservoir within the boundaries of the samples 10-22. At the same time, the distribution of La possesses the largest ionic radius of all the trivalent rare-earth elements; Eu, Sm, Yb, as well as Ce, Pr, Tb are capable of changing valence<sup>17</sup> with the change of redox conditions in the reservoir, which indicates that they carry the required information about the real oil-saturation of the oil-bearing reservoir part. Geochemically, we can assume about their (REE) existence in the trivalent state. Therefore, in terms of gross lanthanide content, in consequence of imposing the insoluble REE part on the mineral and organic movable complexes, in which previously there were established indicator possibilities of the above mentioned lanthanides<sup>7-</sup>

<sup>18</sup>, it becomes simply impossible to solve the specified problem. Hence, it is obvious that the task solution may lie in the results of the analysis of the lanthanide migration with the petroleum fluids in the reservoir and beyond its borders during the extraction of oil and gas hydrocarbons. Such an analysis could probably clarify, on the basis of the changed redox conditions in the reservoir and the forced migration of petroleum fluids, the solution of the given problem in this situation. To confirm our version, there was defined the balance of the REE MMC relative to the formation bank (Figure 10) and the analysis of REE concentrations in the organic part of the formations, highlighted by the alcohol - benzene extraction (Figure 11). The results are presented in the Fig. 10-11.

Here from it follows that the real oil-saturated part can lie between the sampling points 6-15, determined by the maximums of Eu in the lower part and of Tb in the upper part of the section, as a consequence of changes in the initial redox conditions in the reservoir. This is well illustrated by a dramatic shortage in the organic part of the Eu formations in all zones (Figure 11). However, the following should be noted: the ratio: concentration of europium (Eu) within the boundaries of 5 - 16 exceed the concentrations of the same europium (Eu) of the both other parts, and europium (Eu) of the lower part exceeds the value of (Eu) of the upper part that indicates the migration processes vertically from the bottom to the top and forced REE redistributions with petroleum fluids. The more detailed geochemical analysis will be presented in a subsequent paper.

Until now, the solutions of the similar geochemical problems on the basis of REE in petroleum geology were not known. Conducted geochemical analysis, as we have seen, allows to monitor the progress of the life of the field in real time and to assess the geochemical environment in the reservoir.

#### Summary

1. Contrasting differences of the REE spectra and their variations in the fractions of the formation bank suggest the prospect of using REE as geochemical criteria, along with other indicators in the evaluation survey.
2. The ability of the petroleum fluid to change

the redox conditions of the environment in the catagenetic process is always fixed by the **REE reaction**, because of their unusual fundamental chemical properties, especially of lanthanides that can change the valence and ionic radius, which is reflected in the differentiated behavior of individual lanthanides in the REE composition.

3. In sedimentary formations, based on the results of studies of oil and gas deposits in West Siberia and the present work, the informative base in geochemical studies of formations and their fractions is the fixation and differentiation of abnormal behaviors of Ce and Eu, controlled by the values of their relative maxima (Eu\* and Ce\*).
4. In carbonate, oil-bearing formations, where there are different redox conditions (negative anomalies on Eu), as the geochemical criteria of the formation oil-bearing capacity are  $Ce^{4+}$ ,  $Pr^{4+}$ ,  $Tb^{4+}$ , and also the revealed  $Ho^{3+}$  anomalies in the composition of REE.
5. Informative value of the REE, as geochemical parameters, in the sedimentary cycle, with the presence of petroleum fluids is entirely determined by the redox conditions of the interacting environment and chemical properties of the REE themselves, and the REE fractionation itself is defined in the oil fractions (OPABM and MMC), most likely by the transformation of the oil and gas HC structure and the changes of  $C_nH_n$  values of the oil hydrocarbon compounds and bitumen during the catagenetic and (or) migration processes.

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