

# Radioactive (U, Th) elements in technogenic waters of tungsten deposits in Eastern Transbaikalia (Russia)

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**Abstract.** The peculiarities of distribution and migration of uranium and thorium in technogenic waters of seven tungsten deposits located in Eastern Transbaikalia have been studied. It has been established that elevated concentrations of uranium are found in all types of investigated waters, whereas the accumulation of thorium was recorded only in acidic waters (pH < 4). Maximum concentrations of elements were found in the areas of deposits localized in leucocratic and lithium-fluorine granitoids. In acidic waters, uranium and thorium migrate primarily in the form of sulfate and fluoride complex ions, while in neutral and weakly alkaline conditions, carbonate complexes come to the fore.

## 1 Introduction

Eastern Transbaikalia is one of the three largest uranium-bearing regions in Russia. In addition to uranium mineralization, rare metal granitoids are widely distributed here, characterized by significant enrichment of uranium, as well as thorium, which is associated in its natural compounds with rare earth elements and zirconium [1-3]. The connection with rare metal granitoids of tungsten deposits, which owns one of the leading positions in the metallogeny of Eastern Transbaikalia, is also well known. Naturally, it can be expected that the waters draining the tungsten deposits may have increased concentrations of these elements. The aim of the study was to investigate the distribution and migration characteristics of uranium and thorium in the waters of Transbaikalia tungsten deposit areas.

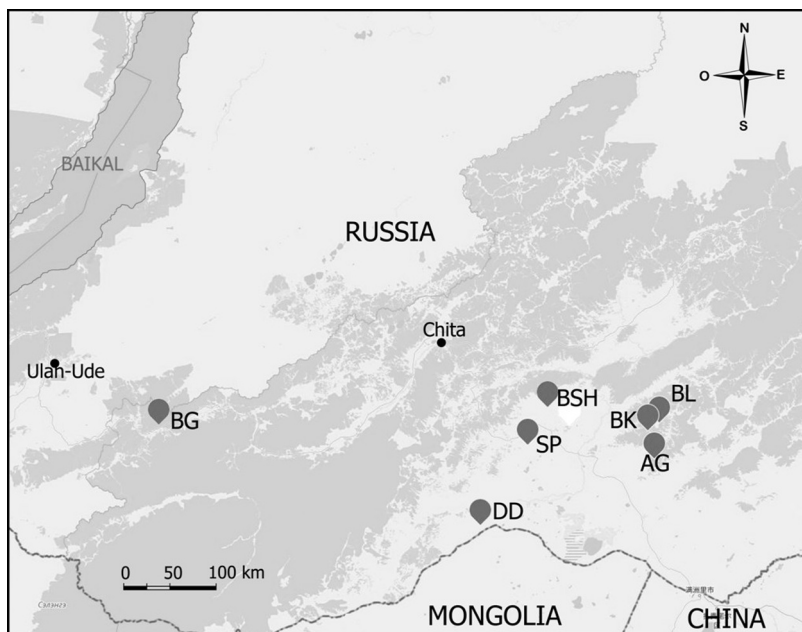
## 2 Materials and methods

From 2013 to 2018, underground and surface waters forming in the areas of operation of seven tungsten deposits located in Eastern Transbaikalia were sampled. These are the quartz-hübnerite-sulfide Bom-Gorhon, quartz-cassiterite-wolframite Dedovogorskoye, greisen tin-tungsten Spokoyinskoye, mercury-antimony-wolframite Barun-Shiveya, as well as vein tin-tungsten Bukuka, Belukha, and Antonovogorskoye deposits (Figure 1). The

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ore objects, with the exception of the Barun-Shiveya deposit, are associated with areas of development of Proterozoic, Paleozoic, and Mesozoic sand-shale deposits, intruded by Mesozoic granitoid intrusions [1, 4-5]. The main ore mineral of the deposits is wolframite. The vein ore bodies of the Antonova Gora, Belukha, Bukuka, and Bom-Gorhon deposits are characterized by high content of sulfides. The hydrothermal Barun-Shiveya deposit has no visible connection with intrusive formations. The rocks enclosing its ore bodies (zones of fine-grained mineralization, ore breccias, and veins) are represented by Proterozoic quartzites with interlayers of mica-chlorite shales [5, 6], with ferberite being the dominant ore constituent. Currently, exploitation of tungsten ores is only carried out at the Spokoyinskoye and Bom-Gorhon deposits. Exploitation at the other deposits has been stopped, and reclamation of mining territories has not been conducted.



**Fig. 1.** Layout of tungsten deposits: BG – Bom-Gorhon; SP – Spokoyinskoye; DD – Dedovogorskoye; BSH – Barun-Shiveya; BL – Belukha; BK – Bukuka; AG – Antonovogorskoye.

A total of 47 water samples were collected in the deposit areas. Mine workings (adits, quarries), drainage from waste dumps, tailings, and barren rocks, tailings ponds, and other water manifestations were sampled. Water sampling and subsequent chemical analysis were carried out using standard methods [7-8] in the certified laboratory of the Institute of Natural Resources, Ecology, and Cryology SB RAS (Chita, Russia). The determination metal (including of uranium and thorium) concentrations in water was performed by the ICP-MS method using the ELEMENT 2 mass spectrometer in the analytical center of the Vinogradov Institute of Geochemistry SB RAS (Irkutsk). The determination of migration forms of radioactive elements was performed by the computational method using the HydroGeo32 software package [9].

### 3 Results and Discussion

Hydrogeochemical systems forming within mining territories significantly differ from natural ones. These differences are most pronounced in areas of deposits with associated sulfide mineralization. For example, the anion composition of the waters in the areas of

operation of the Bom-Gorkhon, Bukuka, Antonovogorskoye and Belukha deposits is mainly  $\text{SO}_4$ ,  $\text{F-SO}_4$ , and  $\text{HCO}_3\text{-SO}_4$ , with leading cations being Ca and Mg. A significant increase in the mineralization of these waters to gram values and a decrease in pH to slightly acidic and acidic ranges have been recorded (Table 1). These conditions are favorable for the migration and accumulation of heavy metals, rare and rare earth elements, as well as uranium and thorium, the concentrations of which in water reach maximum values [10-11].

**Table 1.** Distribution of thorium and uranium concentrations in waters of tungsten deposits.

Deposits	pH	Eh, V	Min. *, g/L	U, $\mu\text{g/L}$	Th, $\mu\text{g/L}$	Th/U
Bom-Gorkhon	3.04-6.18**	0.29-0.51	0.07-3.21	0.28-321	0.03-942.9	0.09-3.53
	4.70	0.39	0.93	71.5	177.3	1.22
Bukuka	2.59-6.74	0.24-0.57	0.28-2.35	1.60-117	0.02-50	0.001-0.61
	4.44	0.42	1.15	41.2	14.7	0.24
Belukha	5.85-6.38	0.26-0.32	0.08-0.37	0.17-0.44	0.02-0.12	0.12-0.28
	6.14	0.28	0.18	0.26	0.06	0.18
Antonovogorskoye	3.3-4.95	0.3-0.53	0.1-0.32	2.0-58	0.09-5.9	0.04-0.1
	4.09	0.41	0.017	17.0	1.5	0.07
Dedovogorskoye	6.51-7.65	0.22-0.35	0.05-0.11	0.04-6.6	0.003-0.12	0.001-0.15
	7.22	0.29	0.08	1.34	0.03	0.06
Spokoyninskoye	6.65-7.96	-0.09-0.22	0.11-1.07	1.50-1863	0.006-0.11	4E-06-0.012
	7.44	0.05	0.5	296.9	0.04	0.003
Barun-Shiveya	7.50-7.70	0.06-0.12	0.15-0.19	0.76-2.02	0.004-0.02	0.002-0.023
	7.60	0.1	0.18	1.57	0.009	0.009
Average content in groundwater of the hypergenesis zone [12]				1.31	0.24	0.18

\*Min. – water mineralization; \*\* – in the numerator – minimum and maximum, in the denominator – average values.

The waters in the field development area of the Spokoyninskoye deposit are predominantly weakly alkaline and neutral with increased mineralization (Table 1), mainly  $\text{HCO}_3$  Mg-Ca type [11]. These conditions are more favorable for the migration of anionogenic elements, the maximum concentrations of which reach (mg/L): W - 1.5; Mo - 0.08; As - 0.61; U - 1.86. In the area of the Dedovogorskoye deposit, fresh neutral and weakly acidic (Table 1),  $\text{SO}_4\text{-HCO}_3$  and  $\text{HCO}_3$  Na-Ca waters are formed, with maximum contents of trace elements at the unit level (Cd, W), tens (Sr, Li, Mo), and rarely hundreds (Al, Mn, Fe, Zn, Cu, As)  $\mu\text{g/L}$  [13]. The waters sampled at the bottom of the Barun-Shiveya deposit quarry are fresh, neutral, and weakly alkaline (Table 1)  $\text{HCO}_3$  Mg-Ca. The trace element water composition is characterized high arsenic content (0.14-0.18 mg/L), as well as ( $\mu\text{g/L}$ ): W (7.5-16.9), Mo (10.7-13.3), Sb (37.1-41.5), Li (10.8-12.2), Al (3.35-47.4), Fe (2.57-41.7), Br (27.7-36.3).

The distribution of uranium and thorium in waters of tungsten deposits (Table 1) is determined by the migration abilities of the elements themselves, the Eh-pH migration conditions, and their content in rocks and ores. Increased concentrations of uranium have been recorded over a wide range of Eh and pH values in waters of both sulfidic Bom-Gorkhon, Bukuka, Antonovogorskoye deposits and low-sulfidic Dedovogorskoye and Spokoyninskoye deposits, while thorium accumulation has only been established in acidic and highly acidic (pH <4) waters (Table 1). The same was previously observed in acidic waters of the mining objects of the Taseevskoye gold deposit [14]. This distribution of elements is explained by the higher migration ability of uranium compared to thorium, which can be transported by solutions of different chemical composition in different physical and geographical conditions, as well as its prevalence in the water-bearing rocks [15-16].

Among natural waters enriched with radioactive elements, uranium waters are distinguished, whose uranium concentrations range from  $n \times 10^{-5}$  to  $n \times 10^{-2}$  g/dm<sup>3</sup> [17], which means that the considered waters containing more than 10 µg/L of uranium should belong to such waters. These are waters of the Antonogorskoye, Bukuka, Bom-Gorkhon, and Spokoyinskoye deposits. The maximum concentrations of uranium were recorded in the waters of the tailings pond and sump at the bottom of the active quarry of the Spokoyinskoye deposit - 0.12-0.43 and 1.86 mg/L, respectively, in the drainage of tailings enrichment at Bukuka - 0.12 mg/L, and under the lower dam of the tailings pond at Bom-Gorkhon - 0.32 mg/L. The highest thorium contents were found in the quarry and waters draining the tails of the enrichment plant at Bukuka (0.03 and 0.02-0.05 mg/L, respectively), as well as in the waters of the settling pond and outlet under the lower dam of the tailings pond at Bom-Gorkhon (0.11-0.94 mg/L). The lowest uranium and thorium contents are characteristic of waters formed in the areas of the Dedovogorskoye, Barun-Shiveya, and Belukha deposits. The anomalously high accumulation of radioactive elements in the waters of the Spokoyinskoye, Bom-Gorkhon, and Bukuka deposits is likely due to their increased content in the enclosing leucocratic and Li-F granitoids [1].

The ratio of thorium to uranium in the waters of deposits is predominantly less than one, which generally corresponds to the distribution of these elements in the groundwater of the supergene zone (Table 1), thus confirming the weaker migration capacity of thorium [15]. An exception is the water draining from the tailings pond of the Bom-Gorkhon deposit, which indicates higher concentrations of this element in its ores compared to other sulfide deposits.

In order to clarify the question of the forms of existence of the considered elements in the waters of tungsten deposits, calculations of the inorganic forms of their migration were performed using the HydroGeo software package [9] (Table 2). The obtained results are in good agreement with the data of other researchers [15, 16]. Thus, in acidic and strongly acidic waters, migration of uranium and thorium primarily occurs in the form of sulfate complexes ( $\text{UO}_2\text{SO}_4^0$ ,  $\text{UO}_2\text{HSO}_4^+$ ,  $\text{UO}_2(\text{HSO}_4)_2$ ,  $\text{ThSO}_4^{2+}$ ,  $\text{Th}(\text{SO}_4)_2^0$ ) and fluoride complexes ( $\text{UO}_2\text{F}^+$ ,  $\text{ThF}_3^+$ ,  $\text{ThF}_2^{2+}$ ). Some amount of uranium is transported as uranyl ion  $\text{UO}_2^{2+}$  and uranyl hydroxyl complex  $\text{UO}_2\text{OH}^+$  (Table 2).

**Table 2.** Migration forms of uranium and thorium (%).

Forms of migration	pH < 4	pH 4 – 6	pH > 6
Uranium			
$\text{UO}_2^{2+}$	0.95 – 12.3	1.04 – 3.08	—*
$\text{UO}_2\text{SO}_4^0$	7.80 – 59.5	5.35 – 19.04	—
$\text{UO}_2(\text{HSO}_4)_2^0$	0.19 – 19.4	—	—
$\text{UO}_2\text{HSO}_4^+$	23.3 – 58.0	3.25	—
$\text{UO}_2\text{F}_2^0$	1.29 – 1.81	0.60 – 9.75	0.39
$\text{UO}_2\text{F}^+$	11.9 – 32.7	9.52 – 63.2	1.69
$\text{UO}_2(\text{CO}_3)_2^{2-}$	—	0.23	22.8 – 66.1
$\text{UO}_2(\text{CO}_3)_3^{4-}$	—	—	0.94 – 54.2
$\text{UO}_2\text{CO}_3^0$	—	10.7	0.14 – 27.06
$\text{UO}_2\text{OH}^+$	0.16 – 1.63	0.85 – 13.1	0.45 – 2.49
Thorium			
$\text{ThSO}_4^{2+}$	0.44 – 10.9	0.11 – 0.29	—
$\text{Th}(\text{SO}_4)_2^0$	5.69 – 84.1	1.00 – 2.40	—
$\text{ThF}_3^{3+}$	2.80 – 13.4	3.45 – 4.15	0.27
$\text{ThF}_3^+$	40.6 – 56.7	18.7 – 72.3	0.11 – 23.7
$\text{ThF}_2^{2+}$	26.7 – 31.4	12.2 – 20.8	3.71
$\text{ThCO}_3(\text{OH})_3^-$	—	0.50	37.3 – 99.5
$\text{Th}(\text{OH})_3^+$	—	10.3	0.13 – 16.2
$\text{Th}(\text{OH})_2^{2+}$	—	48.1	2.58 – 16.9

\* – values < 0.00n

In the process of increasing the pH value of water from 4 to 6, there is a gradual decrease in the quantity of sulfate and fluoride complexes, and the migration in the form of hydroxyl forms intensifies. Uranium complexes, such as uranyl carbonate ( $\text{UO}_2\text{CO}_3$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ), as well as thorium hydroxycarbonate ( $\text{ThCO}_3(\text{OH})_3^-$ ), appear (Table 2). In waters with a  $\text{pH} > 6$ , sulfate forms of uranium and thorium are completely absent, and fluoride complexes play a secondary role. The leading form of uranium migration is uranyl carbonate complexes –  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , and  $\text{UO}_2\text{CO}_3$ . The predominant form of thorium in neutral and weakly alkaline waters is  $\text{ThCO}_3(\text{OH})_3^-$ , while in weakly acidic and neutral conditions, fluoride and hydroxyl complexes such as  $\text{ThF}_3^+$ ,  $\text{Th}(\text{OH})_3^+$ , and  $\text{Th}(\text{OH})_2^{2+}$  play a noticeable role.

## 4 Conclusion

Thus, studying the distribution and migration of uranium and thorium in technogenic-transformed waters of tungsten deposits has revealed the following features:

- Elevated uranium concentrations are found in both acidic and weakly alkaline conditions, while thorium accumulation is only observed in acidic and strongly acidic waters. In particular, the highest concentrations of uranium and thorium are found in areas with sulfide deposits localized in leucocratic granitoids - Bom-Gorkhon, Bukuka, and Antonovogorskoye, as well as the low-sulfide Spokoininskoye deposit associated with Li-F granitoids.
- Waters with uranium concentrations  $> 10 \mu\text{g/L}$ , formed in the areas of the Antonovogorskoye, Bukuka, Bom-Gorkhon, and Spokoininskoye deposits, according to the classification of natural waters enriched with radioactive elements, belong to uranium waters.
- The values of the thorium-uranium ratio in the waters of the Bom-Gorkhon deposit, compared to acidic waters from other deposits, indicate higher thorium contents in its ores.
- In acidic waters, uranium and thorium primarily migrate in the form of sulfate and fluoride complex ions, while in neutral and weakly alkaline conditions, carbonate complexes are predominant.

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