

## Rare Earth Elements and Their Ability to Capture Changes in Borders of Hydrocarbon Saturation in Development of Oil and Gas Deposits

K.S. Tsoi and V.E. Peshkov

Federal State Autonomous Higher Professional Education Institution "Tomsk National Research State University (TSU)" 36. Lenin ave., Tomsk, Russia, 634050.

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Influence is shown of oil fluids redistribution in rare earth elements in the mineral agile complex of rocks in the section of a well by accounting shares - lanthanides balance of the mineral agile complex (MAC) related to rock embankment. Changes in concentration and redistribution of lanthanides in REE composition are considered from the perspective of the impact of oil fluids on the redox conditions in the reservoir and the change in thermodynamic conditions after start of oil and gas deposits development. The possibility has been considered of accumulating individual lanthanides in MAC and the deficit of Eu as a part of REE of an organic complex of rock in the deposit, the main reason of which is changing oxidation - and - reduction of environmental conditions and migration processes within the deposit and through its overlapping screen - top of collector. Also abnormal redistribution of individual lanthanides in REE composition is noted, the consequence of which is specifically the change in reservoir pressure and extraction of fluids from REE along with oil and gas hydrocarbons. Indicator possibilities of REE for establishing the boundaries of most oil-saturated, in fact, in the newly formed part of the deposit in the section of the exploration well have been justified by the behavior of individual lanthanides that are capable of changing valence and of accumulating or impoverishing at the borders of the reservoir deposits resulting from changes in the physico-chemical conditions in the deposit under the influence of technological processes.

**Key words:** oil saturation, migration, rare earth elements, complex formation and valence, ionic radius, differentiation in lanthanides behavior.

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One of the objectives of the petroleum geology is detecting the most oil-saturated part in reservoir section. This problem was solved using geophysical (GIS) methods, and it was possible to solve it using geochemical methods - by the

behavior and distribution of rare earth elements in the rocks earthwork. Previously, identification of oil-saturated strata in well section was determined by concentration of abnormal content of europium (Eu) at the top and base related to the middle part of the reservoir and was identified as the boundaries of reservoir<sup>1</sup>. Then, for such purposes, relative concentrations of (Eu\*)<sup>2</sup> were used as geochemical indicators calculated by the content of neighboring lanthanides - samarium (Sm) and gadolinium(Gd), in mineral and organic components

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\* To whom all correspondence should be addressed.  
E-mail: [geohi70@yandex.ru](mailto:geohi70@yandex.ru)

of the rock:

$$\text{Eu}^* = \text{Eu} / 0.5 (\text{Sm} + \text{Gd}) \quad \dots(1)$$

Use of these geochemical, quantitative parameters or criteria for determining oil-bearing capacity of rock is said to be valid for rocks of clastic complex<sup>3</sup>.

Indicator capabilities of such parameters are well manifested in the presence of petroleum fluids that determine the redox condition towards the recovery process in a closed system of the deposit, when it is viewed as a geometric body. With that, it was found that values (Eu/Sm) N of

**Table 1.** Content of elements in deposit in rocks embankment. g/t

Sample number	1	2	3	4	5	6	7	8	9	10	11	12
<b>element</b>	content. g/t											
Mg	1819	2621	2414	2104	1487	2870	4937	2685	2984	3738	4286	4042
Sr	146	123	151	138	123	134	187	155	147	110	131	117
Y	12.9	12.1	14.1	11.8	8.0	12.8	25.1	15.6	14.5	13.1	14.0	13.1
La	14.4	15.1	19.9	15.7	17.4	18.9	26.3	17.3	21.1	14.6	18.5	16.3
Ce	28.2	33.6	41.0	33.7	35.3	40.0	56.1	36.6	44.7	29.7	37.1	35.2
Pr	3.3	4.0	4.7	4.1	3.9	4.8	6.7	4.6	4.8	3.7	4.3	3.9
Nd	13.5	14.7	18.1	16.9	15.8	18.8	26.6	16.1	18.8	14.7	15.9	14.9
Sm	1.83	2.51	3.73	2.93	3.06	3.14	4.70	2.94	4.21	2.72	3.10	2.76
Eu	0.56	0.69	0.72	0.78	0.90	0.94	1.07	0.85	0.99	0.75	0.67	0.80
Gd	2.48	2.85	3.42	2.89	2.92	4.02	5.56	3.84	4.17	3.18	3.50	3.33
Tb	0.33	0.35	0.36	0.34	0.33	0.50	0.73	0.55	0.52	0.44	0.53	0.40
Dy	2.26	2.36	2.51	2.43	1.76	2.90	5.76	2.55	2.96	2.70	2.76	2.67
Ho	0.49	0.49	0.50	0.47	0.38	0.42	1.08	0.54	0.70	0.49	0.62	0.49
Er	1.05	1.21	1.08	1.20	0.67	1.38	2.82	1.70	1.82	1.24	1.57	1.49
Tm	0.20	0.21	0.24	0.19	0.10	0.28	0.44	0.29	0.26	0.20	0.29	0.26
Yb	1.11	1.27	1.31	1.23	0.65	1.17	3.18	1.67	1.67	1.40	1.48	1.56
Lu	0.17	0.25	0.20	0.20	0.19	0.22	0.32	0.27	0.25	0.23	0.26	0.21
TR	82.84	91.67	111.93	94.86	91.34	110.28	166.40	105.37	121.54	89.08	104.56	97.44
Eu*	0.26	0.26	0.20	0.27	0.30	0.26	0.21	0.25	0.24	0.25	0.20	0.26
Ce*	3.18	3.54	3.33	3.41	3.31	3.38	3.40	3.35	3.45	3.26	3.26	3.47
Sample number	13	14	15	16	17	18	19	20	21	22	23	24
<b>element</b>	content. g/t											
Mg	3727	4085	4655	4740	4606	10025	11515	5916	10438	11696	7643	7074
Sr	126	129	157	166	177	257	312	263	269	297	155	122
Y	12.3	13.8	15.3	16.0	14.3	23.9	26.1	32.5	19.9	35.1	20.8	19.3
La	15.7	16.0	18.9	18.6	17.8	30.8	27.7	29.1	26.9	43.1	21.7	21.5
Ce	31.4	31.2	40.6	36.1	40.4	59.6	62.0	54.0	51.5	87.0	45.7	48.4
Pr	3.9	3.6	4.6	4.2	4.5	6.3	6.9	6.9	5.6	8.8	5.2	5.7
Nd	13.3	12.3	13.6	14.5	16.1	22.5	22.2	26.1	20.6	28.4	16.8	21.6
Sm	3.06	2.68	2.98	2.35	3.41	5.17	4.63	5.39	4.49	7.09	3.52	4.81
Eu	0.80	0.82	0.93	0.85	0.95	1.15	1.20	1.27	1.14	1.71	0.94	1.00
Gd	3.31	3.18	4.53	4.06	3.94	5.78	5.97	6.96	5.31	7.83	5.31	4.98
Tb	0.43	0.41	0.64	0.64	0.63	0.78	0.93	1.16	0.57	1.20	0.65	0.76
Dy	2.32	2.42	2.75	2.74	2.88	4.50	5.24	5.40	3.74	5.63	3.84	3.52
Ho	0.47	0.48	0.46	0.56	0.53	1.13	1.07	1.33	0.82	1.18	0.75	0.81
Er	1.20	1.73	1.74	1.62	1.70	2.78	3.43	4.08	2.48	3.96	2.68	2.54
Tm	0.24	0.25	0.29	0.26	0.27	0.44	0.53	0.61	0.39	0.71	0.45	0.34
Yb	1.52	1.27	1.23	1.42	1.67	2.78	3.33	2.98	1.91	3.95	2.33	2.26
Lu	0.23	0.28	0.27	0.31	0.26	0.55	0.55	0.49	0.42	0.70	0.39	0.37
TR	90.13	90.30	108.78	104.14	109.26	168.21	171.88	178.26	145.79	236.46	131.10	137.90
Eu*	0.25	0.28	0.25	0.26	0.26	0.21	0.23	0.21	0.23	0.23	0.21	0.20
Ce*	3.20	3.18	3.46	3.18	3.63	3.21	3.58	3.00	3.17	3.35	3.39	3.56

the relation in organic complex (OC) of species may differ by 1-2 orders of magnitude from their values in the rocks containing oil reservoir<sup>4</sup>. Additionally, in determining the oil-bearing capacity of rocks, one can use behavior of samarium (Sm) and ytterbium (Yb), that can, same as Eu<sup>2+</sup>, be present and migrate in the form of Sm<sup>2+</sup> and Yb<sup>2+</sup>[4]. It should be emphasized that these regularities persist until field development, when oil and gas deposit is not yet subject to the

influence of the injected deposit water and the influence of surface-active agents (surfactants). This external, forced action appeared to abruptly change REE behavioral nature, especially lanthanides ability to change valence. Violation of initial (before development of the deposit) thermodynamic and redox conditions in the presence of petroleum fluids and fluid migration itself under the influence of changes in reservoir pressure in the deposit is considered in this paper

**Table 2.** Concentration in mineral agile complex (acid extract. 1.8% HCL) of rock samples from oil and gas deposit section. g/t

Sample number	1	2	3	4	5	6	7	8	9	10	11	12
Mg	12833	23957	6187	23412	18477	19146	19646	22498	19319	14752	21268	30492
Ca	2029	776	1135	1265	692	1783	726	1343	1370	1968	1199	720
Y	32.25	34.94	12.15	41.03	63.28	47.65	64.92	49.81	22.82	37.40	50.40	34.55
La	25.44	19.14	13.06	18.43	27.70	23.64	37.27	14.06	32.50	21.94	11.77	18.01
Ce	57.22	51.00	30.97	46.21	81.21	54.27	109.37	33.00	77.48	51.53	31.78	45.69
Pr	7.33	7.53	3.36	5.73	11.51	6.93	16.80	5.04	9.54	6.86	4.72	6.72
Nd	32.52	39.65	13.95	25.11	64.19	31.02	87.74	24.78	36.22	30.17	24.65	32.95
Sm	8.41	12.49	3.75	8.31	25.42	8.03	27.28	10.64	8.48	8.98	11.61	11.18
Eu	2.48	3.56	0.95	3.12	6.11	2.58	6.45	4.19	2.76	2.89	4.77	2.82
Gd	13.41	15.55	4.83	16.09	29.83	16.26	28.10	20.37	9.56	14.79	23.18	12.76
Tb	1.81	1.96	0.86	2.58	3.48	3.06	3.44	3.24	1.48	2.37	3.37	1.73
Dy	9.32	9.67	3.63	11.74	16.45	14.08	16.78	14.43	7.77	11.21	14.96	8.35
Ho	1.30	1.49	0.64	2.15	2.68	2.50	2.77	2.10	1.14	1.76	2.25	1.39
Er	3.72	3.18	1.36	3.90	5.85	6.28	5.62	4.53	2.69	4.03	4.25	3.35
Tm	0.52	0.39	0.20	0.45	0.68	0.72	0.63	0.49	0.37	0.63	0.50	0.43
Yb	1.92	2.23	1.31	2.97	4.44	3.48	3.90	3.15	1.54	2.81	3.47	2.69
Lu	0.33	0.33	0.15	0.41	0.61	0.59	0.55	0.43	0.24	0.43	0.40	0.35
TR	165.73	168.19	78.99	147.20	280.16	173.41	346.69	140.47	191.75	160.40	141.68	148.41
Sample number	13	14	15	16	17	18	19	20	21	22	23	24
Mg	23659	28090	15855	26134	12018	12050	24139	24577	21987	18879	14478	13923
Ca	1415	590	1426	849	1809	2702	1399	1317	1339	1770	1530	1484
Y	40.72	30.16	89.24	47.47	23.99	36.62	47.94	60.18	52.46	43.51	26.54	25.62
La	24.47	14.94	42.10	24.31	20.96	26.52	16.37	11.84	12.41	24.85	24.72	14.69
Ce	57.35	40.74	112.31	70.61	52.68	62.51	40.18	28.41	33.00	59.46	55.94	34.86
Pr	7.33	6.24	18.75	10.94	5.57	8.00	5.30	4.88	4.88	7.48	7.55	4.54
Nd	30.82	31.57	100.11	57.90	25.21	37.07	24.60	25.81	26.29	33.83	31.57	20.90
Sm	8.19	9.17	36.69	17.98	7.15	8.33	10.61	11.90	10.90	8.33	7.02	4.71
Eu	3.17	2.94	11.24	5.38	2.08	2.98	4.27	5.16	4.80	2.80	2.43	2.04
Gd	15.71	13.02	52.20	23.59	9.04	15.15	24.25	24.62	22.80	15.07	11.89	11.47
Tb	2.47	1.70	7.16	3.09	1.69	2.23	3.39	3.92	3.46	2.59	1.89	1.90
Dy	12.43	8.19	29.90	14.13	7.81	11.28	14.68	17.57	15.46	12.04	8.23	6.60
Ho	1.97	1.21	4.47	2.07	1.23	1.64	2.03	2.44	2.12	2.06	1.32	1.20
Er	4.81	2.64	8.81	4.20	2.73	4.14	4.61	4.98	4.39	5.41	3.43	1.81
Tm	0.61	0.33	0.97	0.52	0.37	0.49	0.60	0.60	0.57	0.52	0.46	0.21
Yb	3.28	2.04	5.39	3.08	2.31	3.38	3.16	3.42	3.28	2.65	1.79	1.92
Lu	0.53	0.28	0.87	0.45	0.27	0.34	0.42	0.52	0.34	0.40	0.26	0.28
TR	411.83	368.29	611.34	473.95	506.51	441.74	614.01	396.52	411.74	418.82	377.12	315.70

as the main factor of influence on REE behavioral nature. Here, except for Eu, Sm and Yb, as it will be shown later, the role of geochemical indicators will also appear in the behavior of Tb that is able to migrate from the hydrocarbons of oil and gas in

the form of Tb<sup>4+</sup> and heavy REE in the trivalent form with high complex-forming properties with sodium<sup>5</sup>. This is due to the fact that in transition of Tb<sup>3+</sup> into oxidized state Tb<sup>4+</sup> the ionic radius changes from 1.04 to 0.88, respectfully in

**Table 3.** Share of REE faction (1.8% HC L) of the mineral agile complex relative to their concentrations to samples rock embankment of the oil and gas deposit. %

Sample	1	2	3	4	5	6	7	8	9	10	11	12
weighed quantity	0.0116	0.0955	0.0239	0.0272	0.0647	0.0168	0.0802	0.0337	0.0181	0.0142	0.0480	0.1543
Mg	8.18	10.60	2.97	12.91	14.42	7.74	4.62	9.72	7.51	4.58	5.76	8.75
Sr	16.17	7.32	8.71	10.67	6.52	15.48	4.52	10.06	10.79	20.66	10.62	7.16
Y	2.90	3.34	1.00	4.03	9.22	4.32	3.00	3.71	1.82	3.31	4.18	3.05
La	2.05	1.47	0.76	1.36	1.84	1.45	1.65	0.94	1.78	1.74	0.74	1.28
Ce	2.35	1.76	0.88	1.59	2.67	1.57	2.26	1.05	2.01	2.01	0.99	1.51
Pr	2.57	2.20	0.82	1.64	3.44	1.67	2.91	1.28	2.29	2.18	1.29	1.99
Nd	2.79	3.12	0.89	1.72	4.73	1.91	3.83	1.78	2.24	2.38	1.80	2.56
Sm	5.34	5.77	1.17	3.28	9.63	2.96	6.74	4.20	2.34	3.83	4.34	4.69
Eu	5.15	6.00	1.53	4.65	7.84	3.19	6.99	5.69	3.22	4.47	8.22	4.10
Gd	6.28	6.33	1.64	6.45	11.84	4.69	5.86	6.16	2.65	5.39	7.69	4.44
Tb	6.26	6.58	2.80	8.77	12.08	7.03	5.51	6.85	3.29	6.18	7.43	5.01
Dy	4.79	4.76	1.68	5.61	10.86	5.62	3.38	6.57	3.04	4.82	6.28	3.63
Ho	3.04	3.55	1.48	5.37	8.09	6.92	2.98	4.51	1.89	4.19	4.21	3.26
Er	4.11	3.06	1.45	3.79	10.08	5.26	2.31	3.09	1.72	3.77	3.14	2.60
Tm	3.01	2.13	0.96	2.69	7.92	2.97	1.64	1.95	1.61	3.69	1.98	1.93
Yb	2.01	2.04	1.16	2.79	7.97	3.46	1.42	2.19	1.07	2.34	2.72	1.99
Lu	2.32	1.54	0.86	2.45	3.79	3.12	1.97	1.87	1.08	2.16	1.82	1.95
TR	54.96	53.67	19.07	56.19	111.99	56.16	52.44	51.84	32.06	52.46	56.81	44.00
Eu/Sm	0.96	1.04	1.31	1.42	0.81	1.08	1.04	1.36	1.38	1.17	1.89	0.88
La/Yb	1.02	0.72	0.66	0.49	0.23	0.42	1.16	0.43	1.67	0.75	0.27	0.64
Sample	13	14	15	16	17	18	19	20	21	22	23	24
weighed quantity	0.0214	0.1046	0.0209	0.0754	0.0165	0.0146	0.0253	0.0473	0.0434	0.0167	0.0176	0.0098
Mg	7.36	7.98	3.95	6.40	3.03	1.39	2.43	4.82	2.44	1.87	2.20	2.28
Sr	13.04	5.32	10.55	5.94	11.86	12.18	5.21	5.80	5.78	6.92	11.41	14.16
Y	3.85	2.54	6.78	3.43	1.95	1.78	2.13	2.15	3.05	1.44	1.48	1.54
La	1.81	1.08	2.58	1.52	1.37	1.00	0.68	0.47	0.54	0.67	1.32	0.79
Ce	2.12	1.52	3.21	2.27	1.51	1.22	0.75	0.61	0.74	0.79	1.42	0.84
Pr	2.17	2.00	4.77	3.06	1.45	1.47	0.89	0.82	1.01	0.98	1.68	0.92
Nd	2.69	2.99	8.52	4.65	1.81	1.92	1.28	1.15	1.48	1.38	2.17	1.12
Sm	3.10	3.97	14.30	8.87	2.43	1.87	2.66	2.56	2.82	1.36	2.31	1.14
Eu	4.60	4.18	14.06	7.38	2.55	3.01	4.13	4.72	4.87	1.89	2.99	2.36
Gd	5.51	4.75	13.38	6.75	2.66	3.04	4.72	4.11	4.98	2.23	2.60	2.67
Tb	6.68	4.83	13.07	5.64	3.13	3.34	4.25	3.91	7.00	2.50	3.38	2.90
Dy	6.20	3.93	12.61	5.98	3.14	2.91	3.25	3.77	4.79	2.48	2.49	2.17
Ho	4.91	2.94	11.16	4.30	2.71	1.68	2.20	2.13	3.00	2.02	2.05	1.72
Er	4.67	1.77	5.88	3.01	1.86	1.73	1.56	1.42	2.05	1.59	1.49	0.83
Tm	2.98	1.52	3.89	2.31	1.57	1.30	1.32	1.14	1.69	0.85	1.18	0.73
Yb	2.50	1.86	5.06	2.51	1.60	1.41	1.10	1.33	1.99	0.78	0.89	0.98
Lu	2.69	1.18	3.72	1.67	1.22	0.71	0.88	1.23	0.94	0.67	0.78	0.88
TR	56.49	41.06	123.00	63.33	30.96	28.36	31.79	31.52	40.96	21.64	28.22	21.58
Eu/Sm	1.48	1.05	0.98	0.83	1.05	1.61	1.55	1.84	1.73	1.39	1.29	2.08
La/Yb	0.72	0.58	0.51	0.60	0.85	0.71	0.62	0.35	0.27	0.86	1.48	0.81

octanumerous coordination<sup>6</sup> and approximates by its size to heavy REE, obtaining their complex-forming properties. Therefore, its stability in changed conditions will be determined by the ability of hydrocarbons in oil and gas to act as a stabilizer (screen) against water for Tb<sup>4+</sup> <sup>7</sup>. Otherwise, there is a difference in behaviors of separate lanthanides in the REE in the deposit before and during beginning of development of the deposit. With that, REE behavior obviously varies with the influence of technological

processes. Checking this version is the main objective of REE studies. In addition, the objective is to establish their ability to fixation of changing boundaries of deposit strata oil saturation and the degree of efficiency of using behavior of individual lanthanides as geochemical indicators in changing redox-and-environmental conditions.

In course of development of oil and gas deposits, also exist (or may arise) problems of determining the most oil-saturated part of the collector strata before the end of field

**Table 4.** Aggregated mean values from Tables 1.2.3

Average REE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Rocks														
embankment. g/t	20.97	43.30	4.95	18.04	3.63	0.94	4.30	0.59	3.28	0.68	1.96	0.32	1.85	0.32
Concentration in														
MAC. g/t	21.91	55.81	7.67	36.91	12.05	3.56	17.06	2.45	11.53	1.85	4.06	0.50	2.83	0.40
MAC share %	1.29	1.57	1.90	2.54	4.24	4.91	5.28	5.77	4.78	3.76	3.01	2.21	2.21	1.73
HO1.8% HCl, g/t	19.44	39.98	4.39	15.13	2.65	0.63	2.91	0.39	2.21	0.52	1.48	0.26	1.62	0.27

**Table 5.** Concentration of elements in an extraction of alcohol-benzene mixture of rocks in the section of collector strata of the tested deposit. g/t

Element	Row 1	Row 2	Row 3
Mg	202.1882	155.4561	266.3584
Ca	127.0095	106.0716	91.0105
Sr	1.0451	0.572	0.368
Ba	0.8588	1.3401	0.8274
La	0.0695	0.2363	0.0883
Ce	0.1687	0.5101	0.1844
Pr	0.019	0.0494	0.0208
Nd	0.0669	0.1761	0.0778
Sm	0.0169	0.0343	0.0138
Eu	<b>0.0008</b>	<b>0.0027</b>	<b>0.0015</b>
Gd	0.0214	0.0294	0.0134
Tb	0.004	0.0047	0.0018
Dy	0.0272	0.0288	0.0108
Ho	0.0062	0.0055	0.0029
Er	0.0179	0.0163	0.0066
Tm	0.0032	0.0024	0.0011
Yb	0.0201	0.016	0.0058
Lu	0.003	0.0023	0.0009
TR	0.4448	1.1143	0.4299

Analysis results were obtained from the total of the following samples:

Row 1 - Samples No. 1 - 5, alcohol-benzene mixture fractions - 2.835%; Row 2 - samples No. 6-15 Yield of fractions - 4.9217%; Row 3 - samples No. 15-24, yield of fractions - 6.9972%

development. For whatever reason needed by subsoil user that are of interest for solving this problem for the current period for quantifying remaining hydrocarbon materials. Or, by setting a similar problem, it is necessary to check the possibility of determining additional reserves of growth outside the field contour that is approved by the State Committee for Mineral Reserves (SRC). For these purposes, along with production wells in the part of the deposit that is of interest, an exploration well is usually drilled. The main purpose of drilling such an exploration well is to determine the changed and the most oil-saturated part of the section in the studied deposit. This task is due to the fact that in the zone of influence of the injection well, the front of injection water can significantly shrink due to natural or newly created zone of rocks fracturing. As a result of such forced influence of parts of the deposit and step-by step extraction of hydrocarbon fluids in the area of development, the formation pressure drops, which leads to migration of fluids within the area of the tested area toward the area where development was or is performed. Probably, this process will occur until equilibration of reservoir pressure in the deposit As a result, it is evident that under the influence of the above factors, borders of oil-water contact (OWC) will vary, as

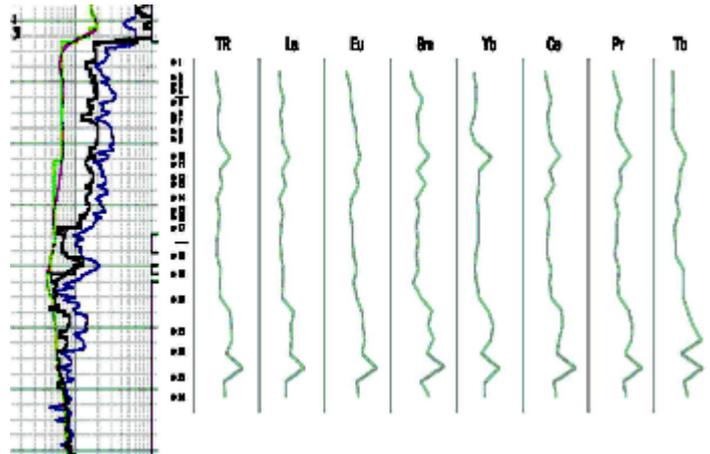


Fig.1. WGR, sampling points and distribution of contents La, TR and lanthanides that are able to change valence, in the embankment of the section of well in the studies deposit

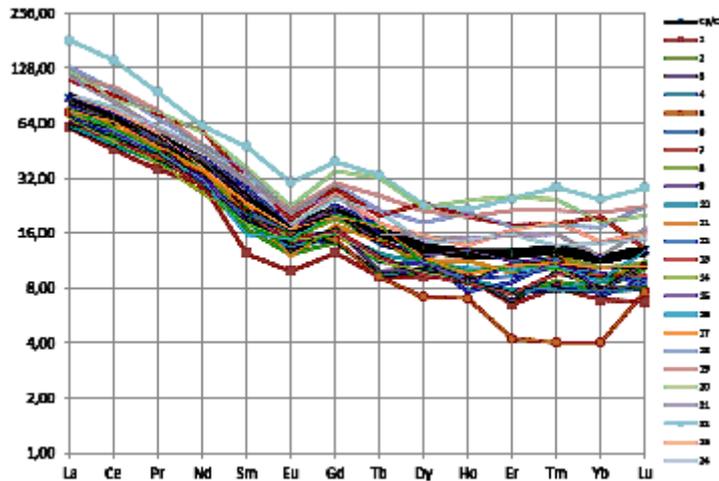


Fig. 2. Variations of REE compositions in the rocks of the deposit under survey. Contents of lanthanides of the embankment of rocks are normalized to chondrite carbonaceous (C1) [11]

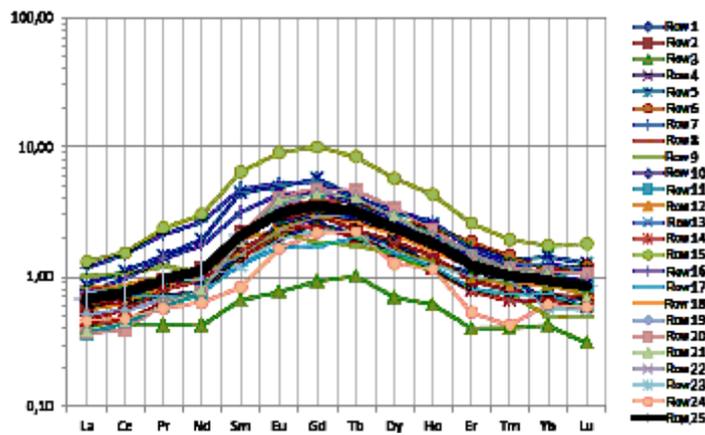


Fig. 3. Variations of REE compositions of the mineral agile complex. REE concentrations are normalized to the North American mudstone (NASG) [9]. Row 25 – average upon the section

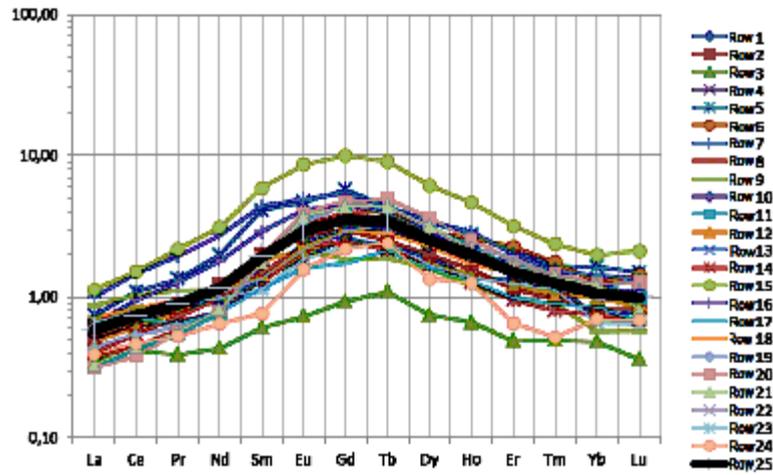


Fig. 5. Distribution of REE shares of the mineral agile complex in the deposit well section, %, from the bottom (sample 24) to the roof (sample 1) of the changed oil saturated part of the deposit

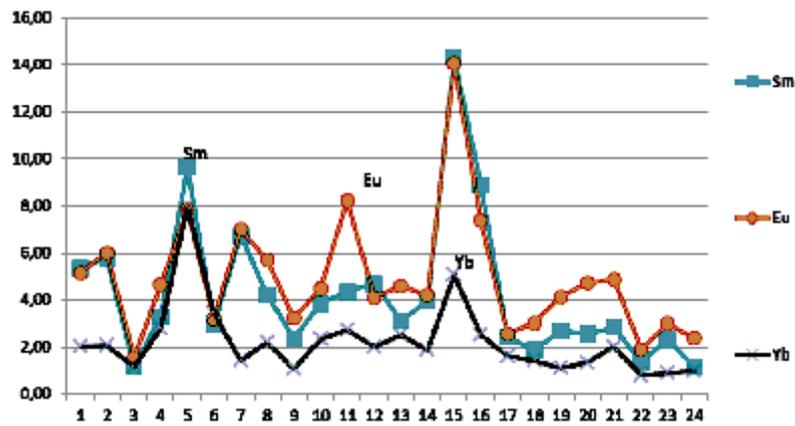


Fig. 5(a). Distribution of REE shares of the mineral agile complex in the well section for Eu, Sm and Yb, %, from Fig.5

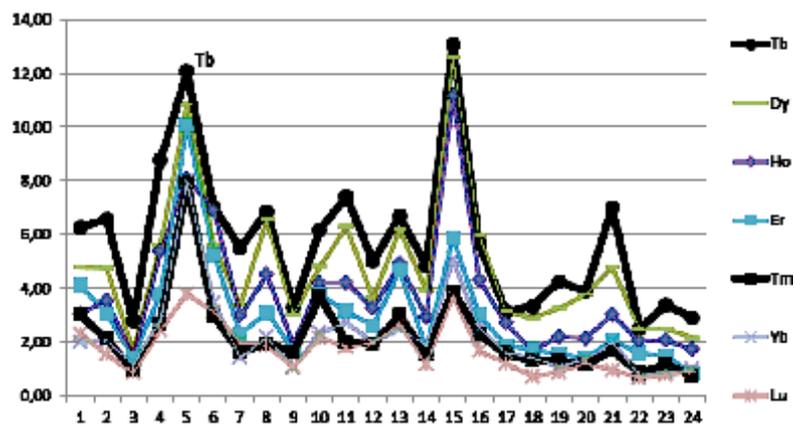


Fig. 5(b). Distribution of REE shares of the mineral agile complex in the well section for representative of heavy REEs, %, from Fig.5

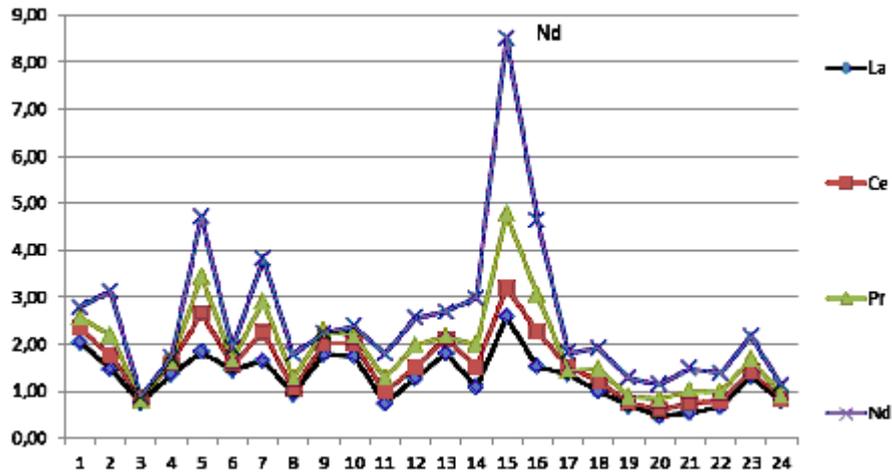


Fig. 5(c). Distribution of REE shares of the mineral agile complex in the well section for representative of light REEs – La.Ce. Pr 8 Nd, %, from Fig.5

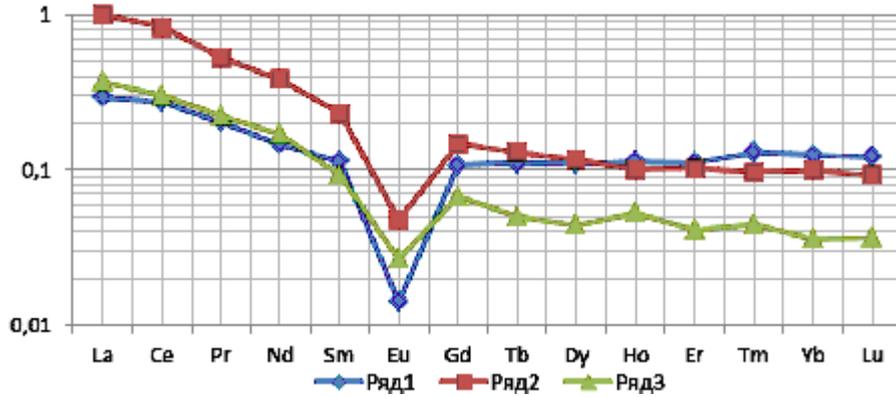


Fig. 6. Variations of REE compositions in the deposit's organic complex of rocks. REE concentrations are normalized to chondrite carbonaceous (!) [11]. Row 1 – samples 1-5 with output of the alcohol - benzene mixture fraction – 2.835%1; Row 2 – samples 6 – 15 with fraction output – 4.9217%; Row 3 – samples 16 – 24 with fraction output 6.9972%. According to Table 5

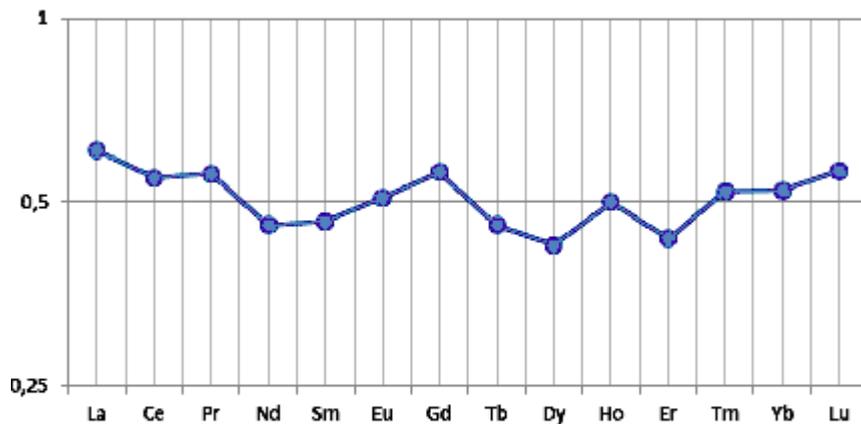
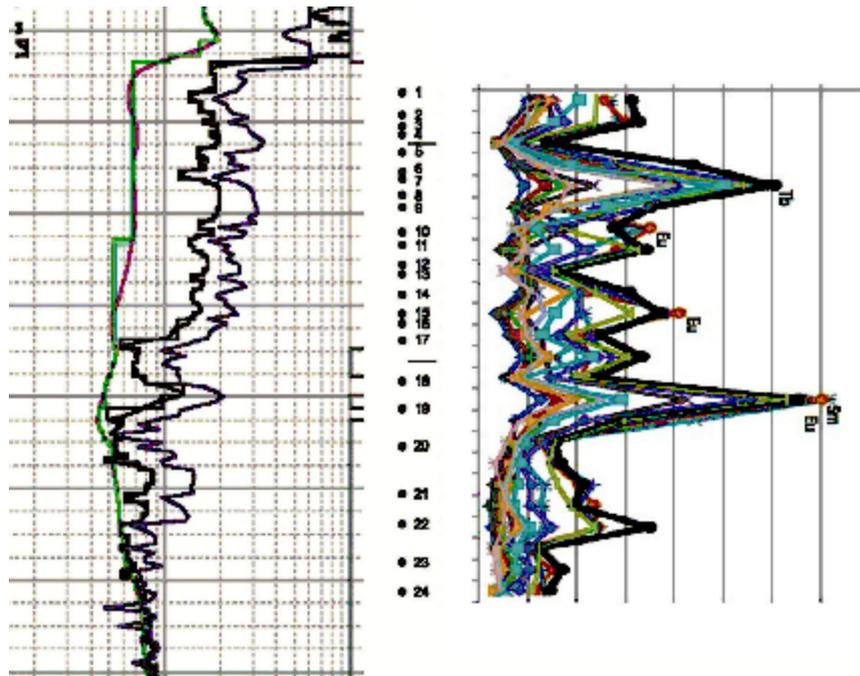


Fig. 7. Spectrum of lanthanides distribution within REE of the non-soluble residue. REE values are normalized to North American slates ( NASC) [9]. According to Table 4



**Fig. 8.** Comparison of results upon oilfield geophysics results (a); geochemical surveys of rare-earth elements (b), where the oil saturated part upon data "a" is defined within the range of 2744.51 - 2755.3 m (sampling points 4.5 - 17.18), upon data "b" - within the range of 2745.33 - 2752.46 m (sampling points 5 - 15)

well as parameters of deposit physics (rock porosity and permeability, etc.) and, most important from the geochemical perspective, medium redox conditions. It is the behavior of lanthanides in these conditions that is used for REE study in this paper. Thus, solution of the problem of quantification of residual hydrocarbon reserves is reduced mainly to determining changes in the boundaries of oil saturation of rock in the test site and quantifying the degree of rocks saturation with petroleum fluid. Such a problem can probably be solved by the method of organic geochemistry, together with geochemical studies of REE behavior. Thus, respectively, on the one hand, to determine the quantitative potential of hydrocarbon of oil and gas, and on the other hand, changed boundaries of the oil-saturated part in the section of the deposit, as the main task. Thus, solution to the task consists of two components: the first one is quantitative determination of potential of the petroleum fluids in the rock in the whole, and release of fractions from petroleum using methods of organic geochemistry, the second one is defining changes in the boundaries of the oil saturated part

by the behavior of rare earth elements in course of deposit development.

#### Object of the research

As the object of study, oil and gas field was chosen with sandstone collector type, in the south-eastern part of Western Siberia. For reaching the set objectives for research, section with well geophysical research (WGR) data is presented as well as core material, lithology of the deposit section and interval of taking samples 1 - 24 at depths 2742.89 - 2764.53 m. (fig. 1).

The mineral composition of unproductive sandstones of the studied area was also involved in research, and breakthrough A-934 is presented, which is characterized by high silica content ( $\text{SiO}_2=93.67\%$ ) and low content of oxides -  $\text{CaO}$  (less than 0.1%) and  $\text{MgO}=0.05\%$ ). From the results of the analysis of a sample taken from the depth of 2711.0 m. made in GI KSC RAS, Apatity.

#### Methods of analysis

Fractional analysis of rocks was used. For geochemical analysis, content of the lanthanides in the embankment, acid extract and organic complexes of rock has been studied. Recovery of

acid extracts, identified with mineral agile complex (MAC), was performed using hydrochloric acid (1.8% HCL) by analogy in works<sup>4-8</sup>, of organic complex - by extracting alcohol - benzene mixture at a ratio of 1:1. Content of rare earth elements in the species and concentration in the fractions was determined using the ICP MS method. Rare earth elements in the organic phase were determined after preliminary concentration by evaporation of the extract until dry residue is obtained and disclosure by nitric acid (HNO<sub>3</sub>) before analysis on the content of the rare earth elements. In discussion of the results, the calculated balance was additionally used between REE mineral agile complex and rock embankment. The results are shown as fractions of individual MAC lanthanides relative to REE content in rocks embankment (table 1 - 3).

## DISCUSSION

From the distribution of lanthanides in section of well and TR (figure 1) it can be seen that it is hard to solve the problem in terms of setting the boundaries of the oil saturated strata. By REE distribution one can only assume location of deposit borders within the boundaries of small peaks in the well section. With that, the used distribution of lanthanides that are able to change valence depending on the redox conditions. By the analysis of rocks embankment did not provide any substantial results for establishing changes in oil saturation. Usually the use of relative maximum distribution and behavior of individual lanthanides in the section of well are well interpreted with the boundaries of oil-bearing strata in clastic rocks<sup>1-4</sup>. These lanthanides include Eu, Sm and Yb in their transition to the divalent state in the form of Eu<sup>2+</sup>, Sm<sup>2+</sup> and Yb<sup>2+</sup> in sharply reducing environment<sup>4</sup>. Indicator capabilities have been defined as well for other lanthanides that can participate in geochemical processes in oxidized form. These include Ce<sup>4+</sup>, Pr<sup>4+</sup> and Tb<sup>4+</sup>. The most interesting in the geochemical context is Tb<sup>4+</sup> and its differentiated behavior from other lanthanides in REE fractions of rocks described in work<sup>3</sup>. Additionally, in Figure 1 for comparison on the background of the WGR. The distribution is shown La that has the largest ionic radius of all trivalent REEs. As it turned out, use of results of distributing

all lanthanides in the rock embankment in well section make it impossible to solve this problem. So far behavior of rare earth elements was considered in study of oil and gas deposits by core material selected from the exploratory drilling, i.e. of objects (oil and gas deposits) without violating initial thermodynamic conditions. So in this paper, an effort was made to solve the task based on conventional chemical properties of REEs by involving the balance of rare-earth elements of the mineral agile complex (MAC) related to rock embankment and lanthanides distribution variations within REEs of the mineral complex of the rock. For comparative analysis and solution of the task, we make a comparative analysis of the REE content variations of oil and gas deposit rocks upon the well section given in Figure 2.

It can be seen from Fig. 2 that spectrums normalized values of lanthanides have almost no differences from sedimentary rocks (Table 4 – average for rock embankment). We do not see any significant deviations in the behavior of individual lanthanides, which is emphasized by visual absence of any fractioning effect among REEs. More informative connection of REEs with rock components of the deposit were obtained in the result of the REE content analysis for the mineral agile complex (MAC).

Normalized concentration of MAC REEs towards North American slates NASG<sup>9</sup> (Fig.3) or clays of the Russian platform RP<sup>10</sup> (Fig.4) show their abrupt impoverishment with light and heavy lanthanides in relation to medium REEs. As known, in natural conditions, such unusual fractioning of REEs has not been observed in sedimentary processes yet. Finally, we observe significant fractioning within REEs. Reasons for such abnormal fractioning can only be the change of thermodynamic conditions in the deposit conditioned by the amount of oil-field water and surface-active reagents (SAR) pumped into the formation site under development that defines decrease of the formation pressure and consequently the process of fluid migration at the surveyed site. As a rule, this results in the change of oxidation-reduction conditions in the boundary zone of the deposit site under survey, which shall be reflected by the behavior of lanthanides due to their unusual chemical properties – ability to change valence and the ionic radius of some

lanthanides and to increase their complex-forming properties from La to Lu<sup>5</sup>. This option will be considered upon the analysis of REEs of the mineral agile complex (MAC) related to rock embankment. Hence, we can suppose that the main reason for such unusual fractioning is forced migration of REEs with oil fluids during their extraction under the action of technological processes. It can be reasonably assumed that impact of technological processes on initial thermodynamic and physical and chemical conditions in the oil-field as well as significant impact on the change of geochemical environment at the oil deposit development site. Such changes shall affect the REE behavior as well, especially on MAC REEs as some REEs are already removed during the operation of the deposit. Hence, we find a further solution of our task – determining and locating of boundary REE abnormalities in the well section and presentation of arguments for the vertical migration of lanthanides with oil fluids. Let's consider the balance of lanthanides shares of the mineral agile complex in relation to the rock embankment upon the well section (Table 3, Fig. 5).

We must also pay attention to the distribution of lanthanides shares and especially the formula of maximums Eu, Sm and Tb in the well section that confines boundaries, e.g., in our opinion the most reliable oil-saturated part of the deposit at the moment of oil surveying (Fig. 5). This conclusion is based on the following assumptions that are, first of all, seen from the distribution of lanthanides in the well section. Accumulation in points confining the assumed oil-saturated part is fixed for most lanthanides among REEs. But largest maximums of accumulations are related to the above lanthanides only that are capable of changing valence and ionic radius in case of changing oxidation-reduction conditions of the environment<sup>6,12</sup>. Now let's consider reasons for such distribution of lanthanides and explain the occurrence of abnormal behavior of individual lanthanides among REEs. Fig. 5 and Table 3 gives clear view of maximum accumulation of Eu and Sm in the zone of bottom boundaries change, and a significant amount of Tb in the zone of a newly formed roof. Hence, the antinomy of accumulation of two lanthanides different in chemical properties within the deposit (Eu<sup>2+</sup>) in the bottom zone and

(Tb<sup>4+</sup>) in the roof zone can be related to various oxidation-reduction conditions of the location of these lanthanides. Such conditions can be seen, as viewed from distribution of these lanthanides, when considering the well section beyond the field limit where the section part is influenced by two different physical and chemical conditions - oxidation (roof zone) and reduction (bottom zone) due to technological processes.

As known, all three elements can change valence and ionic radius in the highly reductive media and can be in the form of Eu<sup>2+</sup>, Sm<sup>2+</sup> 8 Yb<sup>2+</sup> in the organic rock complex. As stated in [4], this promotes their accumulation and migration in bivalent form within the deposit and beyond it with oil and gas hydrocarbons. Hence, we can assume that prior to opening the bed, due to establishment of highly reductive conditions by oil and gas hydrocarbons, accumulations of Eu have been formed in the roof and bottom zones of the oil-bearing bed with impoverishment of the medium part, with ratio of (Eu<sub>roof</sub> > Eu<sub>bottom</sub>), which is typical of deposits with fragmentary complex in the Western Siberia and given in [2.3.4]. Such an assumption is reflected by maximums Eu and Sm in the bottom zone and lower distribution of Eu concentrations in the middle part of the section (Fig. 5 and 50). This assumption is agreed with values of shares in the zone of maximums (sampling point 5) for Eu, Yb and Sm (Fig. 50). Their values correspond to the ratio Eu > Yb > Sm (Table 3) and to the level of change of their oxidation-reduction potentials<sup>4</sup>. This is a sign of reduction priority of this lanthanides and removal (migration) from the roof zone beyond the deposit, e.g., first of all, Eu are removed, then Yb and finally Sm, which is reflected in Fig 50 and Table 3, where shares of these lanthanides in sampling point 5 are: Eu = 7.84%; Yb = 7.97%; Sm = 9.63%. Reasons for such distribution of shares are as follows: first of all, it is related to physical and chemical properties of individual lanthanides to change valence and ionic radius in highly oxidation-reduction conditions of the media. On the other hand, changes of valence for Eu, Yb and Sm are congruent, and the changing priority of their ionic radii in reductive processes is Eu<sup>2+</sup> = 1.25 > Yb<sup>2+</sup> = 1.14A > Sm<sup>2+</sup> = 1.02A in octanumerous coordination [6]. So, the above given distribution of shares Eu, Yb and Sm in point 5 corresponds to the geochemical principle

concerning the capturing of elements with high ionic radius by oil components of fluids [4]. Hence, we see the given priority of removal of these lanthanides along with oil and gas extraction. It should be noted that Eu in the form of  $\text{Eu}^{2+}$  has the largest ionic radius among all REEs. Consequently,  $\text{Eu}^{2+}$  behavior will be determinant for finding its migration pattern with oil and gas hydrocarbons. First of all, those lanthanides are removed that have the largest ionic radius and electropositive potential<sup>13</sup>.

Decrease of concentrations of these lanthanides in sampling point 5 of the well section in relation to the changed bottom part with simultaneous accumulation of terbium (Tb) in the zone of the newly formed roof screen are related to changes in the oxidation-reduction conditions of the media during the development of the oil and gas deposit. Significant amount of water and surface active reagents pumped into the oil formation as stated in<sup>14</sup> has significant influence on geochemical and thermodynamical conditions of the media and will have influence on the surveyed deposit site. This shall be reflected on REEs behavior, especially on accumulation and migration of heavy lanthanides having higher complex-forming properties than average REEs in trivalent form<sup>5</sup>. Ce, Pr and Tb have ability to change valence and ionic radius when oxidation-reduction conditions of the media change towards reductive. As known, such process is possible for cerium ( $\text{Ce}^{4+}$ ), praseodymium ( $\text{Pr}^{4+}$ ) and terbium ( $\text{Tb}^{4+}$ )<sup>7</sup>. Transition from trivalent form to quadrivalent form is defined for these lanthanides by the capacity of the oxidation-reduction potential<sup>15</sup>. Most oxidation-reduction potential of  $\text{Tb}^{4+}$  defines more rigid stability conditions. So, for  $\text{Tb}^{4+}$  stability, organic stabilizers are usually used<sup>7</sup>. In natural processes (possibly) and in oil and gas deposits (quite possible), oil and gas hydrocarbons act as stabilizers<sup>16</sup>. Now let's point out the following aspect that is also important for determining reasons for abnormal accumulations of  $\text{Tb}^{4+}$ . Decrease of ionic radii is maximum in priority  $\text{Ce}^{4+}$ ,  $\text{Pr}^{4+}$ ,  $\text{Tb}^{4+}$ , correspondingly, with the following decreasing order of ionic radii: 0.97, 0.96, 0.88 in octanumerous coordination<sup>6</sup>. Hence, we see that terbium in the form of  $\text{Tb}^{4+}$  with ionic radius 0.88 is the closest in terms of the ionic radius size, and it exceeds ionic radii of  $\text{Yb}^{3+}$  and  $\text{Lu}^{3+}$ , respectively

equal to 0.977 and 0.985. Consequently, the changed ionic radius of  $\text{Tb}^{4+}$  allows locating it next to heavy REEs. Complex-forming properties of  $\text{Tb}^{4+}$  similar to heavy REEs<sup>5</sup> can be seen in Fig. 5b in the form of priority of abnormal accumulation in sampling point 5 of other representatives of heavy REEs. This is a reason to assume interconnection of  $\text{Tb}^{4+}$  with oil and gas hydrocarbons in the result of its screening from water by oil or its derivatives. As a consequence of possibility of such chemical process, we see such redistribution of REEs during the migration of oil fluids in the deposit towards the upper screen non-related to the decrease of deposit's physical parameters (porosity and permeability) and change of oxidation-reduction conditions of the media.

Such an assumption can be checked upon the following results. In the zone of the newly formed roof in sampling point 5, Table 5 gives data for comparing relative maximums of  $\text{Tb}^*$  with values of balance shares of  $\text{Tb}^*$  in the mineral agile complex of rocks. These values are defined from the ratio  $\text{Tb}^* = \text{Tb} / 0.5 (\text{Gd} + \text{Dy})$ . They are respectively equal to:  $\text{Tb}^*_{\text{MAC}} = 0.15$  and  $\text{Tb}^*_{\text{balance}} = 1.06$ , which leaves no doubts that there is terbium in the deposit (difference by 7 times, which is not viewed in natural processes) in the form of  $\text{Tb}^{4+}$ . This statement is assumed on the basis of properties of valent states of lanthanides with changes of ionic radii. This allows assuming that Tb can migrate and be abnormally accumulated only with oil hydrocarbons of fluids in the form of  $\text{Tb}^{4+}$ . There are no other aspects of migration and accumulation in the zone under consideration and within the considered period of time. Consequently, along with  $\text{Tb}^{4+}$  accumulation, accumulation in sampling point 5 shall be seen for other heavy REEs according to high complex-forming properties and in the priority order of changing their ionic radii, which is given in Fig 5b. This priority is probably true for expression of priority of migration properties of heavy REEs under the following scheme:



The ionic radius of  $\text{Tb}^{4+}$  is minimal, but it has the smallest atomic mass in relation to the given trivalent REEs. As seen from Table 3 and Fig. 5b, this principle almost fully corresponds to the given arguments. Consequently, its migration properties shall be largest along with maximum

complex-forming properties in relation to all other heavy REEs, which is reflected in Fig. 5 and 5b and is very well traced upon the average data for shares of the minimal agile complex in the direction Tb > Lu (Table 4). Small discrepancy of values between Tu and Yb is most likely defined by the disposition of Yb<sup>2+</sup>. This is the case when Yb participates as a representative of heavy REEs (Yb<sup>3+</sup>) and at the same time as a representative of lanthanides capable of changing valence in highly reductive conditions (Yb<sup>2+</sup>) under technological processes occurring during deposit development. Changes of the accumulation degree of Yb<sup>2+</sup> in point 15 once more highlight Yb capacity for migration processes, predominantly in its bivalent form.

Due to displaying all shares of lanthanides in Figures 50 – 5c on the same scale, it's easy to view the migration process and increased accumulation of heavy REEs relatively to other lanthanides.

The process of lanthanides migration in the well section during the deposit development, especially at the initial stage, is also very easily traced upon smooth fall of Eu concentrations (Fig. 50, samples 17-21). Vertical migration processes in the well section are proved by Eu deficiency within REEs of the organic complex in the direction from the bottom to the roof of the oil-saturated part of the reservoir bed (Fig. 6).

In this paper, Nd accumulation still remains undefined in the distribution of lanthanides in the well section (Fig. 5c).

Its significant excess and difference as Sm along with Tb. Accumulation due to isomorphism with Ca is excluded as there is no Nd abnormalities in the distribution spectrum of the organic complex (Fig. 6) as shown in<sup>17</sup> in the distribution of carbonate rocks and asphaltenes. Mineral composition of non-productive sandstones of the site under investigation (sample L-934) with traced contents of Ca and Mg oxides proves this as well. Their participation in the generation of hydrocarbons is unlikely possible, as well as in case of lanthanides isomorphism with saturation of rocks with oil fluids<sup>18</sup>. So the only explanation of insignificant Nd accumulation is the quantitative presence of Sm conditioned by the principles of REE geochemistry and influence of adjacent lanthanides in the row La – Lu.

Finally, let's consider the nature of REE distribution in the non-soluble residue after removing the mineral agile complex of rocks. As seen from Fig. 7, the fraction of sedimentary rocks after removal of the mineral agile complex has REEs insignificantly enriched with heavy lanthanides, and as shown in<sup>19</sup>, this is conditioned by the presence of the heavy fraction containing necessary concentrates of REEs resistant to weathering (zircon, etc.)

Now, after having considered the nature of REE distribution in the newly formed oil saturated part of the formation, we can consider the whole mechanism of oxidation-reduction conditions influence on the redistribution of lanthanides with oil fluids beyond the field limit. It can be assumed that initial boundaries of the oil formation were located within the boundaries of the samples under survey. After the start of the development and with the change of the formation pressure in the development area, migration of oil fluids with lanthanides starts from the area under development towards the developed site due to the reduction of formation pressure and further extraction of oil fluids. In its turn, it leads to abrupt change of oxidation-reduction conditions in the deposit and in the site under survey and it changes the whole initial nature of REE distribution in the oil saturated part of the deposit. It can be assumed that the process of changing geochemical conditions goes on as follows: after fluids start migrating from the bottom zone, under reducing conditions, migration of those lanthanides starts that can change their valence in highly reductive conditions – Eu<sup>2+</sup>, Yb<sup>2+</sup> and Sm<sup>2+</sup>. The migration and accumulation will continue until reductive conditions change and oxidizing conditions occur due to water inflow and consecutive pH change. Formation of the boundary zone in our case (sample 15) ends in the zone of maximums of Eu and Sm. Reasons for their accumulation are formation of heavy fractions of hydrocarbons, change of pH and probably porosity and permeability of rocks. From the geochemical point of view, attention should be paid to accumulation of Sm > Eu in the boundary zone, which once more points out the migration of Eu, Sm and Yb in bivalent forms and observation of the principle and priority lanthanides with large ionic radius, so the above ratio Eu < Sm is quite justifiable due to observation of Eu removal priority

in the migration process in relation to Sm and Yb. Further mechanism of oxidation-reduction conditions affecting the REE redistribution can be related to lanthanides possessing an ability to change valence in highly reductive conditions and heavy REEs that have already been considered in this paper.

For illustration purposes, Figure 8 gives the comparison of results upon oilfield geophysics data (0): geochemical studies of rare-earth elements (b), where the oil-saturated part according to data (a) is determined within the range of 2744.51 – 2755.3 m (sampling points 4,5 – 17,18); and within the range between 2745.33 and 2752.46 m for (b) (sampling points 5 – 15). As a result we see almost unchanged upper boundaries of the roof and significant changes in the bottom zone, which clearly specifies vertical migration of fluids.

### CONCLUSION

It follows from the geochemical studies conducted that migrations (emigrations) of REEs within the deposit and an overlapping screen are first of all typical of lanthanides that can change valence and ionic radius in acute reducing conditions. Such properties are possessed by Eu, Sm and Yb in bivalent form, with Eu<sup>2+</sup>, after a change in its valence and ionic radius from 1.06Å to 1.25 [b], becoming the one with the largest ionic radius. Hence, we obtain the priority of its extraction by oil hydrocarbons from the deposit. Displayed redistributions of lanthanides in the well section correspond to the above (Fig. 50).

On the basis of the electrostatic connection of lanthanides with oil components of fluids justified by the ionic connection of cations and anions [20], we can assume the following migration and emigration pattern for light lanthanides according to the decrease of their ionic radii in the row La - Lu in trivalent form. This is clearly shown upon low accumulation of La in the upper screen zone (Fig. 5c), as it possesses the largest ionic radius from all trivalent REEs and is removed first in the result of fluids emigration. Finally, the displayed maximum of Tb<sup>4+</sup> and heavy REEs in Fig. 5b, and especially expression of their maximums in sampling point 5, shows substantiation of accumulation and migration Tb. Such behavior is possible only in the oxidized

condition with changed ionic radius and approaching to the properties of heavy REEs. As is known<sup>5</sup>, with atomic weight increase and ionic radius decrease – the lanthanide contraction law – for all trivalent REEs, in the row La – Lu, complex-forming properties of REEs are increased from La to Lu. In this relation, sedimentary processes<sup>21</sup> show abilities to complex formation of heavy REEs with organic substance. In this paper, we can view this process with these REEs (Fig. 5b). Here we can claim as follows: migration in the deposit and accumulation of heavy lanthanides in trivalent forms in boundary zones are not possible without participation and formation of their complex compounds with oil fluids. So, it would very important to remind of stabilizing properties of oil and gas hydrocarbons for Tb<sup>4+</sup><sup>22</sup>, which is asserted by its abnormal accumulation in the upper screen point (Fig. 5b), which is impossible without screening of Tb<sup>4+</sup> by oil and gas hydrocarbons and their migration to deposits.

### Abstract

The task set in this paper for the quality assessment of oil and gas hydrocarbons, with known parameters of the surveyed site oil saturated part and with attraction of formation physical parameters (porosity and permeability, fluid extraction factor, etc.), as well the established output of fractions of the alcohol-gasoline mixture from the rocks within the intervals of the site under survey, is not only quite solvable, but it also allows calculating the quantitative increase of oil and gas reserves. Finally, the paper shows that despite minimal input data, the tasks set herein can be solved by involving results of geochemical investigations of rare-earth elements.

### CONCLUSIONS

1. Rare-earth elements and valent states of individual lanthanides are geochemical indicators and can be considered as criteria of rocks oil-bearing capacity. Changes of the behavior of individual lanthanides depending on oxidation-reduction conditions also allow substantiating their differentiated behavior within REEs of rock fractions as a part of geochemical surveys.
2. Survey results show that changes of oil saturation boundaries of the deposit can

- be viewed upon the REE shares distribution for the deposit rocks' mineral agile complex. Accumulation maximums of lanthanides capable of changing valence in the well section are identified with a newly formed level of the formation oil saturation, and the degree of oxidation-reduction conditions in the deposit upon the abnormal Eu content among REEs of the organic complex of rocks.
- Survey results show that upon the distribution of REE shares of the mineral agile complex of rocks in combination with the oilfield geophysics data, it's possible to determine the boundaries with largest and smallest watering of surveyed sites beyond the field limit and to perform water shutoff treatment in these zones to direct the pumped liquid to formation beds non-affected by surface-active reagents, which will result in the increase of the oil recovery factor (ORF).

\*The Tomsk State University.

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