# Balance of Rare-earth Elements in Sand Rocks of Western Siberia Oil-bearing Zones

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**Distribution of REEs upon organic substance (OS) fractions of rocks, their clay component, soluble weak 1.8% HCl, and the insoluble reside (IR) is studied. Studies were performed in sand rocks of oil bearing reservoir beds and embedding sedimentary formations of the Western Siberia lowland Jurassic deposit. As a rule, contents of individual lanthanides in OS is lower than that in initial sand rocks, and REEs in OS of oil bearing rocks are distinguished by high enrichment with Eu and heavier lanthanides, especially Yb, and for OS of embedding sand rocks - with REEs, especially La. AE fractions of oil bearing sand rocks are enriched with light and medium REEs, rarely with Yb; AE embedding sand rocks are distinguished by predominant accumulation of medium, and to a lesser extent, light REEs as compared to the initial rock. The composition of mineral constituent rocks (CR) in all sand rocks in relation to other lanthanides is described by the presence of heavier REEs. The degree of abnormal accumulation of Eu and Yb in oil bearing reservoir bed OSs is maximal for the roof, and in the bottom of beds, a significant excess of Eu only is revealed; minimal similar abnormalities in REE redistribution are expressed in sand rocks of the medium part of reservoir beds. No abnormalities on Eu and Yb in embedding sand rock OSs and their presence in reservoir bed OSs is a geochemical criterion for identification of oil bearing rocks and adjustment of geophysical data in studying oil bearing sections of sedimentary rocks.**

**Key words:** Sand, Rock, Western Siberia, Oil bearing

Previously, a selective accumulation effect was noted for the roof and the bottom of oil bearing reservoir beds in oil components of La and lanthanides with variable valence capable of transforming into bivalent state under the influence of reduction environment generated by fluids hydrocarbons[1]. Paper[2] sets a difference in the concentration of rare-earth elements (REE) between fractions of petrologen, asphaltenes and oil, with general tendency towards accumulation of heavier REEs in all types of the organic substance (OS) of sedimentary rocks (Yb and Lu, Fig. 1à), which is related to the increase in stability of complex compounds from La to Lu. Difference in interpretation of results for REEs from OS in papers[1,2], especially Eu (Fig. 16), as well as no data for REEs from OS of sedimentary rocks containing no oil components is a reason for conducting this study.

**Object of study**

To determine quantitative concentrations of REEs in fractions of oil bearing rocks, this paper

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applies samples taken from the zones of roof, bottom and middle part of oil bearing reservoir beds: from bed $J_1$ of the Vasyugan suite of the Khvoynoye deposit (well 38; interval 2,697.7 m – 2,699.3 m; samples 27, 30, 34). Similarly, from the zone of J7 formation of the Tyumen suite, the Gerasimovskoye deposit (well 16Ð; interval 2,757.4 – 2,777.2 m; samples 679, 682 and 746). The Khvoynoye deposit's bed (KB) is represented by sand rocks, the Gerasimovskoye deposit's bed (GB) - by argillites and sand rocks, with denser fine rocks confined to the roof and bottom zones. Both deposits are located in the Western Siberian oil-and-gas bearing basin. Jurassic sand rocks of non-productive formations, in which REE distribution was studied, and fractions were taken in the Severo-Yutymskaya well 198 from interval 2,713.0 m (sample 51474) and in the Krapivvinskaya well 203 from interval 2,711.0 m (sample L-934).

KB sand stones in the roof, middle and bottom have the following concentration, respectively (%): $SiO_2$ 82.0 – 78.0, 3.0 - 80.6; $Al_2O_3$ 11.2 – 10.2-9.7; $Fe_2O_3$ 4.0 – 1.4 – 2.4; $CO_2$ 2.2 – 1.4 – 1.2 and Corg. 1.08 – 1.05-1.39. In the GB section, from the bottom and the roof, changes of the chemical composition are found, reflected as follows (%): for Fe 3.9 – 1.2 – 11.8; for $CO_2$ 1.7 – 2.5 – 23.2 and Corg. 1,61 – 1.06 – 2.67. Composition of

sand stones (51474 and L-934) of non-productive formations is given in Table 1. These rocks are distinguished by high silica acidity as compared to KB sand rocks, lower $CO_2$ concentration and Corg.

Sand rocks L-934 and 51474 were analyzed in the chemical laboratory of GI KNC RAN. Average for Russian platform (RP) siltite-sand rocks upon data[4].

**Methods for separation fractions and REE analysis**

REEs were studied in each case upon the embankment of rocks (ER), and individually upon OS fractions, acid extract (AE) and insoluble residue (IR). Methodology for performing individual fractions includes rock crushing to achieve natural fineness of sand rock. Then the quartered part is taken for REE analysis in the embankment of rocks, and the basic mass of the sample is treated with a special ethyl alcohol and benzene mixture (1:1). For OS extraction, a sub-sample is placed into a cone flask 200 mL and after adding the benzene mixture (100-150 mL), the sample is subject to automatic agitation during 2 hours. After sedimentation, the extract is filtered. Re-extraction was performed after manual agitation. The third portion of the extract is filtered in 24 hours and the sample is washed by a 4-fold extract portion. Combined filtrates were used after

**Table 1.** Chemical composition for RP sand rocks and siltite-sand rocks (mass %).

| Oxides | L-934 | 51474 | Average for RP [4] | |
|---|---|---|---|---|
| $SiO_2$ | 93.67 | 86.54 | 70.57 | 73.68 |
| $TiO_2$ | 0.08 | 0.29 | 0.40 | 0.50 |
| $Al_2O_3$ | 2.6 | 5.62 | 8.15 | 7.16 |
| $Fe_2O_3$ | 0.18 | 0.33 | 3.05 | 2.45 |
| FeO | <0.05 | 0.59 | 1.36 | 1.43 |
| | | | 0.07 | 21.43 |
| MnO | <0.003 | 0.02 | 0.072 | 0.06 |
| MgO | 0.05 | 0.41 | 2.04 | 1.61 |
| CaO | <0.10 | 0.12 | 4.00 | 3.75 |
| $Na_2O$ | 0.52 | 1.56 | 0.63 | 0.46 |
| $K_2O$ | 0.94 | 1.75 | 2.21 | 1.91 |
| $H_2O-$ | <0.08 | <0.08 | 0.78 | - |
| PPP + $H_2O^+$ | 0.91 | 1.03 | 1.01 | 2.83 |
| $CO_2$ | <0.10 | 0.23 | 3.61 | 3.27 |
| Corg. | 0.17 | 0.99 | 0.22 | 0.27 |
| $SO_3$ (total) | 0.1 | 0.00 | 0.33 | 0.33 |
| $P_2O_5$ | 0.03 | 0.09 | 0.126 | 0.22 |
| Σ | 99.95 | 99.57 | 99.9 | 99.93 |

**Table 2.** REE concentration in oil and gas bearing reservoir beds, g/t

| Fractions | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Yb | Eu/Sm | Eu* | $(Eu/Sm)_N$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Khvoynoye deposit, roof (No. 27, interval 2696,7 m.) | | | | | | | | | | | | |
| Sand rock | 22.500 | 56.200 | 39.000 | 21.800 | 5.200 | 1.600 | 1.015 | 0.430 | 0.400 | 0.300 | 1.640 | 0.790 |
| OS | 0.065 | | | | 0.080 | 4.900 | 2.462 | 0.024 | 0.590 | 61.250 | 128.000 | 161.200 |
| AE | 41.000 | 261.000 | 173.750 | 86.500 | 12.900 | 7.400 | 4.250 | 1.100 | 1.800 | 0.570 | 3.100 | 1.500 |
| IR | 19.200 | 39.500 | 28.300 | 17.100 | 0.900 | 0.900 | 0.660 | 0.420 | 0.300 | 0.210 | 1.100 | 0.550 |
| Middle part (No. 30, interval 2698.2 m) | | | | | | | | | | | | |
| Sand rock | 29.600 | 61.000 | 37.650 | 14.300 | 5.100 | 0.900 | 0.590 | 0.280 | 0.900 | 0.170 | 1.020 | 0.440 |
| OS | 0.018 | | | | 0.030 | 0.100 | 0.063 | 0.025 | 0.130 | 3.300 | 6.500 | 8.700 |
| AE | 589.000 | 1670.000 | 977.000 | 284.000 | 51.900 | 6.400 | 4.575 | 2.750 | 18.700 | 0.120 | 0.760 | 0.310 |
| IR | 20.500 | 39.100 | 25.150 | 11.200 | 4.100 | 0.740 | 0.490 | 0.240 | 0.610 | 0.180 | 1.080 | 0.470 |
| Bottom (No. 34, interval 2699.3 m) | | | | | | | | | | | | |
| Sand rock | 36.300 | 72.000 | 48.050 | 24.100 | 3.800 | 1.500 | 0.950 | 0.400 | 3.200 | 0.390 | 2.010 | 1.020 |
| OS | 0.870 | | | | 0.052 | 2.500 | 1.263 | 0.026 | | 48.070 | 127.000 | 126.500 |
| AE | 1560.000 | 3100.000 | 2030.000 | 960.000 | 110.000 | 52.000 | 27.800 | 3.600 | 51.300 | 0.470 | 3.200 | 1.230 |
| IR | 9.900 | 28.600 | 19.750 | 10.900 | 2.350 | 0.540 | 0.450 | 0.360 | 1.550 | 0.230 | 1.020 | 0.600 |
| Gerasimovskoye deposit, roof (No. 679, interval 2757,4 m) | | | | | | | | | | | | |
| Argillite | 46.400 | 71.400 | 54.750 | 38.100 | 7.700 | 2.920 | 1.785 | 0.650 | 3.400 | 0.380 | 2.080 | 1.000 |
| OS | 0.400 | | | | 0.180 | 1.180 | 0.609 | 0.037 | 1.120 | 6.500 | 26.300 | 17.100 |
| AE | 6.300 | 20.900 | 18.450 | 16.000 | 5.100 | 3.090 | 1.790 | 0.490 | 0.540 | 0.400 | 3.600 | 1.570 |
| Middle part (No. 682, interval 2764.9 m) | | | | | | | | | | | | |
| Sand rock | 19.400 | 39.900 | 27.350 | 14.800 | 3.000 | 1.000 | 0.660 | 0.320 | 0.800 | 0.330 | 1.750 | 0.870 |
| OS | 0.240 | | | | 0.810 | 0.830 | 0.675 | 0.520 | 0.510 | 1.030 | 1.400 | 2.710 |
| AE | 9.000 | 7.500 | 11.750 | 16.000 | 4.500 | 3.400 | 2.235 | 1.070 | 0.720 | 0.750 | 3.100 | 1.970 |
| Bottom (No. 746, interval 2777.2 m) | | | | | | | | | | | | |
| Argillite | 35.200 | 59.500 | 42.750 | 26.000 | 5.200 | 1.600 | 1.065 | 0.530 | 3.700 | 0.300 | 1.600 | 0.790 |
| OS | 3.000 | | | | 0.440 | 5.000 | 2.630 | 0.260 | 1.140 | 11.400 | 30.500 | 30.000 |
| AE | 44.900 | 100.000 | 82.500 | 65.000 | 19.500 | 4.500 | 3.125 | 1.750 | 3.000 | 0.230 | 1.300 | 0.600 |

**Table 3.** REE content in the embankment of rocks and concentrations in individual fractions, g/t

| Fraction | Sub-sample | La | Ce | Nd | Sm | Eu | Gd | Dy | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Sand rock L-934 (non-productive) | | | | |
| Embankment of rocks | 0.9464 | 3.7800 | 7.5270 | 3.3490 | 0.6783 | 0.1537 | 0.5922 | 0.6493 | 0.4259 | 0.4308 | 0.0680 |
| Organic substance | 1.6710 | 0.2710 | 0.2868 | 0.1033 | 0.0170 | 0.0042 | 0.0133 | 0.0122 | 0.0065 | 0.0047 | 0.0007 |
| OS, ash residue | 0.0082 | 55.2000 | 58.4200 | 21.0400 | 3.4600 | 0.8540 | 2.7100 | 2.4850 | 1.3200 | 0.9800 | 0.1400 |
| Acid extract | 0.0178 | 141.6000 | 277.5000 | 125.5000 | 25.9600 | 5.9100 | 20.6500 | 16.1500 | 7.7820 | 5.1640 | 0.6860 |
| Insoluble residue | 0.8916 | 2.8600 | 5.6630 | 2.4390 | 0.4977 | 0.1149 | 0.4397 | 0.5269 | 0.3540 | 0.3880 | 0,062* |
| | | | | | | | Sand rock 51474 (non-productive) | | | | |
| Embankment of rocks | 0.5841 | 17.1000 | 36.1500 | 16.3300 | 3.0370 | 0.6632 | 2.4500 | 2.0480 | 1.1600 | 1.1000 | 0,154* |
| Organic substance | 0.2699 | 0.2160 | 0.2921 | 0.1108 | 0.0205 | 0.0042 | 0.0163 | 0.0121 | 0.0067 | 0.0054 | 0,0009* |
| OS, ash residue | 0.0342 | 17.0700 | 23.0600 | 8.7450 | 1.6200 | 0.3310 | 1.2570 | 0.9550 | 0.5290 | 0.4260 | 0.0710 |
| Acid extract | 0.0633 | 158.9000 | 325.9000 | 180.3000 | 43.0800 | 9.6640 | 38.2100 | 26.2200 | 9.8520 | 6.5230 | 0,8* |
| Insoluble residue | 0.4964 | 14.7500 | 31.8100 | 13.5000 | 2.4570 | 0.5442 | 1.8090 | 1.6730 | 0.9990 | 1.0150 | 0.1470 |
| Blank run | | 0.0240 | 0.0390 | 0.0136 | 0.0014 | 0.0003 | 0,0008* | 0.0008 | 0.0006 | 0.0004 | 0.00006 |

REE analyses were performed using mass-spectrometry with isotope dilution in GI KNC RAN (Apatity).    *Values calculated upon proportion to other REEs.

vaporization and annealing to determine the concentration of REEs in the sand rock OS. % output of OS fraction was estimated upon the extraction residue. Aliquots of samples after extraction were used to extract the mineral agile complex (MAC) of sand rocks (acid extract) by treating each sample with 1.8% HCl during 2 hours. After separating the acid extract by filtration, the residue was dried, and the AE % output was calculated upon weight loss. AE fractions of the insoluble residue were used for REE analysis.

Determination of REEs in oil bearing rocks and their fractions (Table 2) was performed by instrumental neutron activation analysis (INAA). The activity was measured and radionuclides were identified using the nuclear data processing system Lp 4900, a large capacity DCP and an X-ray detector by ORTEC (Tomsk). Analysis precisions was as follow, %: La – 4-5, Ce – 8-12, Nd – 7-14, Sm – 7-18, Eu 6-16, Tb – 11-30, Yb – 10-18. Assessment correctness of lanthanides concentration is checked by analyzing standard samples TV, KN and SA.

REE contents in non-productive sand rocks and their concentrations in fractions were determined by mass spectrometry with isotopic dilution using MI 1201-T tool after chemical decomposition of samples and separating REEs from them. The primary chemistry procedure includes sample decomposition with $HF+HCl+HCCO_4$, removal of acid fumes by heating-up, solution of the residue in 1,5N HCl and transferring the solution to the chromatographic column filled with DOWEX 50õ8 resin (200-400 bags). Elution was performed with 4N HCl. The precision of the mass spectrometry is higher than ±1% (rel.) for Ce, Nd, Sm, Eu, Gd, Er, Yb and Lu, and around ±2% for La [4]. The correctness of REE analysis was checked by determining these elements in standard basalt BCR-1[5]. The results of REEs analysis is given in Table 3. It also includes data of the blank experiment reflecting the background addition for each element, which was considered when calculating REE concentration in samples (REE analysis was performed by I.V. Sharikov and O.G. Sherstennilkova in the Geological Institute KNC RAN, Apatity).

Studies of samples, included into this article, in the organic substance and high molecular compounds of oils from various deposits to

**Table 4**. REE share in fractions relative to the embankment of rocks for oil reservoir beds, %

| Fraction name | Fraction output | La | Ce | Nd | Sm | Eu | Tb | Yb |
|---|---|---|---|---|---|---|---|---|
| | | | Roof sand rock (27), Khvoynoye deposit | | | | | |
| Organic substance | 1.08 | 0.003 | | | 0.030 | 3.200 | 0.060 | 1.400 |
| Acid extract | 9.4 | 18.300 | 40.900 | 34.700 | 23.900 | 45.200 | 21.700 | 38.100 |
| Insoluble residue | 89.52 | 81.700 | 59.100 | 65.300 | 76.100 | 51.600 | 78.300 | 60.500 |
| | | Sand rock of the reservoir bed middle part (ZO), Khvoynoye deposit | | | | | | |
| Organic substance | 1.05 | 0.001 | | | 0.006 | 0.100 | 0.100 | 0.200 |
| Acid extract | 1.6 | 32.000 | 41.200 | 29.200 | 17.200 | 12.200 | 14.800 | 33.700 |
| Insoluble residue | 97.35 | 68.000 | 58.800 | 70.800 | 82.800 | 87.700 | 85.100 | 66.100 |
| | | | Bottom sand rock (34), Khvoynoye deposit | | | | | |
| Organic substance | 1.39 | 0.030 | | | 0.020 | 2.300 | 0.100 | |
| Acid extract | 1.8 | 74.500 | 66.800 | 62.000 | 46.800 | 62.900 | 15.600 | 38.000 |
| Insoluble residue | 96.81 | 25.500 | 33.200 | 38.000 | 53.200 | 34.800 | 84.300 | 62.000 |
| | | | Roof argillite (697), Khvoynoye deposit | | | | | |
| Organic substance | 1.08 | 0.009 | | | 0.030 | 0.340 | 0.060 | 0.300 |
| Acid extract | 0.32 | 0.040 | 0.080 | 0.100 | 0.100 | 0.340 | 0.150 | 0.030 |
| | | | Sand rock of the bed part (682), Khvoynoye deposit | | | | | |
| Organic substance | 0.71 | 0.010 | | | 0.200 | 0.600 | 1.200 | 0.500 |
| Acid extract | 0.34 | 0.150 | 0.050 | 0.340 | 0.330 | 1.000 | 0.900 | 0.200 |
| | | | Bottom argillite (746), Gerasomovskoye deposit | | | | | |
| Organic substance | 1.75 | 0.140 | | | 0.190 | 0.250 | 0.750 | 0.540 |
| Acid extract | 3.52 | 3.600 | 4.500 | 10.200 | 10.200 | 3.100 | 9.400 | 2.200 |
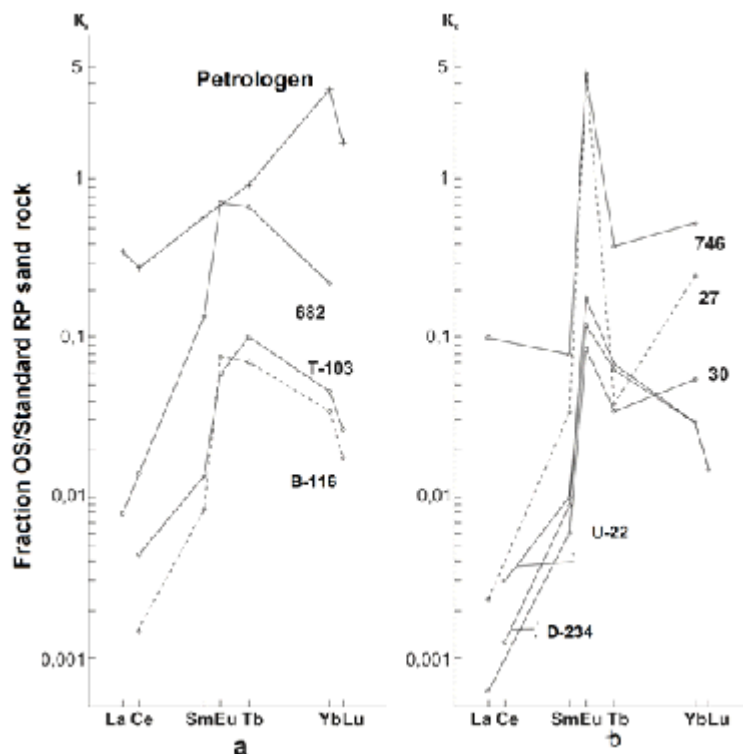


**Fig. 1.** Differences in REE concentration between fractions of petrologen, asphaltenes and oil in paper [2] (Ò-103, B-116, U-22 and D-234) and our data for rocks' OS (682, 746, 27 and 30)

**Table 5.** REE balance upon sand rock fractions, %

| Fraction | Fraction Output | La | Ce | Nd | Sm | Eu | Gd | Dy | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sand rock L-934 (non-productive)** | | | | | | | | | | | |
| Embankment of rocks | 100 | 3.78000 | 7.52700 | 3.34900 | 0.67830 | 0.15370 | 0.59220 | 0.64930 | 0.42590 | 0.43080 | 0.06800 |
| Organic substance | 0.87 | 0.00230 | 0.00250 | 0.00090 | 0.00015 | 0.00004 | 0.00012 | 0.00011 | 0.00005 | 0.00004 | 0.000006 |
| Acid extract | 0.73 | 1.03400 | 2.02600 | 0.91600 | 0.18950 | 0.04310 | 0.15070 | 0.11790 | 0.05680 | 0.03770 | 0.00500 |
| Insoluble residue | 98.81 | 2.82600 | 5.57200 | 2.40000 | 0.49000 | 0.11310 | 0.43270 | 0.51850 | 0.35000 | 0.38340 | 0.06130 |
| Total for all fractions | 100 | 3.86000 | 7.60000 | 3.31700 | 0.67930 | 0.15620 | 0.58350 | 0.63650 | 0.40690 | 0.42110 | 0.06630 |
| Total for all fractions to rock embankment | 1 | 1.02100 | 1.01000 | 0.99000 | 1.00100 | 1.01600 | 0.98500 | 0.98000 | 0.95500 | 0.97700 | 0.97000 |
| **Sand rock 51474 (non-productive)** | | | | | | | | | | | |
| Embankment of rocks | 100 | 17.10000 | 36.15000 | 16.33000 | 3.03700 | 0.66320 | 2.45000 | 2.04800 | 1.16000 | 1.10000 | 0.15400 |
| Organic substance | 0.99 | 0.00210 | 0.00290 | 0.00110 | 0.00020 | 0.00004 | 0.00016 | 0.00012 | 0.000066 | 0.000053 | 0.000009 |
| Acid extract | 1.63 | 2.59000 | 5.31200 | 2.93900 | 0.70220 | 0.15750 | 0.62880 | 0.42740 | 0.16060 | 0.10630 | 0.01300 |
| Insoluble residue | 97.38 | 14.36400 | 30.97700 | 13.14600 | 2.39200 | 0.52990 | 1.76160 | 1.62920 | 0.97280 | 0.98900 | 0.14300 |
| Total for all fractions | 100 | 16.95600 | 36.29000 | 16.09000 | 3.09500 | 0.68740 | 2.38450 | 2.05700 | 1.13340 | 1.09500 | 0.15600 |
| Total for all fractions to rock embankment | 1 | 0.99100 | 1.00400 | 0.98500 | 1.01900 | 1.03600 | 0.97300 | 1.00400 | 0.97700 | 0.99500 | 1.01300 |

**Table 6.** REE share in sand rock fractions, %

| Fraction | Fraction output | La | Ce | Nd | Sm | Eu | Gd | Dy | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Sand rock L-934 | | | | | | | |
| Organic substance | 0.87 | 0.060 | 0.030 | 0.030 | 0.020 | 0.030 | 0.020 | 0.020 | 0.010 | 0.010 | 0.010 |
| Acid extract | 0.73 | 26.770 | 26.660 | 27.620 | 27.880 | 27.580 | 25.830 | 18.520 | 13.960 | 8.950 | 7.540 |
| Insoluble residue | 98.81 | 73.170 | 73.310 | 72.350 | 72.100 | 72.390 | 74.150 | 81.460 | 86.030 | 91.040 | 92.450 |
| | | | | Sand rock 51474 | | | | | | | |
| Organic substance | 0.99 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 | 0.010 |
| Acid extract | 1.63 | 15.280 | 14.640 | 18.270 | 22.700 | 22.910 | 26.120 | 20.780 | 14.170 | 9.700 | 8.330 |
| Insoluble residue | 97.38 | 84.710 | 85.350 | 81.720 | 77.290 | 77.080 | 73.870 | 79.210 | 85.820 | 90.690 | 91.660 |
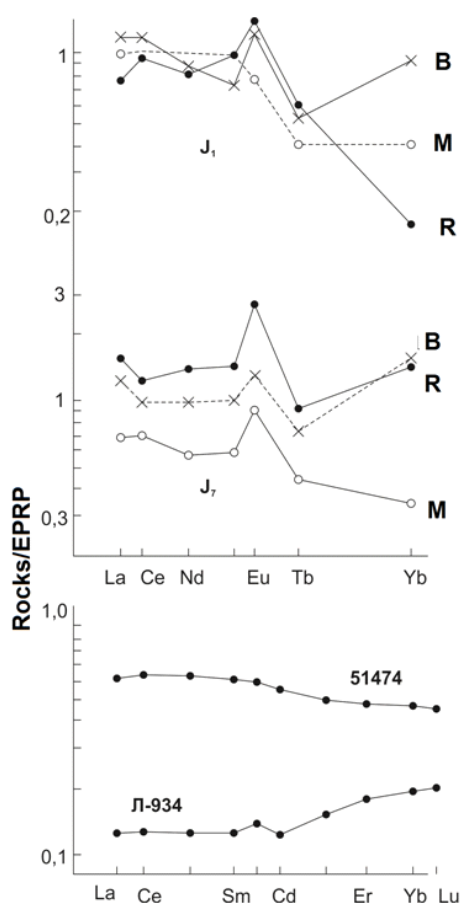


**Fig. 2.** Distribution of REEs in rocks of oil bearing formations and non-productive sand rocks of Jurassic sediments of the Western-Siberian lowland. REE contents of rocks are normalized upon the standard sample of Phanerozoic sand rocks of the Russian Platform (EPRP) [4]. $J_1$ – Khvoynoye, $J_7$ – Gerasimovskoye, where R - roof, B - bottom, M - middle part of oil bearing reservoir beds. 51474 and L-934 -non-productive sand rocks.

determine their REE contents were performed using ICP MS (Plasma LLC. Tomsk). All major results are given in Tables 2 – 7.

Degree of Eu* accumulation in relation of adjacent Sm and Gd in the rock and fraction is calculated according to the content of these elements in EPRP (Gd concentration was assessed upon Sm and Tb normalized values).

Analyses were performed using INAA (Tomsk). $(Eu/Sm)_N$ – upon lanthanides values normalized to carbonaceous chondrite ($\tilde{N}1$) [8].

**RESULTS AND DISCUSSION**

**REEs in rocks**

To compare REEs distribution in sand and argillites under consideration, the content of REEs in each rock was compared (normalized) with REEs of the standard general averaged samples of Phanerozoic sand rocks of the Russian Platform (EPRP), which REE concentration was determined using mass-spectrometry with isotope dilution in GI KNC RAN (Table 3). As seen from Fig. 2 for oil bearing reservoir beds, significant differentiation of predominantly heavy REEs (Yb) is typical, and relative accumulation is found almost in all rocks Eu/Eu* = 0.73-1.36 at 0.678 in EPRP).

In sand rocks of the Khvoynoye deposit (Fog. 3), the content of light REEs (La-Sm) is close to the prevalence of these lanthanides in EPRP, and in the section for the Gerasimovskoye deposit, argillites of the roof and bottom are enriched with all REEs similarly to the middle zone sand rocks. It can be stated that non-productive sand rocks of Jurassic sediments of the Siberian platform are slightly differentiated in REE content in relation to

**Table 7.** Distribution of OS (Corg.), resins and asphaltenes upon INAA data upon the section of J7 formation of the Gerasimovskoye deposit

| No. of samples | Sampling interval | OS and its fractions | Content of OS and fractions in HC, % | HC share from OS, % | REE content, g/t | | | | (Yb/La)N* | | (Eu/Sm)N** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | La | Sm | Eu | Yb | EPRP | C1 | EPRP | C1 |
| Sand rocks above the reservoir bed roof | | | | | | | | | | | | |
| 1-3 | 2754.7-2755.1 | OS total | 1.390 | 100.000 | 1.600 | 0.050 | 2.700 | 1.930 | 15.300 | 1.770 | 247.000 | 142.300 |
| | | Resins | 0.264 | 19.000 | | | | | | | | |
| | | Asphaltenes | not found . | | | | | | | | | |
| Reservoir bed roof argillites | | | | | | | | | | | | |
| 679-680 | 2757.4-2757.9 | OS total | 1.330 | 100.000 | | | | | | | | |
| | | Resins | 0.200 | 15.000 | 2.740 | 0.840 | 1.140 | 1.380 | 6.100 | 0.740 | 6.500 | 3.570 |
| | | Asphaltenes | 0.090 | 6.700 | 4.190 | 0.490 | 2.870 | 1.800 | 5.300 | 0.640 | 26.300 | 19.400 |
| Reservoir bed middle part sand rocks | | | | | | | | | | | | |
| 698-706 | 2766.8-2767.9 | OS total | 0.780 | 100.000 | 1.760 | 0.140 | 0.240 | 0.280 | 1.300 | 0.230 | 7.300 | 4.530 |
| | | Resins | 0.027 | 3.300 | | | | | | | | |
| | | Asphaltenes | not found . | | | | | | | | | |
| Sand rocks and argillites of reservoir bed bottom | | | | | | | | | | | | |
| 743-746 | 2776.2-2776.9 | OS total | 1.330 | 100.000 | | | | | | | | |
| | | Resins | 0.015 | 0.920 | 0.100 | 0.310 | 0.510 | 0.880 | 110.000 | 13.010 | 7.800 | 4.330 |
| | | Asphaltenes | 0.052 | 3.200 | 0.700 | 0.210 | 0.650 | 1.140 | 20.400 | 2.400 | 15.000 | 8.130 |

Fractions are extracted from OS in IHN SO RAN (analysts N.V. Pshenichnaya, V.M. Bembel). Asphaltenes were not found in the middle part and behind the reservoir bed roof.

* Ratios (Yb/La)N and **(Eu/Sm)N in the fraction are normalized to EPRP [4] and Ñ1 [8]

REE determination in OS, resins and asphaltenes was performed using INAA (Tomsk)

the RP standard sample. The REEs concentration is gradually decreased in them according to the increase in the sand rock maturity level from EPRP to sample 51747 and L-934 ($SiO_2$ growth, respectively, 86.5, 54-93, 73.0 %, Table 1), and the ratio Eu/Eu* is insignificantly increased towards the same direction (0.678-0.721-0.725, respectively).

**REEs in OS fractions**

OS fraction output in both reservoir beds is almost similar (KB 1.05-1.39%; GB 0.71-1.75%)

and close to that observed in non-productive sand rocks (0.87-0.99). But REEs distribution significantly differs from that observed in the rock itself (Fig. 2 and 3): in all OS fractions of oil bearing rocks of reservoir beds, minimal content of La is noted, along with maximum Tb è Yb with constant abnormal high relative enrichment of Eu. There are definite differences in ratios of individual REEs among the roof, bottom and middle part of reservoir beds, which was noted before[1]. The latter is seen

**Table 8.** Comparison of La, Sm, Eu and Yb values in
resins/asphaltenes ratios extracted from oils of various deposits

| Fraction | Tsoy et al. | | | | |
|---|---|---|---|---|---|
| S/A | La | Sm | Eu | Yb | Eu/Sm |
| G-M (roof) | 0.65 | 1.71 | 0.4 | 0.77 | 0.23 |
| G-M (bottom) | 0.14 | 0.48 | 0.78 | 0.77 | 1.62 |
| KK-DN (N) | 0.6 | 0.68 | 1.73 | 0.59 | 2.54 |
| UB-ON (N) | 1.31 | 1.41 | 0.47 | 0.22 | 0.33 |
| RS-DN (N) | 1.04 | 0.86 | 1.5 | 1.53 | 1.74 |
| RS-ON (N) | 0.43 | 0.3 | 0.4 | 0.45 | 1.33 |
| TA (N) | 9.85 | 0.87 | 0.16 | 0.61 | 0.18 |
| KDU (N) | 0.75 | 0.87 | 0.6 | 0.66 | 0.69 |

GM - Gerasomovskoye deposit (from OS rocks)
KK-DN (Karazhanbas deposit (Kazakhstan), produced oil
UB-ON - Urshak deposit (Bashkiria), residual oil
RS-DN - Samatlorskoye deposit (Russia), produced oil
RS-ON - Samatlorskoye deposit (Russia), residual oil
TA - Ashalchinskoye deposit (Tatarstan), bitumen
 KDU - Kokdumalakskoye oil and gas deposit (Uzbekistan)
Concentrations of lanthanides in GM position are determined using INAA, others
- by ICP MS.

The same from paper [10] on studies of oils of ancient platforms

| Fraction | | Gottikh et al. | | | | |
|---|---|---|---|---|---|---|
| No. | Element | La | Sm | Eu | Yb | Eu/Sm |
| 1 | SSB/A | 0.06 | 0.1 | 0.19 | 0.15 | 1.9 |
| 2 | S/A | 0.22 | 0.14 | 0.16 | 0.16 | 1.14 |
| 3 | S/A | 0.14 | 0.13 | 0.145 | 0.06 | 1.11 |
| 4 | S/A | 0.18 | 0.1 | 0.05 | 0.01 | 0.5 |
| 5 | S/A | 0.2 | 0.12 | 0.15 | 0.2 | 1.25 |
| 16 | SB/A | 0.014 | 0.013 | 0.013 | 0.02 | 1.0 |
| 16 | SSB/A | 0.05 | 0.065 | 0.065 | 0.052 | 1.0 |
| 16 | AUV/NPUV | 1.36 | 1.3 | 1.69 | 3.25 | 1.3 |

S/A - resins/asphaltenes                    S - resins
A - asphaltenes                    SSB - alcohol-benzene resins
SB - benzene resins                    AUV - aromatic hydrocarbons
NPUV - naphtha-paraffin hydrocarbons
REE concentrations in samples 1 – 5 and 16 from paper [10].
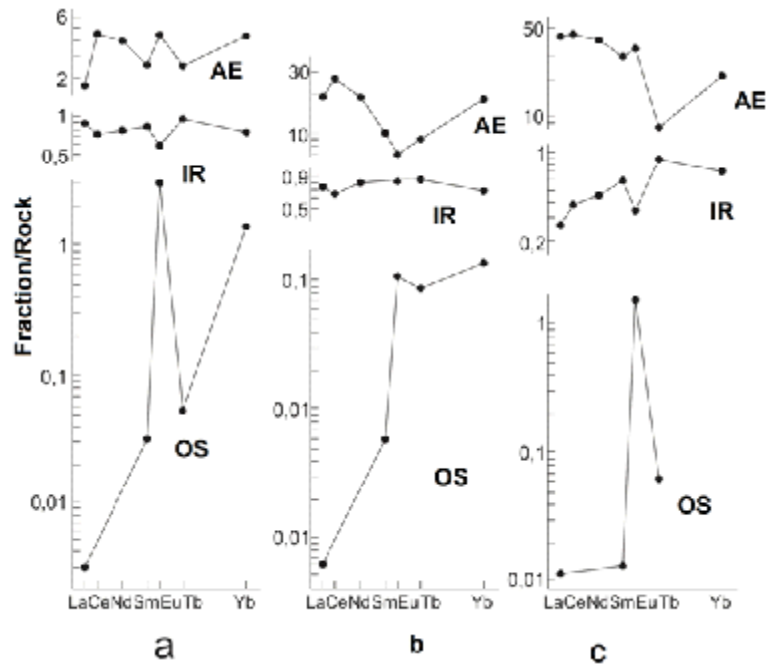
**Fig. 3.** REE content differences among fractions of OS, AE and IR of oil bearing sand rocks of Khvoynoye deposit formation $J_1$ REE prevalence in fractions is normalized upon REEs of rocks, where a - roof, b - middle, c - bottom of the formation
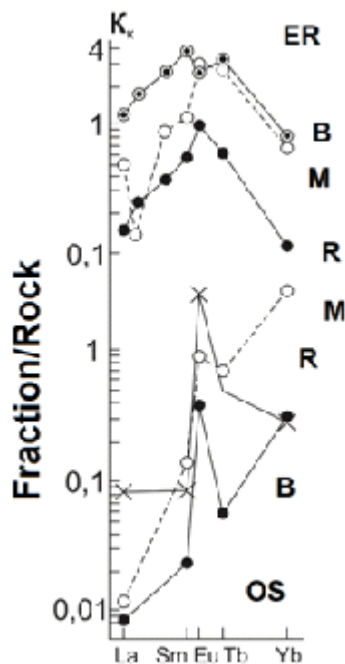


**Fig. 4.** Differences of REEs contents among OS and AE fractions of oil bearing rocks of Gerasimovskoye deposit formation $J_7$ (R- roof, M - middle, P - formation bottom)

from values $(Tb/La)_N$, $(Yb/La)_N$ in OS normalized upon the same ratios of initial rock, and Eu* - Eu enrichment degree in OS as compared to the initial rock:

Thus, roof and bottom OSs on both reservoir beds are at maximum enriched with Eu in relation to the middle part, roof - Yb as compared to other zones of the reservoir bed, the middle - Tb (Fig. 4). Unlike oil bearing rocks, in OSs of non-productive sand rocks, another ratio of REEs is found, with total reduced REEs content (Fig. 5): As compared to the initial rock, OSs of both sand rocks are enriched with light lanthanides, especially with La. REEs relations in OSs normalized upon the rocks for both sand rocks are as follows: (Tb/La calculated as average between Gd/La and Dy/La):

| Sample | (Tb/La)N | (Yb/La)N | Eu* |
|---|---|---|---|
| L-934 | 0.29 | 0.15 | 1.14 |
| 51474 | 0.5 | 0.39 | 0.95 |

It follows from the analysis of individual lanthanides that contents of REEs in OSs of oil
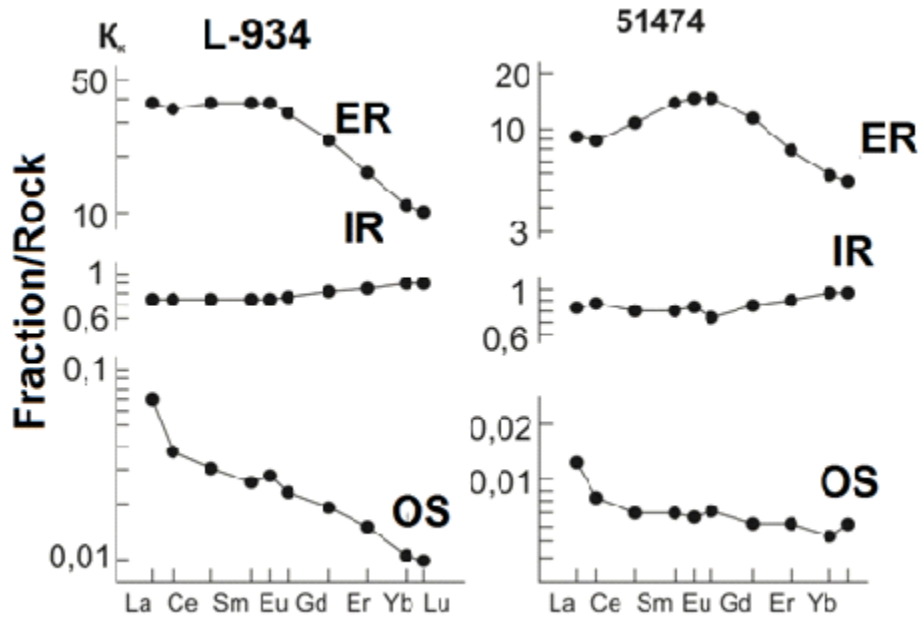
**Fig. 5.** REE content differences among fractions of OS, AE and IR of non-productive sand rocks of Western-Siberian lowland Jurassic sediments. L-934 - Kraviniskaya well, 51474 - Severo-Yutymskaya well
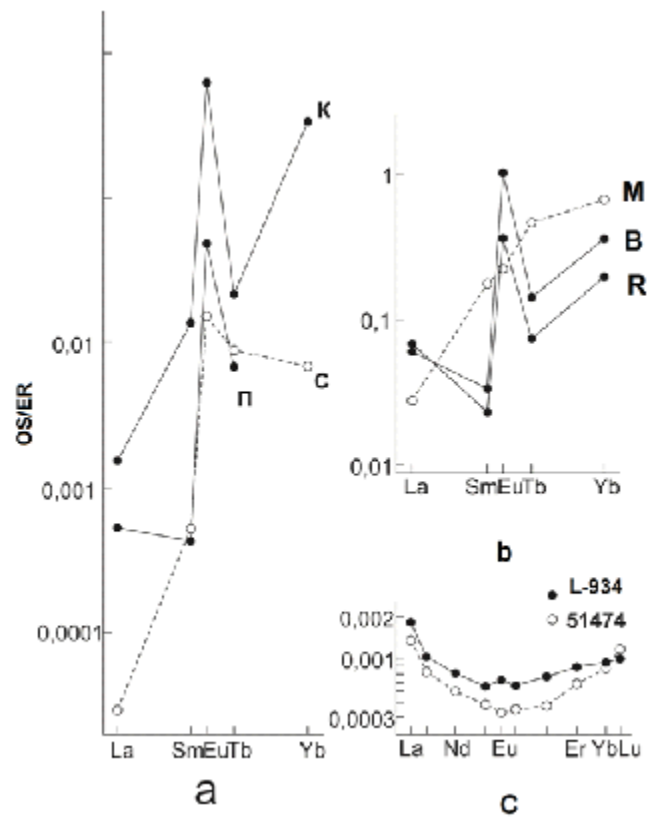


**Fig. 6.** Comparison of contents and concentrations of OS and AE REEs from oil bearing sand rocks (a, b), where R - roof, B - bottom and M - middle part of the reservoir bed and non-productive sand rocks (c)
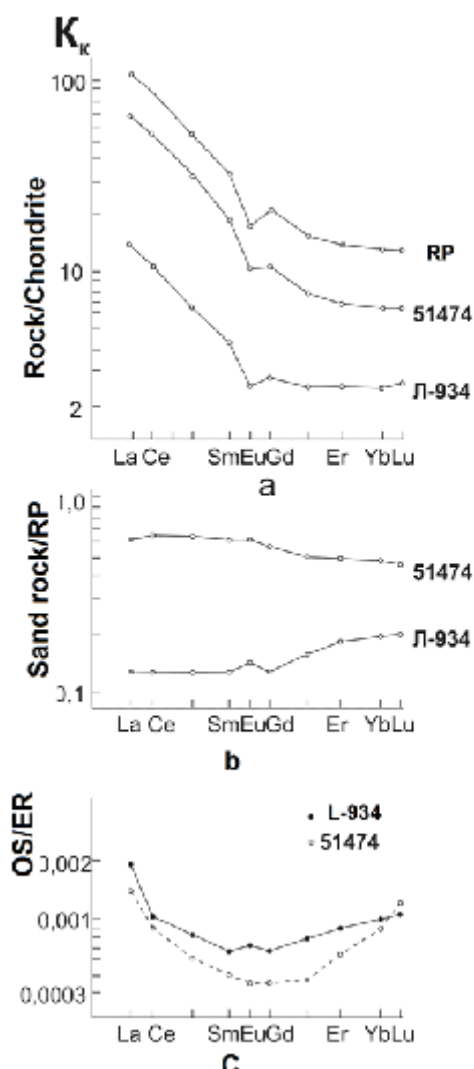
**Fig. 7.** Comparison of normalized values of REE composition of non-productive sand rocks and their differences in the content of OS and AE REEs

bearing and no-productive rocks are radically opposite, with almost no positive abnormalities in OSs of the latter in terms of Eu (Fig. 6, 7, 8).

EEs relations in OSs normalized upon the rocks for both sand rocks are as follows: (Tb/La calculated as average between Gd/La and Dy/La):

| Sample | (Tb/La)N | (Yb/La)N | Eu* |
|---|---|---|---|
| L-934 | 0.29 | 0.15 | 1.14 |
| 51474 | 0.50 | 0.39 | 0.95 |

It follows from the analysis of individual

lanthanides that contents of REEs in OSs of oil bearing and no-productive rocks are radically opposite, with almost no positive abnormalities in OSs of the latter in terms of Eu (Fig. 6, 7, 8). It can be especially well observed in REE distribution spectrum for chondrite-normalized from contents in fractions of non-productive sand rocks in Fig. 8 - in the organic substance REE distribution.

Consequently, abrupt increase in Eu value in rocks of reservoir beds shall be considered as a sign of oil bearing capacity; moreover, maximums of Eu in the roof and bottom of reservoir beds testify bed capacity. In parallel with high Eu-abnormalities, the sign of relative enrichment with medium and heavy REEs in the organic phase of oil bearing rocks compliments such interpretation of results. Balance calculations upon fractions on the basis of data from Tables 4, 5 and 6 with respect to the output of individual fractions (%) showed that the share of each light REE (La-Sm) in OS of oil bearing reservoir beds is 0.001-0.2% of their content in initial rocks. For heavier REEs it exceeds 0.7-1.4%, and only for Eu in the roof and bottom of the bed it can reach 2-3% (Table 3). In non-productive sand rocks, the share of individual REEs in OS does not exceed 0.01-0.03%, and only for La it reaches 0.06% from their content in initial rocks (Table 6).

Thus, the prevalence of medium and heavy REEs and especially Eu in OSs of oil bearing rocks by several levels exceeds the content of these lanthanides in ordinary sand rocks, which once more points at the connection between the REE concentration and peculiarities of the ratios in OSs of oil bearing rocks with oil components.

To specify, with which hydrocarbons and how REEs interact, the REE distribution in resins and asphaltenes was studied for OS extracted from rocks in the section of Gerasimovskoye deposit oil formation $J_7$. Output of OS fractions ($C_{org}$, Table7) shows that asphaltenes are predominantly concentrated in the formation bottom, and only their small part is concentrated in the roof. Content of resins is gradually increased from the bottom to the roof (just as he share of resins in OS), and some amount of resins emigrates beyond the bed to overlapping and rocks. Both fractions of hydrocarbons are described by enrichment with medium and heavy lanthanides, and according to high ratio of Eu/Sm (6.5-247 relative to EPRP and
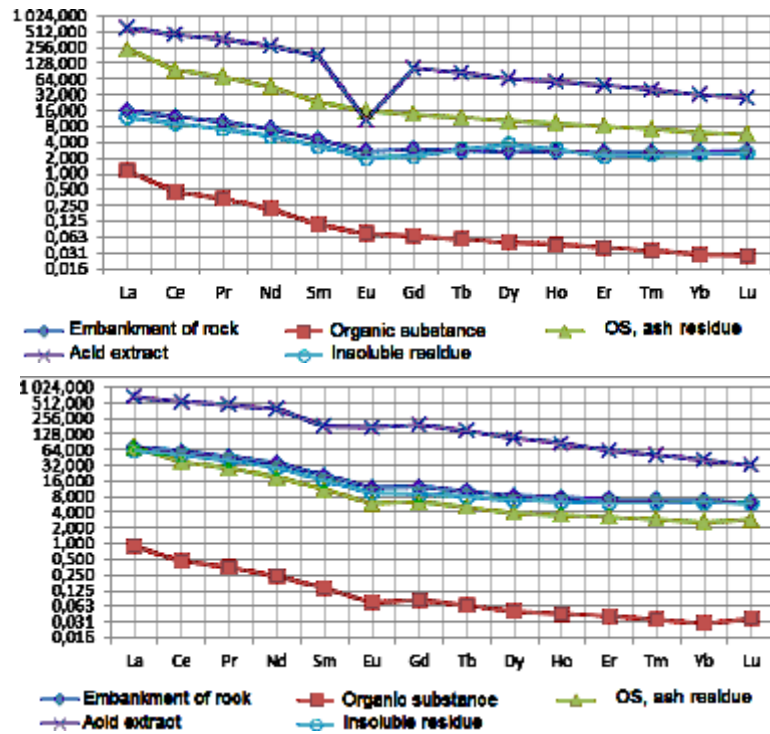
**Fig. 8.** Variations of REE distribution in non-productive sand rocks and their fractions.
REE values are normalized to carbonaceous chondrite (Ñ1) [8] (upon data from Table 3).
Pr, Tb, Ho, Tm are calculated upon mean concentrations of adjacent lanthanides
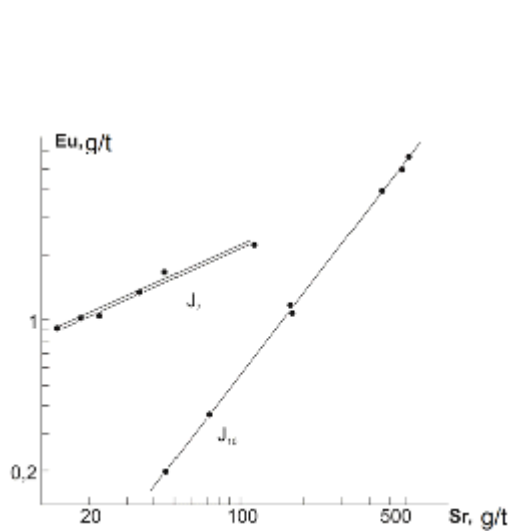


**Fig. 9.** Direct correlation between Eu and Sr content in OS of oil bearing formation $J_7$ and $J_{10}$ of the Gerasimovskoye oil and gas bearing deposit (well 18.)
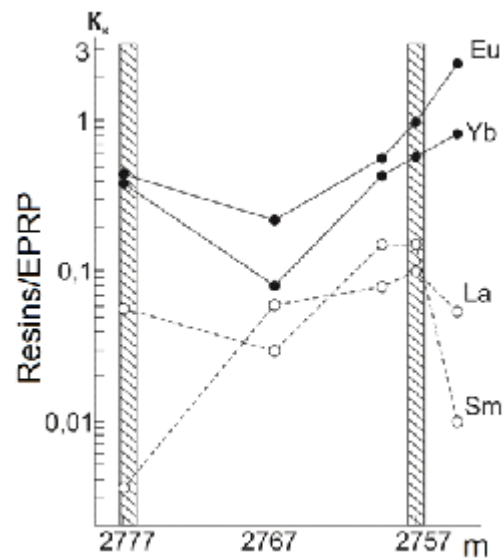


**Fig. 10.** Changes of concentrations of individual REEs from the bottom to the roof and above the roof in resins from OS extracted from respective zones of the Gerasimovskoye deposit oil bed ($J_7$) Resin REE concentration is normalized upon EPRP.

Ñ1 (Table 7) - by excess of Eu.

As in ordinary sedimentary rocks, Eu/Sm is 1, high Eu/Sm ratio for both hydrocarbons roves selective enrichment of Eu. This is agreed with data for Eu in OS of all studied oil bearing rocks of both beds, where Eu for OS is 1.4-128 relative to EPRP (Table 2). Eu abnormal enrichment is also noted for oil asphaltenes from Jurassic and Cretaceous deposits of the Western Siberia in paper [2]. The only possible explanation for selective Eu accumulation as compared to adjacent Sm, Gd and Òb - change of Eu valence, as Eu differs in chemical properties from adjacent trivalent REEs only in $Eu^{2+}$ [1]. Based on latest data on the size of ionic radii of REEs in octamerous coordination [9], we can see that $Eu^{2+}$ has the largest ionic radii equal to 1.25 Å as compared to $Eu^{3+}$ (1.04 Å) and adjacent trivalent ions ($Sm^{3+}$ = 1.079 Å; $Gd^{3+}$ = 1.053 Å; Tb = 1.04 Å). Hence, we can claim along with preferred extraction, proposed in [2], about hydrocarbon compounds of heaviest REEs with minimal ionic radii, and we can also talk about predominant concentration of largest cations in OS. As the ionic radius of $Eu^{2+}$ coincides with $Sr^{2+}$, we can expect parallel accumulation of Sr in OS in the deposit section. Such a version was checked by correlation of these elements for OS of alcohol-benzene mixture of two oil bearing formations of the Gerasimovskoye deposit (Fig. 9).

As seen from Fig. 9, a straight dependency exists between Eu and Sr. The determination of such dependency within oil bearing deposits is an additional argument for the change of Eu valence and its extraction by oil and gas hydrocarbons, predominantly in $Eu^{2+}$ form. Hence, we can expect emergence and acquiring of such properties by other REEs as well, capable of changing valence in reduction media (Sm, Yb). On the other hand, the combination of accumulation of heaviest and lightest REEs in OS points at the possibility of selective capture of individual REEs by various OS fractions. Both these provisions are proved when comparing the REE content of resins and asphaltenes extracted from the same OS. Thus, for the roof and bottom of the Gerasimovskoye deposit (Table 7), not only the difference in the REE enrichment level is found, but also, in both cases, an unusual Sm value is noted as compared to asphaltenes, which points at possible partial redistribution of Sm in $Sm^2$ form.

| Formation zone | Fraction | La | Sm | Eu | Yb |
|---|---|---|---|---|---|
| Roof | Resins/ asphaltenes | 0.65 | 1.71 | 0.40 | 0.77 |
| Bottom | Resins/ asphaltenes | 0.14 | 1.48 | 0.78 | 0.77 |

Then, during the analysis of REE redistribution in resins, upon $J_7$ formation section (Fig. 10), differential mobility of individual elements is revealed, and La fractioning inside the bed from the bottom to the roof differs in more intensity and consecutive accumulation to the roof as compared to other REEs, for which the maximum is found in the bed's middle zone; on the contrary, Eu and Yb accumulation and abrupt decrease in La and Sm contents is found in the resin beyond the reservoir bed. Separation of Eu and Sm beyond the formation underlines the difference in chemical properties of both elements in this zone, which can be interpreted simply as a sign of Eu accumulation in $Eu^{2+}$ form, which is possibly true for Yb as well (transfer in $Yb^{2+}$ form). In this connection, we shall pay attention to predominant Yb enrichment of asphaltenes and petrologen as compared to adjacent lanthanides ($Lu^{3+}$) that can't change valence according to paper[2, 9]. We should also remind that the decrease in the relative accumulation degree in OS of oils in the row Eu-Yb-Sm is agreed with the difference of their redox potential[1].

We should note that the aggregate of data obtained for REEs in OS and its fractions extracted from oil bearing rocks, and in hydrocarbon fractions of oils, allows making the following geochemical interpretation of REE behavior: REE fractioning is related to processes of predominant accumulation of heavier lanthanides due to the increase in strength of complex REE compounds in the row La-Lu. Impact on individual lanthanides in a highly reductive environment created by hydrocarbons of oil fluids conditions the change of Eu, Yb and Sm valence. Consequently, the change of redox conditions towards highly reductive is the main reason for transition of these lanthanides into the bivalent form and formation of complex compounds with oil hydrocarbons.

Relation of these two processes can be

assessed more precisely by investigating the REE content of the mineral agile complex (MAC) of initial rocks.

**REE in acid extracts**

In this paper, similarly to [**6**] and others, REEs extracted from rocks are taken as MAC REEs, with their treatment by 1.8% ÍÑl (AE). As a rule, REEs absorbed on lutaceous fractions of sedimentary rocks and REEs of authigenic minerals are transferred into the solution. REE concentrations in AE of sand rocks is 2-4 times higher than the prevalence of REE in initial rocks (Fig. 3 and 4), and in aleurolites of the Gerasomovskoye deposit, the REE concentration in AE is decreased 90.2-4 as compared to the initial rock). Differences in REE accumulation in AE for sand rocks and aleurolites reminds about a similar change in REE content for the lutaceous fraction <2m among sands, aleurolites and clays upon the facial profile of the Upper Pennsylvania sedimentary basin. Comparison of REE concentrations in fractions <2m shows that REEs of oil bearing sand rocks is 5-10 times higher than the initial concentration of non-productive sand rocks, and in aleurolites and clays it is only 1.5-0.6 of REEs of rocks[7].

Among AE REEs and fractions <2m of sand rocks, relative accumulation of medium and light REEs is found, for which Yb enrichment is typical of AE of oil bearing rocks. As REEs of the mineral agile complex (MAC) of sedimentary rocks are the source for extracting some REEs to OS, REE redistribution between OS and AE reflects the essence of REE fractioning that depends on the OS chemical structure, sorption and migration properties of oil components. It follows from the comparative analysis that the organic substance of research objects - oil bearing rocks and non-productive sand rocks - is enriched both with light (La) and heaviest REEs (Fig.6). Difference of oil bearing OS sign is expressed in predominant accumulation of heavy REEs with Eu excess, whereas non-productive sand rocks have maximum enrichment in OS La with no visible changes in Eu* relative concentration (Fig. 6, 7, 8).

**REEs in insoluble residue**

The fraction of sedimentary rocks after the removal of OS and AE almost in all cases (Fig. 2.5) contains REEs that are insignificantly enriched with heavier lanthanides. As shown in paper[7], this is conditioned by the presence of heavy fraction containing accessory concentrates of REEs resistant to weathering (zircon, etc.) In the balance of rocks REEs, the insoluble reside (IR) is 25-90% of individual lanthanides (Table 5 è 6).

Thus, it follows from the geochemical analysis and REE balance of oil bearing and non-productive sand rocks and their fractions that migration possibilities in trap zones of Eu, Yb and Sm deposit are conditioned by bivalent state of these lanthanides in a highly redox environment created by oil and gas HC.

This version is also confirmed and well seen when comparing the results of REE analysis in fractions of extracted and residual oils at the background of REE concentration of these high-molecular compounds of oils and ancient platforms given in paper[10].

From Table 8 we can see that Eu values - ratios from KK-DN deposit (Eu/Sm)=2,54, and produced oil significantly exceed similar values of these ratios in residual oil of UB-ON (0.33). Similar behavior of these lanthanides is observed in the Samatlorskoye deposit as well. All these prove the initial significant accumulation of Eu, Yb è Sm in bivalent form in the bed prior to the deposit development and their further extraction from the deposit along with oil and gas HCs during industrial use. So, first of all, lanthanides with large ionic radius – $Eu^{2+}$, $Yb^{2+}$ and $Sm^{2+}$ - are subject to migration processes. From trivalent REEs, $La^{3+}$ has the largest radius, so its presence in the organic phase is rather consistent.

A general preliminary conclusion is that the differentiated, abnormal behavior of individual lanthanides with the valence change is possible in highly redox conditions and only in the presence of sufficient amount of oil and gas hydrocarbons in fluids of sedimentary rocks, e.g., these processes are of local and indicative nature within oil and gas bearing sediments. To prove the correctness of such a conclusion, we would like to give similar ratios according to paper[10]. As seen from Table 8, values Eu/Sm in S/A ratios of oils from different deposits differ significantly, whereas these relations according to paper[10] almost equal to 1 and correspond to values Eu/Sm considered in sedimentary processes[11,12].

REEs as geochemical criteria of oil-bearing capacity of rocks in the sedimentary cycle.

The practice of exploration drilling considers geophysical logging as the major method for preliminary assessment of oil bearing formation boundaries. But diagnostics using this method is complicated by the presence of water bed, fractures and other geological factors. When studying REEs in fractions of sedimentary rocks, all sections of the core used for this purpose from the above wells were described by geophysical data and were referred to oil formations, according to the latter. In reality, only for the Khvoynoye and Gerasimovskoye deposits, the geophysical forecast is proved upon geochemical abnormalities in OS - Eu excess and enrichment with heavy REEs. In two other cases, we dealt with non-productive sand rocks, which REE concentration, along with that in individual fractions, was absolutely different from oil bearing rocks. In other words, geophysical interpretation in ratios of both sand rocks as oil bearing ones was not confirmed.

## CONCLUSION

The geochemical analysis experience showed that the information concerning REEs of the organic substance in diagnostics of oil bearing capacity is unambiguous if sings of abnormal Eu/Eu* accumulation in OS are used. Moreover, we can determine the most oil saturated part of reservoir beds upon the existence of maximum Eu values in the roof and bottom OS. So, despite the use of early investigation results as compared to the results of previous years, the paper is considered to be up-to-date as the possibilities of applied geochemistry of REEs in oil geology are far from end and are urgent at the moment. Considered behavior of REEs in the reduction environment created by oil and gas hydrocarbons allows assuming participation of other lanthanides apart from Eu, Sm and Yb in determining geochemical criteria of oil bearing rocks. These lanthanides can be Ce, Pr and Tb that are also capable of changing valence and non-specific behavior of Y and Ho in sedimentary processes with participation of oil fluids. It's easy to notice that this paper contains no explanations on Tb behavior in the organic complex of rocks along with La, Eu, Sm and Yb and given paper [1]. Hence, we see that further studies are impossible without combined consideration of formation processes

of oil and gas hydrocarbons and the mechanism for transformation of the buried organic substance considered in papers[13-17] with geochemical studies of REEs. The main thing is that they are impossible without determining reasons for REE relation to oil components, especially with its highly molecular part.

The selection of REEs in geochemical studies and in the paper in particular is sufficiently justified due to the presence of significant chemical differences of REEs from other elements[18,19,20]. Against the background of differences and fundamental properties of REEs[11], the mechanism of using REEs is defined for geochemical studies in oil and gas bearing sediments, where significant differences of their functions are reflected. Consequently, there is practicability for further studies of REE behavior in sedimentary rock with oil fluids.

1.  When investigating REEs in rocks and fractions of OS, AE and IR of oil bearing formations and no-productive sand rocks of Jurassic sediments, a difference in the content and concentration of REEs in OS was found, which is conditioned by specific content of OS fraction and redox conditions created by fluid oil components in the deposit, which is shown and implemented by high relative enrichment of Eu and heavier REEs in OS of oil bearing rocks as compared to standard sedimentary rocks, where OS is enriched by La with light REEs.

2.  Signs of selective fraction of Yb and Sm in OS fractions of oil rocks were found by analyzing REE balance in them, and we can assume migration in bivalent state.

3.  Large abnormalities of Eu accumulation in OS of oil bearing rocks and especially in the bottom and roof of reservoir beds are a geochemical sign showing the presence of oil and boundaries of oil formation in the well section.

Sharkova (isotope geochemistry and geochronology laboratory of the Geological Institute KNC RAN, Apatity, and N.V. Phenichnaya; V.M. Bembel for extraction of resins and asphaltenes from alcohol-benzene mixture of oil bearing rocks of the Khvoynoye and Gerasimovskoye deposit beds (IHN SO RAN), Gerasomova N.N. (IHN SO RAN) for extraction of HC fractions of oils from extracted and residual oil of various deposits. Special acknowledgment is given to Balashov Y.A., Doctor of Geological Sciences, Professor of TIN KNC RAN for careful attention to this paper and recommendations.

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