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Distribution of Rare Earths in Uranium Oxides of the Main Types of Uranium Deposits: Causes and Genetic Meaning

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Abstract—Three groups of industrial uranium deposits that differ in the distribution of lanthanides in U oxides have been recognized. A dependence of the REE distribution type on the Yttrium content and Yttrium index $YI = (La + Ce)/Y$ that controls the formation of REE phases capable of selective accumulation of lanthanides has been discovered. This indicates the important role of crystal–chemical fractionation in the distribution of lanthanides. Preferable accumulation of Sm–Gd by U oxides has been found to occur at relatively low contents of Y. In Proterozoic uranium deposits, the yttrium specialization of oxides predominates, while in most Phanerozoic deposits the lanthanum–cerium specialization is typical. These results extend the possibilities of using REEs in ores for purposes of study of the genesis of various uranium deposits.

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The type of distribution of rare earth elements (REEs) in minerals is widely used to determine the conditions of their formation and the sources of ore-bearing fluids in various deposits. The REE distribution in rocks and minerals is a cumulative effect of their fractionation in processes of magma differentiation, fluid migration, and mineral crystallization. Variation in the REE, Zr, Th, and U concentrations in evolution of granitic magmas [1] is one of many examples of their fractionation in conjugate phenomena of fluid–magmatic interaction and crystallization. The reasons for such behavior can be subdivided onto geochemical and crystal–chemical. The former relate to the chemical properties of the REEs and determine their fractionation in melts and fluids. The latter are caused by differences in the structure of crystalline phases and lead to the separation of rare earth elements during deposition of minerals from melts and aqueous solutions.

These mechanisms of REE fractionation are combined and can be repeated several times during formation of minerals concentrating individual REEs or their groups: light (L, La–Nd), intermediate (I, Sm–Tb) and heavy (H, Dy–Lu) [2]. The most common REE-selective phases are monazite–phosphate of Ce and LREEs and xenotime–phosphate of Y and LREE–HREE. Oxides of U (uraninite and pitch-

blende), the ore minerals of most uranium deposits, are also selective minerals accumulating IREEs [3].

Variations in the indicator ratios such as the yttrium index ($YI = (La + Ce)/Y$), La/Yb, Eu/Sm, and patterns in spider diagrams (chondrite–normalized REE content in oxides [4]) reveal different distribution types of rare earth elements in ores of the main industrial genetic classes of uranium deposits [5] and demonstrate their dependence on the content of yttrium and the value of the YI in U oxides [6]. This index reflects not only the $(La + Ce)/Y$ value in U oxides, but, perhaps, also a number of REE-selective mineral microphases (monazite and xenotime), since these elements constitute more than 70 wt % of their composition.

Analysis of the literature [7–12] and our own data on the contents of REEs in U oxides from ores of uranium deposits (obtained by ICP–MS, SIMS, and ID–TIMS) has allowed systematization of these data and identification of the causes of REE fractionation. Three groups of U oxides have been identified (Table 1, Figs. 1–3).

The first group has a positive distribution type and a dome-shaped spider diagram pattern with increasing concentrations of lanthanide from Sm (Pr) to Er (Tm). It has an inherent value of La/Yb 0.01–0.47, YI 0.004–0.17 and a lack of a negative Eu anomaly and dominance of Y, whose content exceeds $(La + Ce)$ many times (Table 1). Such a uraninite with an age of more than 1275 Ma form rich ores of the Canadian unconformity–type U deposits (Fig. 1a): Sue, Shea Creek, McArthur River, in Northern Australia (Fig. 1b), and Nabarlek, Pine Creek, and others were found in

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REE content (ppm) and values of indicator ratios in oxides of U deposits in the groups distinguished

	Deposit	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	Eu/Sm	$\text{La}/\sqrt{\Sigma}$	YI	Source
Type 1a	Shea Creek	6527	28	221	138	888	559	200	nd	177.6	1184	220	434	55	178	8	4291	0.36	0.16	0.04	[7]
	McArthur River	6988	9	20	15	116	141	128	nd	134	839	145	233	28	102	7	1917	0.91	0.09	0.004	[7]
	Sue	1127	0.38	6.12	1.83	13.87	5.49	7.95	97.30	32.11	274.1	40.61	68.37	8.46	25.59	2.06	584.2	1.45	0.01	0.01	ad
Type 1b	Nabarlek	2448	69.38	354.9	40.26	167.9	108.9	44.04	1021	89.95	524.9	90.58	182.7	29.78	185.3	6.40	2916	0.40	0.37	0.17	[8]
	PainCreek	nd	5.5	43	11	77	79	24	153	55	329	55	128	89	nd	nd	1049	0.30	nd	nd	[9]
	Mistamisk	nd	212	2374	507	3148	1452	238	1335	276	1788	332	796	94	447	41	13040	0.16	0.47	nd	ad
Type 2	Gurvanbulag	232.6	115.7	71.65	8.80	44.32	21.61	1.13	111.0	4.92	27.94	0.59	1.59	0.96	5.05	0.13	415.4	0.05	22.92	0.81	ad
	Shea Creek	3276	272	477	189	754	526	211	nd	nd	1177	nd	308	nd	267	11	4192	0.40	1.02	0.23	[7]
	Pen Ar Ran	753	309	505	37.3	170	42.1	7.34	479	9.64	33.5	6.22	18.6	1.88	22.5	0.39	1645	0.17	13.73	1.08	ad
Type 3	Limousine	537.3	224.4	1295	207.8	805	424.9	62.30	2543	42.45	122.3	16.31	47.89	6.28	101.2	1.29	5890	0.15	2.22	2.83	ad
	Schlema–Alberoda 1	nd	91.27	49.51	3.52	9.92	1.69	0.47	6.85	0.22	1.22	0.26	0.53	nd	12.63	0.02	178.1	0.28	7.23	nd	ad
	Schlema–Alberoda 2	nd	84.87	43.22	nd	15.98	2.57	0.81	6.71	nd	3.13	nd	1.82	nd	1.06	nd	160.2	0.31	79.92	nd	ad
	Roll–front 1	nd	320	380	34	90	11	3.5	15	1.6	9.9	2.8	8.2	1.1	6.2	0.7	884	0.32	51.61	nd	[10]
	Roll–front 2	nd	990	1200	52	120	6.2	1.2	17	0.8	3.6	0.4	1.2	0.4	2	0.5	2395	0.19	495.0	nd	[10]

nd, not determined; ad, the authors' data.

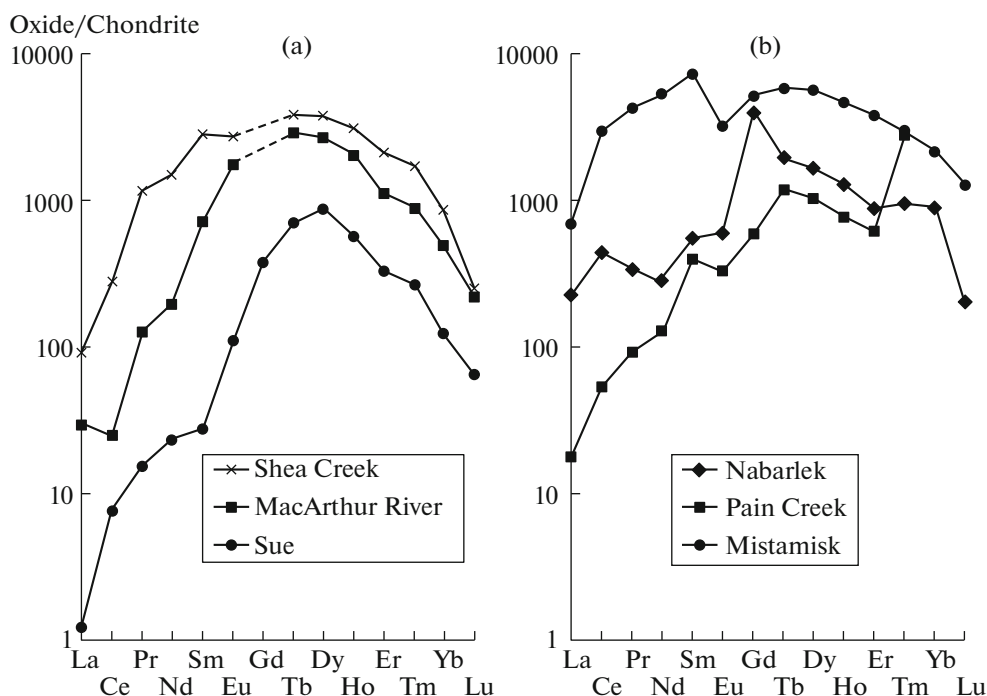


Fig. 1. REE pattern of the first group of U deposits.

metasomatic albitite ore of the Proterozoic U deposit Mistamisk (Canada) [7–9].

The second group demonstrates the sub-chondrite or negative type of REE distribution with local peaks in the Sm–Dy and Sm–Gd area. It differs from the first group by higher values of La/Yb (1–23) and YI (0.23–2.83) and a negative Eu anomaly (Table 1, Fig. 2). This type is dominant in pitchblende of the Mesozoic vein uranium deposits in France (Pen Ar Ran, Limousine), U–Mo deposits of the Streltsovskoe (Russia) [11] and Dornot (Mongolia) ore fields, and the Paleozoic U deposit Vostok, Northern Kazakhstan [12]. The same REE distribution has been found in the late pitchblende of Mesozoic age (60–130 Ma) in rich ores of the Shea Creek deposit (Table 1).

The third group of oxides differs sharply by the negative type of REE pattern with a distinct positive peak of Gd (Fig. 3). It is characterized by the highest value of La/Yb reaching 495 (Table 1). This type has been identified in pitchblende of the Late Palaeozoic Schlemma–Alberoda deposit (eastern Germany) [1, 2] and roll-front deposits of South Kazakhstan [10]. The latter show high values of ΣREE 884–2395 ppm, La/Yb > 50, and distinct positive anomalies of Gd (Table 1, Fig. 3).

French researchers, applying ion probe and laser ablation techniques, studied the REE distribution in 66 U oxide samples from uranium deposits from around the world, targeting their genetic classification [10]. These data were not used here completely due to lack of data on the concentrations of Y, Yb and Gd,

which are indicative elements when analyzing the REE distribution. The patterns of the spider diagrams obtained by those researchers are also similar to the REE distributions described above for a number of

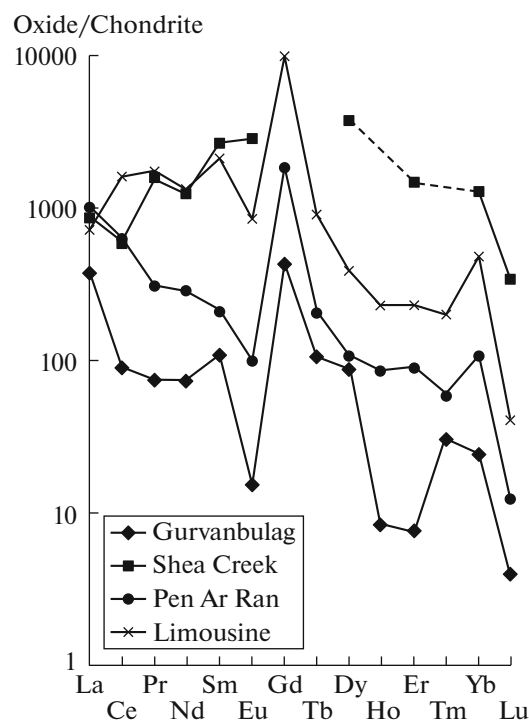


Fig. 2. REE pattern of the second group of U deposits.

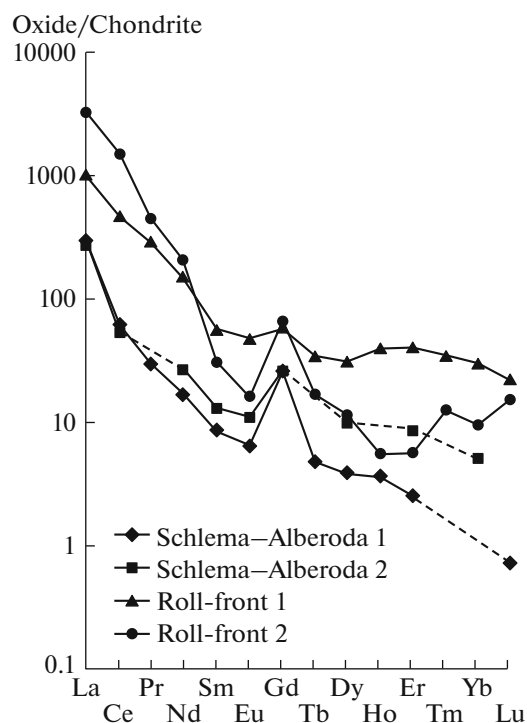


Fig. 3. REE pattern of the third group of U deposits.

uranium deposits. The pattern of the first type is found in uraninites of a wide range of deposits of an ancient unconformity type in Athabasca (Canada), Cigar Lake, Eagle Point, Sue, Millennium, and the Alligator River (Australia) and Nabarlek and Coongarra. Distribution of the second type is characteristic of pitchblende from U–Mo deposits of Strel'tsovskoe ore field (Russia) and vein U deposits in granites (France). Those researchers considered the distribution of REEs in U oxides as one of the indicators of the formation conditions of uranium deposits, which may become the basis of a genetic classification [10, 13]. They suggested that REE fractionation was caused by geochemical factors affecting REE behavior in solutions and melts with different ligands at different temperatures and pressures. Thus, elevated IREEs–HREEs in uraninites from unconformity-type deposits was explained by sorption of LREEs in aluminum phosphate–sulfates formed earlier [14] and then their removal from the mineral-forming medium.

Thus, the studied U oxides of the main industrial–genetic classes of endogenous uranium deposits can be divided into three types according to the pattern of their spider diagrams and different values of the indicator element ratios. The dependence between the REE distribution type and relative content of Y in U oxides and the value of YI has been revealed. In turn, the YI value determines the possibility of formation of minerals, selectively absorbing LREEs or IREEs–HREEs [2, 3]. The capability of U oxides themselves to accumulate IREEs (Sm–Gd) occurs at relatively

low contents of Y, i.e., at high values of YI. For the first time we found in U oxides a relation between the REE distribution patterns and the crystal–chemical properties of deposited rare earth minerals, the composition of which was determined by the YI value in ore fluids.

As conclusions the following should be noted. It was determined that the REE distribution in U oxides is mainly influenced by crystal–chemical fractionation. This conclusion is based on identification of the REE distribution dependence on the value of the YI, which determines the possibility of formation of minerals selectively incorporating REEs. The ability of U oxides to accumulate IREEs at different values of YP has also been demonstrated.

Dominance of Y or (Ce + La) in the studied U oxides permitted recognition of two groups of deposits. The first has yttrium specialization (the first type of REE distribution) and is characteristic of ancient Proterozoic deposits, the second one with a cerium–lanthanum specialization (types two and three) is typical for most of the Phanerozoic deposits (Table 1). The causes for the differences are in various compositions of the ore-forming solution that determines formation of microphases of either xenotime or monazite. The dependence of the REE distribution in U oxides on the mineral-forming medium allows identification of possible sources of polychronous U deposits. These data can be used in the development of a genetic version for classification of uranium deposits [15].

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