

Rare Earth Elements and Yttrium in Carbonate Reef Deposits Containing Hydrocarbons of Oil and Gas

Klimenty Sergeevich Tsoy

Federal State-financed Educational Institution of Higher Professional Education
“National Research Tomsk State University” (TSU), Tomsk, Russia

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Abstract: For the first time anomalies in the behaviour of cerium and europium simultaneously among other REE are discovered in the processes of sedimentation.” The reasons of differentiation of certain lanthanides in the composition of REE and fractioning of REE in reef deposits fractions are considered with the presence of hydrocarbons of oil and gas as the main components affecting the stabilization of an unusual valence state of certain lanthanides able to change valence depending on the oxidation-reduction conditions in sedimentary cycle. According to the recorded anomalies of certain lanthanides in the range of REE the arguments are given supporting the possibility of REE isomorphism occurrence with the displacement of Ca and Mg by Nd and Tb and yttrium by holmium. Also the possible factors are considered defining relationship of REE with the derivatives of oils and bitumoids, namely with their high-molecular compounds (tars, oils and pyrobitumens containing N, S and O).

Key words: Rare earth elements • Hydrocarbons of oil and gas • Valence • Ionic radius • Isomorphism • Differentiation • Fractionation

INTRODUCTION

The differentiation of lanthanides in rare earth elements (REE) of the sedimentary cover rock was considered generally in a number of papers [1-5 and others]. The spread and abnormal behavior of certain REE are connected in the first place with the deficit or excess of Ce and Eu in REE, which can have two forms, Ce^{4+} and Ce^{3+} and Eu^{3+} and Eu^{2+} [1] depending on the oxidizing or reducing conditions in magmatic, metamorphic, hydrothermal [2-5] and other processes. The detailed analysis of the variety of REE mineral concentrators will not be conducted here, although many of them are usual components of marine and river deposits. Only zircons from sedimentary complexes which are particularly researched in recent years due to the rigidity of the structure and used as the indicators of different types of rocks generation conditions will be mentioned [4]. This reflects to some extent the interconnection with the sedimentary deposit generation, but not with the generation of buried organic matter (OM). However, these processes (magmatic, metamorphic, hypergene, hydrothermal and others) overlapping with

sedimentary form epigenetic (secondary) mineral movable complex (MMC) able to interact with the organic complex (OC) of sedimentary rocks [Error! Reference source not found.6]. Such interaction involving hydrocarbons of oil and gas under certain oxidation-reduction conditions leads to the differentiation of certain lanthanides in REE, including Ce and Eu. The synchronism of the appearance of Ce and Eu negative anomalies in certain fractions has been first noted (Pic.1-5) despite their contrast oxidation-reduction properties [2,5,8]. This can be considered as a sign of the presence of REE organo genetic components in oil-bearing systems.

So far there have been no information sources concerning genetic relationship of microelements including REE with buried organic matter (OM), oil and its components. This information is critical for oil-bearing complexes analysis, which is given in this paper.

The fundamental statement of the question about the possibility of causal relationship between REE and oil, especially with its high-molecular polycyclic compounds containing atoms of N, S and O - gums and pyrobitumen, as well as with its saturated and aromatic hydrocarbons, can solve the above-mentioned problem of oil-bearing

complexes analysis. The assumption about the possibility of REE migration in the form of metal organic complexes, particularly due to REE presence in the bituminous phase of subsurface reduced fluids was made in the paper [9].

Another assumption is made in the given paper: the presence of REE in oil fluids and oil fractions due to REE complexing properties and their transfer from mineral moveable rocks (MMR) to the hydrocarbon phase after the formation of oil fluids from buried OM (kerogen) inside the sedimentary cover. This assumption is based on the results of the analysis and behavior of the REE of the fractions of rocks and oils from Western Siberia oil-bearing collectors zones. REE balance in the rocks and oils fractions (correlation of REE concentration in mineral and organic parts) proved the possibility of such relationship and the reasons of differentiation of certain lanthanides in rocks organic complex (OC) [9]. So, it is obvious from the previous researches [7, 6] that the relationship between MMC REE and OC REE can exist during the process leading to the change of REE chemical properties (oxidation-reduction medium and others) and the possibility of such relationship can only be connected with the formation and presence of oil fluids in sedimentary rocks.

One of the ways of extracting oil fluids is the benzyl alcohol mixture (BAM) extraction (1:1) of test samples with further filtration of the solution through a paper filter whose pores size are 1-10 micrometers. The molecule size of naphthalenes and other compounds is not bigger than 100 Å (pyrobitumens - 50-100 Å) and the molecule size of the microparticles of the oil fluids colloidal solution can be from 10 to 10000 Å [10]. Therefore, the composition of the received product BAM presents the whole complex of naphthalenes of water-saturated rocks and is a complex system of relationship between mineral and organic phases in the oil-bearing deposits pores system. That is why according to the concept under consideration, the only factors of REEs interaction between the given phases are probably the processes of the formation and spread of oil itself. According to the researches Tisso B. Velte D.[10] and others, migration and transfer of oil and gas components is possible through the pores of sedimentary rocks in colloidal, micellar molecular solutions, which means that all interaction processes between REE and naphthalenes in the sedimentary process are also connected and occur with hydrocarbons of oil and gas under the influence of thermodynamic conditions in the complex system of carrier beds pores and in the conditionally closed system of trap-deposit.

Hence it is possible to compare, in the first case, the mechanism of a part of REE transfer in rocks with oil-bearing deposits with the similar mechanism in ocean suspension [2,3]. The only difference is that processes of transfer and exchange occur in different thermodynamic conditions and environment, especially in the closed system of oil collector as a geometric body in the enclosing rock.

In the second case the REE fractionation processes are connected with:

- Sorption properties of the hydrocarbons of oil and gas components and chemical properties of REE due to the ability of these REE to change valence and ionic radius in oxidation-reduction medium;
- Increasing of complexing properties from La to Lu;
- REE ability to isomorphism as a result of monotone change ("lanthanide compression" effect) of lanthanides ionic radii in La-Lu series.

Today ICP MS methods allow to define a wide range of microelements including full composition of REE in tar, oils and pyrobitumens as well as innaphthene-paraffin (NPHC) and aromatic (AHC) hydrocarbons [9]. From the structure of pyrobitumens by Yen given in [8], microelements (M) and possibly REE can be a part of intermolecular or intramolecular packets i.e. interlayer packet space as a result of electronegativity of BMC (organic ligands) and positivity of REE ions (cations).

It can be assumed that REE due to complexing properties with organic matter (OM) can enter into the composition of these complex high-molecular compounds.

Such interpretation is most likely possible only for pyrobitumens on the assumption of macrostructure of pyrobitumens in the classical understanding of oil geochemistry. However, tar is highly unstable and present a one-layer structure in the pyrobitumen structure. In this case, the occurrence of REE in resins as well as in other oil derivatives (oils, aromatic and saturated hydrocarbons) can be explained by the presence of metal-organic components in oil fluids different from the structure of porphyrins (V and Ni compounds between N atoms) which form as a result of direct interaction with carbon atoms like in cyclopentadienyl REE derivatives (C_5H_5)₃Ln [01]).

Such version can be proved on the basis of fundamental physicochemical properties of REE [2,8] and on the researches on synthesis of metal-organic REE compounds [11]. To support the idea of the possibility of metal-organic REE complexes formation in oil fluids, the following can be taken from the paper [11] analysis:

Table 1: Rare-earth elements concentration (g/t) in North American schist (NASC), clays of Russian platform (RP), chondrites (C1) and insoluble residue of benzyl alcohol mixture (IR) of the given paper

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Source
NASC	32	73	7,9	33	5,7	1,24	5,2	0,85	5,2	1,04	3,4	0,5	3,1	0,48	[0]
RP	37,5	74,8	8,6	32,2	6,2	1,3	5,21	0,79	4,88	0,96	2,78	0,41	2,73	0,41	[Error! Reference source not found.]
C1	0,237	0,613	0,093	0,457	0,148	0,056	0,199	0,0361	0,246	0,0546	0,16	0,0247	0,161	0,0246	[0]
IR	1,5	0,66	0,22	0,74	0,14	0,028	0,17	0,027	0,22	0,079	0,137	0,018	0,09	0,017	Sample 1

- Lanthanides belong to strongly positive elements. The sizes of their standard electrode potentials are close to the corresponding values of alkali and alkali-earth metals;
- High electro-negativity of organic ligands is enough for the formation of REE compounds;
- High complexing properties of REE compounds are caused at the first place by the presence of vacant 5d₂-orbitals;
- The big enough size of REE ions the presence of available vacant 5d-orbitals make them strong Lewis acids which helps the formation of the “L_n- organic ligand” connection;
- Metal-organic REE compounds (Sm, Eu и Yb) are soluble in aromatic hydrocarbons which are usually oils and bitumoids compounds;
- The properties of REE organic complexes are well described in terms of ionic models i.e. first, by electrostatic interaction of REE ions with the molecules of organic ligands and then probably by covalent bonds between them;
- The most important observation from the paper [13] is also the following: “the wide-spread coordination number (CN) in metal-organic REE compounds is 4, but CN can reach 9 and even 12, as a rule the quantity of the molecules of coordination-bonded ligand depends on the method of extraction of the complex from the solution. At the same time some kinds of compounds cannot be received free from coordination ligands”, which is possibly one of the reasons of REE fractioning between the fractions of oil and bitumen-like substances.

The presence of the full specter of lanthanides as an established fact has been discovered in many examined fractions of oils from the sedimentary rocks of oil-bearing deposits by ICP MS method.

In the given paper OC BAM signifies a complex of organic and mineral components received as a result of the extraction of rock samples by benzyl alcohol mixture. Due to the known reason there are no data in the paper concerning acid extract (1,8% HCl) as the cut is presented

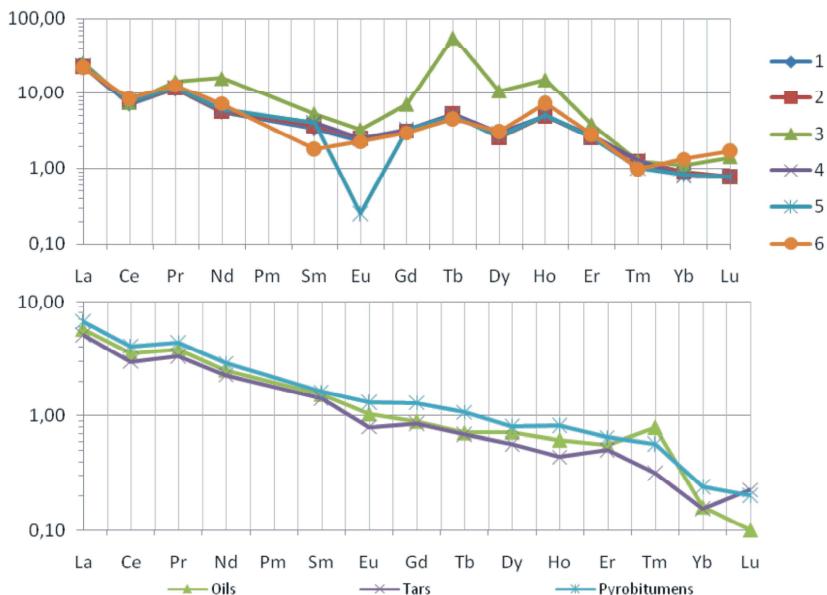
by limestones (biomorph-coral deposits). The variations of REE composition in OCBAM and in an insoluble residue (IR) and geochemical processes are considered in comparison with REE values of these fractions, normalized for REE composition in chondrites (C1) because the content of REE in insoluble residue is more comparable with lanthanides content in C1 [12] than in North American schist (NASC) or clays of Russian platform (RP). For the interpretation of geochemical processes the data on the size of ionic radii in octantal coordination are used [1].

In the total, despite the absence of comprehensive information about the reasons of anomalies of certain lanthanides in oil-bearing deposits, particularly about the abnormal behavior of Ce and Eu, as well as, Tb, Pr and Ho and the absence of the records of these anomalies in the REE composition of carbonate deposits, it is possible to set the task of geochemical analysis of REE in the investigated areas.

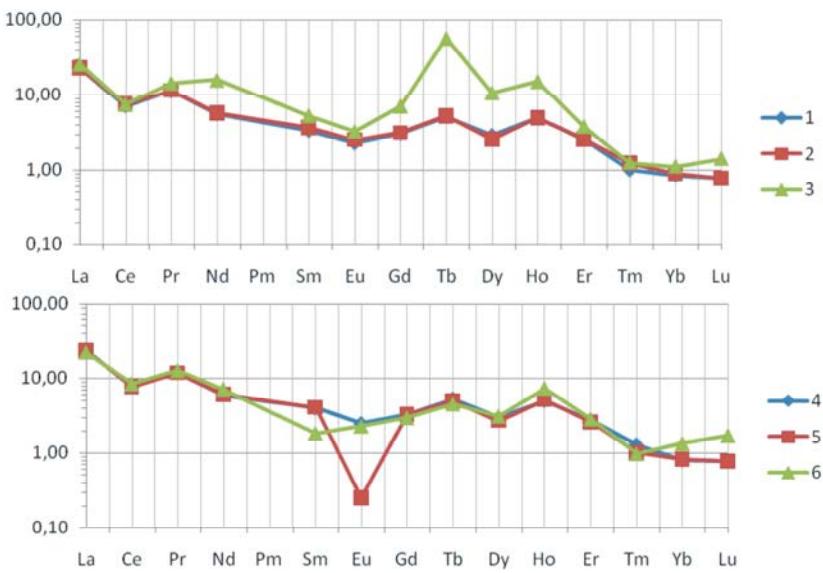
RESULTS AND DISCUSSION

Anomalies of Tb and Pr were recorded during the researches of reef deposits in the open-cast well 12 of Kokdumalakskoe oil and gas field situated in the Republic of Uzbekistan. The open cast is presented by biomorph-coral deposits, in the top - by anhydrite and halite, in the bottom - by detrital and clay deposits. The age of the deposits is upper Oxford /low Kimmeridge epoch. REE analysis are performed in BAM samples and in insoluble residue. Also, the concentration of REE is defined in oils, tars and pyrobitumens, extracted from the sum of samples of OC BAM, the results are given in the Tables 2,3.

It is important to point out the difference in average concentration of REE sum (total return - TR) in insoluble residue - 8,435 gpt and TR in OC BAM - 24,422 gpt (Table 2). TR in OC BAM is 2,89 times higher than TR in insoluble residue, what is not typical for similar values of TR in oil-bearing deposits of clastic complexes. TR balance, according to [6], varies from 30 to 70% between MMC and OC.



Pic. 1: The contrast of the allocation of the chondrite-normalized values of REE in OC BAM (a) and in the oil fractions of Kokdumalakskoe oil and gas field



Pic. 2: Chondrite-normalized differences in REE allocation in OC BAM of oil and gas fields.

Considering, regardless weight losses (Table 4), the sum of REE in source rock equal ($TR_{OC\ BAM} + TR_{IR} = TR_{REE}$), it is obvious that $TR_{OC\ BAM} \gg TR_{IR}$ and makes 70% of TR_{REE} . So, in the given paper a reverse balance of $TR_{OC\ BAM}$ of carbonate deposits is observed - 70% of TR_{REE} , while in clastic rocks $TR_{OC\ BAM}$ makes 30% [6, 9]. As a result, it is possible to assume the presence of significant influence of organic component of the original rock on geochemical behavior of REE in carbonate reef deposits with the presence of hydrocarbons of oil and gas.

The pic. 1 shows significant difference in abundance of certain lanthanides in REE of OC BAM and in REE of oil fractions. The differentiation of certain lanthanides observed in REE OC BAM show that anomalous behavior of Tb, Pr and Ho can be definitely associated with OC BAM and OC BAM can be considered as a complex system of REE transfer, where the exchange of REE between mineral and organic parts of oil fluids occurs. As colloid solutions may contain non-sedimentalsubmicroparticles, there could be the exchange and transfer of REE by microparticles,

Table 2: REE concentration in IR and in OC BAM in the samples of the well 12 of Kokdumalaksoe oil and gas field

No	Element	IR						
		Assay number	1	2	3	4	5	6
1	La		1,5	1,3	1,9	1,5	1,1	2,2
2	Ce		0,66	0,77	1,87	0,83	7,01	0,65
3	Pr		0,22	0,22	0,42	0,23	0,11	0,28
4	Nd		0,74	0,62	1,51	0,76	0,32	1,02
	Pm							
5	Sm		0,14	0,11	0,2	0,15	0,09	0,16
6	Eu		0,028	0,03	0,051	0,032	0,019	0,044
7	Gd		0,17	0,16	0,24	0,22	0,16	0,27
8	Tb		0,027	0,023	0,053	0,037	0,027	0,038
9	Dy		0,22	0,23	0,53	0,27	0,18	0,31
10	Ho		0,079	0,083	0,212	0,092	0,004	0,123
11	Er		0,137	0,085	0,118	0,145	0,087	0,164
12	Tm		0,018	0,015	0,013	0,017	0,012	0,028
13	Yb		0,09	0,084	0,092	0,088	0,072	0,167
14	Lu		0,017	0,015	0,015	0,02	0,012	0,031
15	Y		4	4,3	8,6	4,1	1	6,5
16	TR		8,046	8,045	15,824	8,491	10,203	11,985
	OC BAM							
No	Element	Assay number	1	2	3	4	5	6
1	La		5,4	5,5	6,1	5,6	5,6	5,3
2	Ce		4,38	4,58	4,59	4,75	4,69	5,16
3	Pr		1,03	1,07	1,34	1,11	1,09	1,17
4	Nd		2,55	2,62	7,25	2,73	2,77	3,27
	Pm							
5	Sm		0,5	0,55	0,78	0,59	0,6	0,27
6	Eu		0,13	0,144	0,183	0,14	0,0143	0,128
7	Gd		0,61	0,63	1,41	0,65	0,65	0,59
8	Tb		0,185	0,191	2,052	0,191	0,179	0,164
9	Dy		0,71	0,64	2,62	0,73	0,66	0,76
10	Ho		0,271	0,273	0,831	0,273	0,28	0,398
11	Er		0,417	0,418	0,608	0,438	0,415	0,454
12	Tm		0,025	0,031	0,031	0,032	0,025	0,024
13	Yb		0,137	0,143	0,179	0,13	0,133	0,215
14	Lu		0,019	0,019	0,035	0,019	0,019	0,042
15	Y		4	4	13,2	3,7	3,6	4,4
16	TR		20,364		20,809	41,209	21,083	20,7253
								22,345

In the tested assays the samples are grouped in the following way:

- No 1: 77-474, 77-475: approximate interval 2961,0 - 2961,5 m.
- No 2: 77-485, 77-486: approximate interval 3024,0 - 3024,5 m.
- No 3: 77-490: approximate interval 3026,5 m.
- No 4: 77-492, 77-493, 77-494: approximate interval 3027,5 - 3028,5 m.
- No 5: 77-500, 77-501, 77-503 и 77-558, 77-559: approximate interval 3047,0 - 3048,0 - 3074,5 m.
- No 6: 77-585, 77-586, 77-587 и 77-598: approximate interval 3054,0 - 3087,0 - 3087,5 - 3093,5 m.

* - REE concentration in OC BAM are given considering the blank experiment (a filter after the extraction of BAM) TR = the sum of lanthanides and Y. All analyses are performed with ICP MS method.

Table 3: REE concentration in oils, tars and pyrobitumens*

OC BAM fractions, concentration, gpt	La	Ce	Pr	Nd	Sm	E	u
	Gd	Tb	Dy	Ho	Er	T	m
	Yb	Lu	Y	TR			
Oils	1,38	2,18	0,36	1,16	0,23	0 , 0 6	
	0,18	0,03	0,18	0,03	0,09	0 , 0 0	
	0,03	0,00	1,35	7,26			
Tars	1,21	1,83	0,31	1,04	0,21	0 , 0 5	
	0,17	0,03	0,14	0,02	0,08	0 , 0 1	
	0,03	0,01	1,19	6,31			
Pyrobitumens	1,61	2,53	0,41	1,33	0,24	0 , 0 7	
	0,26	0,04	0,20	0,05	0,10	0 , 0 1	
	0,04	0,01	1,50	8,40			

* Analyses are performed with ICP MS method

which can be proved by difference between the REE composition of OC BAM and REE of oils, tars and pyrobitumens, in which there is no differentiation of Tb, Pr and Ho in REE composition (pic 1b).

In the REE composition (pic.1,2) we observe unusual allocations of certain lanthanides followed by positive anomalies of Tb, Pr and Ho with the deficit of Ce and especially Eu in all samples with weak differentiation of Yb and Lu in the composition of REE. This tendency is observed in oil and gas zones of the field. The only difference is that sharp Eu deficit is recorded in the bottom of the oil and gas field (sample 5, pic.2).

The presence of the hydrocarbons of oil and gas in clastic complexes is usually followed by records of Eu anomalies and its accumulation in oil and gas traps in the form of Eu²⁺ [6]. In the given research such effect is not observed, as well as the presence of highly reducing environment, which shows that Eu participates in the geochemical process in the 3-valent form and is represented by the values (Eu/Sm)_N, (Eu*)_N and (Eu/Eu*)_N.

It was earlier established that these correlations in OC BAM of the clastic complexes in the deposit zones are 1-2 and more orders of magnitude higher [6]. In the range of the chondrite-normalized values of REE composition the unusual one is Ce deficit and clear excess of Pr, Tb and Ho (pic. 2). Even more contrast distribution of lanthanides is observed in REE BAM normalized for the sum (C1+IR) with adding of Y to the composition of REE of OC BAM (pic. 3,4). Two peculiarities are clearly observed: the excess of Tb and Ho in both zones and at the same time difference of REE composition in the values (Ho/Y)_N in these zones (Table 6). The effect of the presence of Tb and Pr anomalies and the excess of Ho relative to Y is typical for the oil zone. The attempt of such interpretation was made in order to reduce the mineral component

Table 4: TR balance in carbonate reef deposits

No	Total mass of original rock	OC BAMoutcrop, %	TROC BAM, gpt	TR IR, gpt	Part of TR REE in OC BAM, %
1	66,53	0,362	20,634	8,046	71,6
2	58,51	0,272	20,809	8,045	72,1
3	41,27	0,252	41,209	15,824	71,5
4	51,58	0,894	21,083	8,491	71,3
5	138,06	0,652	20,725	10,203	67,0
6	137,89	0,432	22,345	11,965	65,1

Table 5:

Sample	1	2	3	4	5	6
(Eu/Sm) _N	0,68	0,68	0,61	0,62	0,06	1,25
(Eu*) _N	0,71	0,74	0,52	0,68	0,07	0,95
(Eu/Eu*) _N	0,71	0,65	0,52	0,68	0,07	1,24

Table 6:

Sample	1	2	3	4	5	6
(Tb/Yb) _N	6,02	5,94	51,2	6,61	6,04	3,41
(Ho/Y) _N	1,80	1,80	1,81	2,12	2,23	2,60
(Ho/Yb) _N	5,83	5,61	13,7	6,25	6,24	5,48

Table 7:

Sample	1	2	3	4	5	6
CFC(Ce/Ce*) _N	0,42	0,43	0,37	0,46	0,43	0,48
IR (Ce/Ce*) _N	0,34	0,14	0,48	0,30	3,93	0,17

Table 8:

Sample	1	2	3	4	5	6
OC BAM(Ho/Yb) _N	5,83	5,61	13,7	6,25	6,24	5,48
IR (Ho/Yb) _N	2,57	2,92	6,80	3,10	0,16	2,16

influence on organic, liquid phase of oil fluids and to record Tb, Pr and Ho anomalies with the aim of explaining their appearance.

Next, consider the correlations $(\text{Tb}/\text{Yb})_N$, $(\text{Ho}/\text{Y})_N$ and $(\text{Ho}/\text{Yb})_N$ in the researched samples.

The absence of average data on REE in oil fluids and oils does not allow to compare the composition of REE of OC BAM with other objects and to make a detailed interpretation of the interaction process between REE of mineral and hydrocarbon parts of carbonate deposits. Nevertheless, a multiple increase of these values on the oil-gas interface is clearly observed in $(\text{Tb}/\text{Yb})_N$ correlations (sample 3). The same concerns the correlations $(\text{Ho}/\text{Yb})_N$ and the correlation $(\text{Ho}/\text{Y})_N$ additionally shows the difference of these values in oil and gas zones. So, pic. 3 and table 6 show the presence of Tb and Ho anomalies which definitely indicates the occurrence of the geochemical processes in oil fluids that have not been observed before.

The Analysis of Ree in an Insoluble Residue: In the REE composition of the samples the distribution of lanthanides is the most contrast in the oil zone, where we can observe

a positive Ce inversion which is obviously connected with the changing of the oxidation-reduction environment in the reef bottom zone (water-bearing zone) and with the possibility of Ce^{3+} to Ce^{4+} transfer. (sample 5, table 7, pic.4).

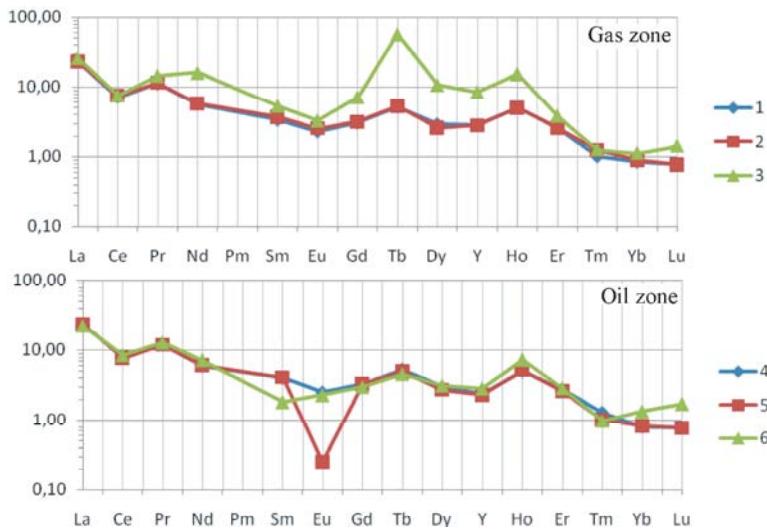
In the same sample we observe a negative Ho inversion which can not be explained from the point of view of valence changing as Ho is not capable of changing its valence and always has the form Ho^{3+} in geochemical processes.

Analysis of REE in Oil Fractions: Oil fractions - oils, tars, pyrobitumens are extracted from the sum of OC BAM of the researched samples. The corresponding fractional yield (%) is 92,0; 7,1 and 0,9. Assuming that reef deposits are formed in the marine basin, it is logical to compare the distribution of lanthanides in REE of these fractions relatively to the REE distribution (according to average data) in marine water [2] and in the oil fractions of clastic rocks [8]. As the pic.5 shows, the common properties are:

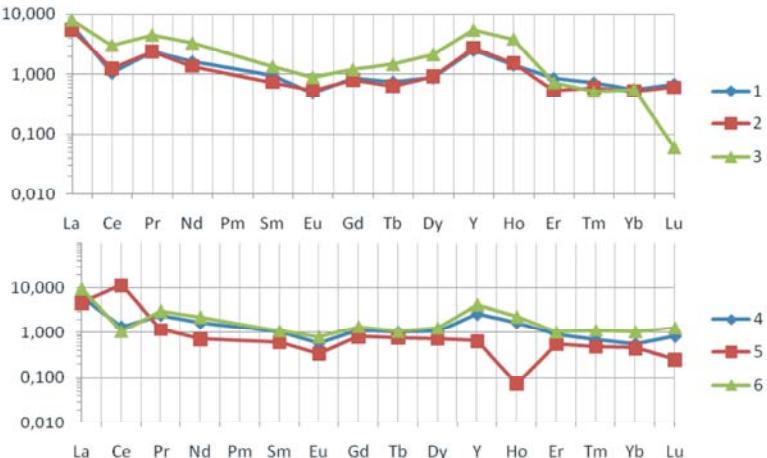
- Enrichment by light lanthanides (La-Sm);
- Deficit of Ce and Eu;
- Insignificant fluctuations of medium and heavy REE (Gd-Lu) relative to Gd.

The difference between REE in oil fractions of the given paper (pic5b) and REE in the fractions of clastic rocks (pic5c) [7] consists in Eu deficit in all samples (pic.5b), which indicates the absence of highly reducing environment in the deposit. Practically, the identity of the distribution of the lanthanides in marine water REE (pic.5a) and REE of oil fractions (pic.5b) indicates a possible basic source of REE in carbonate reef deposits and heredity of lanthanides distribution in oil fractions from the composition of REE of marine basin. The same assumption about the hereditary distribution of elements in sedimentary rocks is made in the collected articles [13].

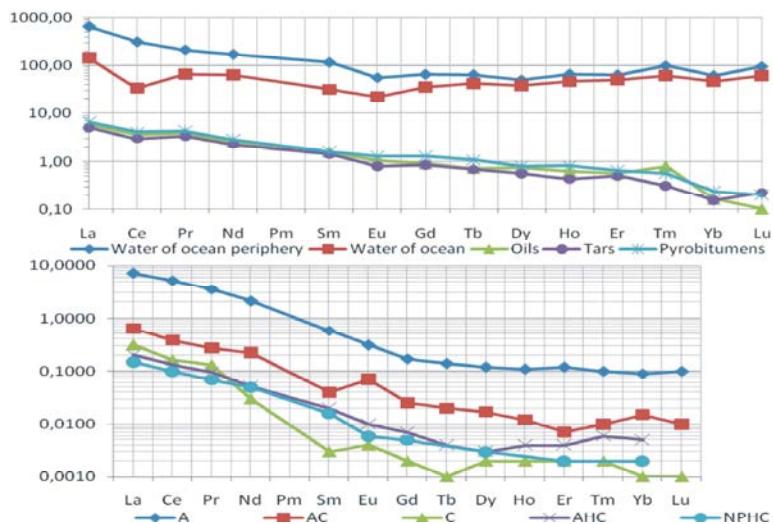
Analysis of Research Results: The reasons of anomalies appearance in the composition of REE of oil fluids (BAM) and changing of lanthanides concentration in the samples



Pic. 3: Normalized (C1+IR) distribution of lanthanides and Y in the REE of OC BAM in oil and gas zones.



Pic. 4: Ce and Ho inversions in the chondrite-normalized distributions of lanthanides and Y in the REE of IR.



Pic. 5: Chondrite-normalized differences of REE composition of oils and marine water fractions [1] - a, the given paper - b, paper [9] - c. A - No16, AC - No12, C - No15.

from OC BAM and IR of oil and gas deposit, considering modern knowledge about geochemistry of REE, can be:

- REE behavior depending on the oxidation-reduction conditions of the environment;
- Isomorphism;
- complexing properties of REE;
- Physical parameters of the stratum (porosity, permeability);
- Thermodynamic properties of the deposit influencing the abundance and specific transfer of certain lanthanides from mineral phase to organic in oil fluids.

One of the reasons of the appearance of Tb and Pr anomalies in rock fractions of reef deposits can be oxidation of these lanthanides and their participation in the geochemical process in the form of Tb^{4+} и Pr^{4+} . The presence of the oxidation media in the considered paper is illustrated by Eu deficit in the composition of REE (pic.2). As it is known [14], the formation of the ions Tb^{4+} и Pr^{4+} is possible with the appearance of stabilizing factors, which can be hydrocarbons of oil and gas (other factors do not exist) in the considered media. One of the mechanisms of lanthanides' unusual valent state appearing is displacement of water by another solvent and (or) formation of heteropolylanthanide compounds for stabilization (screening) of lanthanide ions in 2- or 4-valent states [14].

Consider in detail the opportunity of Ce, Pr and Tb oxidation. The appearance of Ce, Pr and Tb anomalies in REE of IR and OC BAM is connected, in the first place, with the possibility of transfer of these lanthanides to the 4-valent state. According to the theory of classic chemistry of REE, it is known [8] that Ce, Pr and Tb form oxides in which they have valence more than three. The most stable among these lanthanides is cerium in the form CeO_2 . Praseodymium is capable of forming an oxide of the same composition, but it is formed under specific oxidation conditions [8]. In general, oxidation of Ce and Pr is defined by the value of oxidation-reduction potential [5] and the degree of easiness of the 4-valent 4f-electrone detachment. Terbium in this group of lanthanides does not form oxides of LnO_2 type [8], however, [14] describes characteristic (the most stable) valences in water solutions for Pr^{4+} and So, from the sources mentioned above we can assume that Ce and Pr anomalies are connected with the oxidation of these lanthanides. This is observed in the composition of REE of IR with no Tb

accumulation (pic.4). Consequently, Tb anomalies in OC BAM cannot be explained by its oxidation into 4-valent state and accumulation in the form of LnO_2 [8]. However the possibility of Tb oxidation into Tb^{4+} is not excluded in the presence of stabilizer [14], most likely a hydrocarbon of oil and gas. If it is so, the further process will be probably connected with the formation of a complex " Tb^{4+} - organic component of oil fluids" and the formation of Tb anomaly. In fact, significant accumulation of Tb и Pr in REE composition in the area of decreased rock porosity (sample 3, pic.2,3) emphasizes the possibility of Tb^{4+} Pr^{4+} presence together with oil components. As a result of Tb valence change from Tb^{3+} to Tb^{4+} it occurs that Tb has the least radius ($0,88\text{\AA}$) relative to all REE regardless of their valences ($Lu^{3+} = 0,977\text{\AA}$) and consequently Tb receives the highest complexing properties.

The special role of REE complexation is strengthening of these properties from La to Lu, i.e. contraction of ionic radii in the La-Lu series [8]. As an example consider Ce^{3+} in the form Ce in natural processes. Hereby the connection of Ce^{4+} complexation with carbonate and bicarbonate compounds is emphasized [2].

The same is probably correct for Tb and Pr given hydrocarbons of oil and gas as stabilizing factors. This allows to consider the further mechanism of Tb and Pr anomalies in the order of changing of these lanthanides ionic radii.

In geochemical processes Ce, Tb and Pr valence change to 4-valent state is followed by changing of their ionic radii (\AA):

- For $Ce^{3+} \rightarrow Ce^{4+}$, correspondingly from 1,143 to 0,97;
- For $Tb^{3+} \rightarrow Tb^{4+}$, correspondingly from 1,04 to 0,88 and
- $Pr^{3+} \rightarrow Pr^{4+}$ correspondingly from 1,125 to 0,96.

Besides, the mechanism of sorbing Ce^{4+} , Pr^{4+} and Tb^{4+} complex compounds by oil fluids in carbonate media with organic components also includes the following:

- Atomic weight of $Tb > Pr > Ce$, consequently, the field intensity and the complexing properties of these lanthanides increase correspondingly, which does not contradict regular increasing of complexing properties of these lanthanides in the La-Lu series;
- According to the essence of ionic bonds theory, the chemical bond occurs due to electrostatic attraction of the formed ions, consequently, the interrelation is realized through the interaction of anions and cations of different atoms having different valence - positive

or negative as a result of receiving or losing electrons [15]. This implies, that most elements composing oil basis(C, H, O, Cl, S and others) have negative valence, that is why high-molecular compounds of oil fractions create a negative field for attraction positive ions - cations.

Thus, if hydrocarbons of oil and gas help to stabilize ions Tb^{4+} and the size of ionic radius is favorable for increasing the Tb^{4+} complexing properties relative to all REE, its accumulation should be expected in the composition of REE, especially in the area of the least rock porosity, which is observed in the pic.3. Another reason of abnormal accumulation of certain lanthanides is isomorphism effect.

It is known from the paper [10], that organic acids as important surface-active substance for the solvation of hydrocarbons in natural environment form insoluble salts with cations Ca^{2+} and Mg^{2+} . Consequently, Ca and Mg can be displaced by Tb^{4+} and Nd^{3+} correspondingly as a result of heterovalent isomorphism. Before considering such version, note certain growth of Nd in oil-gas interface (pic.1-3). Let us compare the radii of these elements and the possibility of their displacement.

$$Nd^{3+} = 1,109 \rightarrow Ca^{2+} = 1,12, \Delta = 0,011 \text{ \AA}; Tb^{4+} = 0,88 \rightarrow Mg^{2+} = 0,89, \Delta = 0,01 \text{ \AA}.$$

As it is seen, the given data do not exclude the possibility of these lanthanides isomorphism as one of the factors of Tb and Nd accumulation in the composition of REE of OC BAM.

Abnormal behavior of Ho in REE of OC BAM can also be explained by the displacement of Y^{3+} ions by Ho^{3+} ions as a result of isovalent isomorphism. Ionic radius (\AA)

$$Ho^{3+} = 1,015 \rightarrow Y^{3+} = 1,019, \Delta = 0,004 \text{ \AA}.$$

Hereby there are doubts concerning the existence of Y and Ho isomorphism in natural conditions. There are no data or published works on isomorphism occurrence of Y^{3+} and Ho^{3+} at present time. There are data about the version of such displacement appearance as a result of "lanthanide compression" effect. However, the proximity of ionic radii with 0,004 \AA difference probably led the researches to the idea of principle impossibility of isomorphism for these REE.

Consequently, while interpreting geochemical processes, Y and Ho are mentioned separately as heavy REE in La-Lu series [4]. In the given paper during the

analysis of REE distribution in an insoluble residue and in OC BAM after adding Y between Dy and Ho (pic.3,4) the contrast distribution of Y and Ho in the composition of REE is observed.

As it is seen from the pic.4, REE of the insoluble residue show deficit of Ho relative to Y and on the contrary, in the spectrum of OC BAM there is a clear excess and anomaly of Ho relative to all other REE (pic.2) indicating the possibility of Y displacement as a result of isovalentisomorphism. The possibility of Y and Ho isomorphism is also determined by the correlation and their concentration in an insoluble residue and OC BAM ($TR_{OC\ BAM} \gg TR_{IR}$). Such effect is also observed in the correlations $(Ho/Yb)_N$ and is characterized by insignificant fluctuations of Y in the composition of REE (pic.5b). This makes obvious the fact that abnormal accumulation of Ho in OC BAM and deficit of Y are impossible to explain by any other geochemical process.

Another reason probably lies in the elements' nature, including REE. The thing is that the composition of most elements in natural mixture consist of several isotopes possessing different physicochemical properties (e.g. U^{235} - 0,72%, U^{238} - 99,27%). The table of isotopes of elements composition shows that some elements' abundance in nature is 100%. The abundance of Tb, Pr and Ho is 100%. If we assume the possibility of REE isotopes fractioning in natural processes, the increase of Tb and Pr can be logically determined by the increase of general mass of complex compounds due to 100% abundance in nature. At the same time the mass of other REE complex compounds must be less despite the bigger atomic weight due to the presence of several isotopes. This is only an assumption, as it is not known which isotope's efficiency prevails in certain physicochemical processes during a sedimentation cycle with hydrocarbons of oil and gas presence. These are the further prospects of research in this direction.

CONCLUSION

In sedimentary processes with the presence of hydrocarbons of oil and gas as stabilizers of lanthanides unusual valence state and the effect of "lanthanide compression" all unusual conditions of lanthanides can be practically realized: Sm, Eu and Y in 2-valent state [9], Tb, Pr in 4-valent state; isomorphism of REE can be observed, which was considered impossible in sedimentary processes and was not [5] explained due to the absence of enough information about sizes of ionic radii and full data on the Earth composition.

Undoubtedly, such conclusion could not be done without understanding of researches previously conducted by many scientists in such areas as organic geochemistry [16-18], geochemistry of REE of sedimentary processes [19-21, 25] and synthesis of organic REE derivatives [21-24, 26] and others.

- The appearance of Tb and Pr anomalies in oil fluids is determined in the first place by Tb and Pr oxidation into the 4-valent state and also possible as a result of displacement Mg^{2+} by terbium in the form Tb^{4+} due to heterovalent isomorphism. Similar is the increased value of Nd in BAM with the possibility of displacement Ca^{2+} by neodymium in the form Nd^{3+} .

Abnormal behavior of Ho is connected with the possibility of isovalent isomorphism, i.e. with the displacement of Y^{3+} by holmium in the form Ho^{3+} in oil fluids in oil-and-gas-bearing deposits.

Under highly reducing conditions in clastic rocks deposits the displacement of Sr^{2+} (1.26\AA) by europium in the form Eu^{2+} (1.25\AA) is possible with the difference of 0.01\AA [6, Error! Reference source not found.]. In carbonate deposits, without highly reducing conditions displacement of other elements is also possible: Ca, Mg by Nd, Tb correspondingly.

Hereby, both in clastic and carbonate deposits, hydrocarbons of oil and gas can be stabilizing factors of unusual valence state of certain lanthanides and, contacting with oil fractions and water, can form the place and environment of REE transfer between mineral and organic parts of deposit.

- In oil fluids REE of oil fractions obviously have a hereditary character of the distribution of the lanthanides in the composition of REE of marine water.
- In practice, the results of the research can be used in oil exploration for getting information about the possibility of separation of oil and Gas zones in oil and gas traps in carbonate reef deposits and others on the basis of lanthanides behavior in the composition of REE.

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REFERENCES

1. Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr*, pp: 751-767.
2. Balashov, Y.A., 1976. Rare earth elements geochemistry. Moscow: Nauka, pp: 159-164.
3. Dubinin, A.V., 2006. Ocean geochemistry. Moscow, pp: 359.
4. Balashov, Y.A. and S.G. Skublov, 2011. Contrast of magmatic and secondary zircons geochemistry. *Geochemistry*, 4: 1-12.
5. Geology of rare elements fields, 1959. Moscow: Edited by Ginzburg. 3: 125.
6. Balashov, Y.A. and K.S. Tsoy, 1989. The role of oxidation-reduction conditions in Eu^{2+} , Yb^{2+} and Sm^{2+} . *ASR*, 5(389): 1189
7. Tsoy, K.S., 1989. Rare earth elements geochemistry in oil and gas deposits of Western Siberia. PhD thesis, (Geochim. AS USSR.).
8. Ryabchikov, D.I. and V.A. Ryabuhin, 1966. Analytical chemistry of rear earth elements and yttrium. Moscow: Nauka, pp: 380.
9. Goettlich, R.P., S.F. Vinikurov and B.I. Pisotsky, 2009. Rear earth elements as geochemical criteria of endogenous sources of microelements in oil. *SAR*, 425(2): 1-3.
10. Tisso, B. and D. Velte, 1981. Formation and distribution of oil. Moscow: Mir, pp: 501.
11. Bochkarev, M.N. and G.S. Kalinina, 1989. Organic derivatives of rare earth elements. Moscow: Nauka, pp: 229.
12. McDonough, W.F. and S.S. Sun, 1995. The Composition of the Earth. *Chemical Geology*, pp: 223-251.

13. 1984. Association of elements with organic matter in the sedimentary deposits of Siberia. Collection of scientific papers, IGG, AS, Sib. Dep. Novosibirsk, pp: 157.
14. Panyushkin, V.T. and Y.A. Afanasyev, 1980. Lanthanides. Simple and complex compounds. Rostov University publishing house, pp: 17-25.
15. Ugay, Y.A., 1997. Valence, chemical bond and oxidation degree as the main concepts of chemistry. Moscow: Chemistry. Vyssh. Shk, pp: 53-57.
16. Bailey, N.L., C.R. Evans and C.D. Milner, 1974. Applying petroleum geochemistry to search of oil, examples from western Canada Basin. Am. Assoc. Pet. Geol. Bull, 58: 2284-2294.
17. Evans, C.R., M.A. Rogers and N.L. Bailey, 1971. Evolution and alteration of petroleum in Western Canada. Chem. Geol., 8: 147-170.
18. Rogers, M.A., N.L. Bailey, C.R. Evans and J.D. McAlary, 1972. An Explanatory and Predictive Model for the Alteration of Crude Oils in Reservoirs in the Western Canada Basin. Proc. Int. Geol. Congr. Montreal, Canada, Mineral Fuels Sec., 5: 48-55.
19. Haskin, L.A., *al. et*, 1966. Rare earth in sediments. JGR, 71: 6091.
20. Taylor, S.R. and S.M. McLennan, 1979. Chemical relationship among irghizites, zhamanshinites Australasian tektites and Henbury impact glasses. GCA, 43: 1551.
21. Masuda, A. and N. Nakamura, 1973. Geoch. etcosmochem. acta, V. 37: 230-248.
22. Hayes, R.G. and J.L. Thomas, 1971. Organometal Chem. Rev., A. 7: 1-50.
23. Wilkinson, G. and J. Birmingham, 1954. Amer. Chem. Soc., 76(23): 6210-6213.
24. Shannon, R.D., 1984. Actacrystallogr. A, 32(5): 751-767.
25. Migdisov, A.A., Y.A. Balashov and I.V. Sharkov, 1994. Distribution of rare earth elements in the main lithological rocks of the Russian Platform sedimentary cover. Geochemistry, 6: 789-803
26. Gromet, L.P., R.F. Dymek, L.A. Haskin and R.L. Korotev, 1984. The North American shale composite: Its compilation, major and trace element characteristics. Geochem. etcosmochem. Acta, 48(12): 2469 - 2482.