Rare Alkali Metals in the Waters of Lithium-containing Deposits in Eastern Transbaikalia

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Abstract. The results of hydrogeochemical studies on the content of rare alkaline elements in man-made waters of mining facilities at Zavitinsky, Orlovskoye, and Etykinskoye rare metal deposits of Eastern Transbaikalia are presented. Concentrations of these elements are determined both by the content in the ores and rocks of deposits and by their water-migration properties. It was found that the acidic sub-basement waters of the Orlovskoye and the quarry waters of the Zavitinsky deposit contain abnormally high concentrations of lithium, up to 3.74 and 3.88 mg/L, respectively. The high content of lithium (Li) in the waters of these deposits was determined relative to the average values for the waters of the hypergenesis zone, as well as the standards of maximum permissible concentrations (MPC) of chemicals for water bodies used for fisheries, drinking water, and other activities.

1. Introduction
Eastern Transbaikalia is the largest lithium-bearing province in Russia. Currently, 7 deposits and more than 200 ore occurrences of rare metals of industrial importance are known within the region. Of particular interest in connection to the value and significance of the application are rare alkali metals, which are widely used in the chemical, electrochemical, radio engineering, and nuclear industries; optics and medicine; rocket and space, nuclear, and military equipment; and other important industries.

Despite the widespread use of lithium, rubidium and caesium, they are classified as rare and scattered elements. The content of rare alkaline elements in the Earth's crust is Li – 32, Rb – 150, and Cs – 4 g/t [1]. The content of alkaline elements in ocean water varies within the limits of Li - 0.15–0.2, Rb - 0.12–0.2, and Cs - 0.0003 mg/L. The range of changes in the content of rare alkaline elements in groundwater is very large and amounts to Li - 0.001–700, Rb - 0.001–960, and Cs - 0.001–20 mg/L. There are also several geochemical types of groundwater in the Earth's crust that contain maximum concentrations of rare alkaline elements. A detailed description of these types of waters is given in the work [2]. In general, about 55% of the world's lithium reserves, 40% of rubidium, and 35% of caesium are concentrated in natural waters. Granite pegmatites account for about 97% of the prospective lithium reserves [2].

The main factors that determine the behavior of alkali metals are associated, firstly, with the proximity of the properties and sizes of Li ions with magnesium (Mg), a Rb, and Cs with potassium (K), which leads to their scattering in the minerals of the host elements (mainly silicates), and, secondly, with the formation of compounds with volatile components. This, in turn, contributes to
their accumulation in residual melts and the formation of pegmatite deposits of rare alkaline elements [3].

The largest lithium deposit in Russia is Zavitinskoye. The extraction of lithium pegmatites at this deposit was started in 1937. The main ore minerals are spodumene (LiAlSi2O6) and beryl (Be3Al2Si6O18), with accompanying minerals of petalite (LiAlSi4O10), cassiterite (SnO2), and columbite-tantalite (FeTa2O6). In 1997, the mine was mothballed due to rising energy prices and a sharp deterioration in economic indicators [1]. However, the ore potential of the Zavitinskoye deposit has not been fully exhausted, and its richest areas are considered investment-attractive objects for the extraction of high-quality spodumene raw materials [4-5]. Currently, overburden dumps and two quarry lakes are located in the contours of the deposit, which are actively used by the local population for recreation and fishing.

Significant lithium reserves have also been noted for ores of the Orlovskoye and Etykinskoye tantaloniobate deposits associated with amazonite-albite granites with increased concentrations of tantalum (Ta) and related elements. The main carriers of Li, Rb, and Cs in these deposits are lepidolite (KLi2Al(Al, Si)O10(F, OH)2) and zinnwaldite (KLiFe2Al[Si2AlO10][F, OH]),. Rubidium and caesium in the ores of the Orlovskoye deposit are present in quantities of 0.16-0.03 % and 20-0.005 %, respectively, which allows them to be extracted along the way. Ore-bearing granites of the Etykinskoye deposit contain 0.0108-0.0192 % Rb [1]. Both deposits are currently also mothballed.

Recently, there has been increased interest in the study of rare metal deposits, including those mentioned above, which are associated with the development of the mineral resource base of Russia, in particular, the lithium industry [4-9]. Equally important is the study of issues related to the migration and accumulation of rare alkaline elements in technogenically transformed waters in mining areas. Many researchers have studied the hydrogeochemistry of Li, Rb, and Cs in the conditions of technogenesis. Thus, according to the data [10] in the acidic waters of the Kul-Yurt-Tau (pH 2.9) and Makanskoye (pH 4.2) quarry lakes formed after the mining of pyrite deposits in Bashkortostan, the range of rare alkali metal contents was Li – 13.5-47.1, Rb - 0.10-15.1, and Cs – 0.16–1.90 µg / L. After the mining of the Bakr-Tau pyrite deposit, also located in Bashkortostan, the content of Li – 70.7-89.4, Rb – 1.13-2.04, and Cs – 0.044–0.095 µg / L was determined in the formed quarry lake [11]. In the slightly alkaline drainage ditches of the Tyrynauz tungsten-molybdenum deposit, higher concentrations of rare metals were noted: Li – 1.40, Rb – 0.50, and Cs – 0.60 mg / L [12]. A hurricane content of Li – 13.9–300 and Rb – 1.9–32.5 mg / L was found in the drainage waters of the Udachnaya tube quarry in Western Yakutia [9]. In the technogenically transformed waters of the Bukukinsky and Bom-Gorkhonsky tungsten deposits and Bugdainsky molybdenum deposits of Eastern Transbaikalia, the maximum concentrations of rare alkali metals reached the values of Li – 589.0–1062, Rb – 45.0-74.9, and Cs – 3.67–49.0 µg / L [13–14].

2. Data and methods

The purpose of this work is to study the prevalence of lithium, rubidium, and caesium in the technogenic waters of the mining facilities of the Zavitinskoye, Etykinskoye, and Orlovskoye rare metal deposits of Eastern Transbaikalia. Hydrogeochemical testing of technogenically disturbed areas of the above-mentioned deposits was carried out in the summer periods from 2015 to 2021. A total of 46 water samples were taken. The objects of testing were quarry lakes, drainage drains from under dumps, tailings ponds, and drilling holes made for blasting operations during the development of deposits.

Water samples were taken in plastic bottles with a capacity of 1.5 liters each. pH and Eh were measured on site. For atomic absorption analysis of cations and trace elements, the samples were filtered through a paper filter with a pore diameter of 2–3 microns into plastic cups with a volume of 100 ml and acidified with concentrated nitric acid (1:1) of the OSCH brand. For mass spectrometric analysis by inductively coupled plasma, samples under pressure were filtered using a syringe through a membrane filter with a pore diameter of 0.45 microns into plastic tubes or glasses and acidified in the same way immediately after filtration. Chemical and analytical studies of water samples for macro
components and some trace elements were carried out in a certified laboratory of INREC SB RAS (Chita). Analyses of water samples by inductively coupled plasma mass spectrometry (ICP-MS) were performed at the analytical center of the Vinogradov Institute of Geochemistry SB RAS (Irkutsk).

3. Results and discussion
The results obtained on the chemical composition of the tested technogenic waters of mining facilities of rare metal deposits are presented in the table 1.

Table 1. Physico-chemical characteristics of technogenic waters of rare metal deposits of Eastern Transbaikalia, Li-Cs based on the results of ICP-MS analysis.

| Parameters, units | Orlovskoye | Deposit Zavitinskoye | Etykinskoye |
|-------------------|------------|---------------------|-------------|
| pH                | 3.5-7.96\(^a\) | 7.08-8.01 | 4.47-7.5 |
| Eh\(^b\), mV       | -87-575 | -86-172 | 238-418 |
| PO\(^c\), mgO L    | 348 | 113.8 | 316.2 |
| HCO\(_3\), mg L    | 20.7-226 | 39.6-281.8 | 4.27-67.7 |
| SO\(_4\)\(^2-\)    | 1073 | 408.8 | 132.9 |
| Cl\(^-\)           | 0.92-26.3 | 2.34-40.5 | 0.65-1.97 |
| F\(^-\)            | 4.4 | 23.4 | 1.02 |
| NO\(_3\)\(^-\)     | 0.72-56.5 | 0.31-21.5 | 0.36-17.9 |
| NO\(_2\)\(^-\)     | 33.5 | 3.08 | 5.12 |
| NH\(_4\)\(^+\)     | 0.009-0.74 | 0.009-30.4 | 0.006-0.033 |
| Ca\(^2+\)          | 28.3-801.9 | 37.1-327.1 | 4.30-159.8 |
| Mg\(^2+\)          | 201.3 | 146.4 | 28.9 |
| Na\(^+\)           | 6.61-339.0 | 2.69-87.9 | 0.70-38.4 |
| K\(^+\)            | 81.8 | 36.0 | 6.38 |
| \(\sum\) ions      | 3.78-28.8 | 13.4-50.7 | 2.28-11.7 |
| Li, \(\mu g / L\)  | 13.6 | 33.7 | 5.25 |
| Rb                 | 0.57-19.6 | 1.42-9.87 | 0.65-4.42 |
| Cs                 | 4.07 | 5.88 | 2.14 |
|                    | 2.12-4232 | 240-1624 | 52-1768 |
|                    | 1070 | 817 | 325.6 |
|                    | 26-3740 | 14.2-3877 | 6.86-868.8 |
|                    | 799.1 | 1247 | 131.3 |
|                    | 2.68-97.2 | 1.67-61 | 1.07-91.8 |
|                    | 34.5 | 27.0 | 39.8 |
|                    | 0.01-13.1 | 0.03-102 | 0.04-27.2 |
|                    | 2.91 | 36.8 | 5.66 |

\(^a\) In the numerator – the minimum and maximum, in the denominator – the average values.
\(^b\) Redox potential.
\(^c\) Permanganate oxidizability.

Strongly acidic pH (3.5) values were noted for the majority of water samples taken from the drainage channels of dumps and boreholes of the Oryol deposit (table 1). Similar results were noted
for the sub-basement waters of the overburden rocks of the Etykinskoye deposit (pH 4.47). The quarry waters of the Zavitinskoye, as well as the waters of the settling ponds of the Orlovskoye and Etykinskoye deposits, are neutral and slightly alkaline. The pH of these waters varies from 7.08–8.01. High Eh values (418 and 575 mV) are also characteristic of acidic waters, and lower and negative values (–86 and –87 mV) were noted in samples taken from a stream near the village of Pervomaisky and in the tailings pond of the Orlovskoye deposit.

The peculiarities of the man-made waters of these deposits also include a significant increase in mineralization (up to 3 g / L or more) in acidic waters, a high concentration of sulfate ions, and an abnormally high metal content (Al, Fe, Mn, Zn, Sr, As, W, U).

Abnormally high concentrations were also noted for rare alkaline elements. Thus, the maximum values for Li were recorded: 3877 µg / L in the neutral quarry waters of the Zavitinskoye and 3740 and 869 µg / L in the acidic sub-basement waters of the Orlovskoye and Etykinskoye deposits, respectively (table 1). The content of Rb in man-made waters of rare metal deposits ranges from 1.07-97.2 µg / L and Cs from 0.01-102 µg / L.

Comparison of the contents of rare alkaline elements relative to the average values for the waters of the hypergenesis zone [15] showed a significant excess of lithium, rubidium, and caesium, with values of Li – 95.9, Rb – 14.5, and Cs – 141.5 times the average for the technogenic waters of the Zavitinskoye deposit. For the waters of the Orlovskoye and Etykinskoye deposits, the indicators are respectively as follows: Li – 61.5, Rb – 18.5, and Cs – 11.2 times the average and Li – 10.1, Rb – 21.4, and Cs – 21.8 times.

To assess the ecological state of man-made waters of mining facilities of rare-metal deposits, the average values of concentrations of Li with maximum permissible concentrations (MPC) of substances for water bodies of fisheries [16] and those for drinking and cultural water [17] use were also compared. The results obtained, presented in the figure, indicate their significant excess over the standards. So, for the waters of economic, drinking, cultural, and household values, the excess over the MPC for Li is up to 26.6, 41.6, and 4.4 times; for waters of fishery value up to 9.98, 15.6 and 1.64 times for the Orlovskoye, Zavitinskoye and Etykinskoye deposits, respectively (figure 1).

![Figure 1. Comparison of the average values of Li concentration in the waters of the Orlovskoye (OR), Zavitinskoye (ZV) and Etykinskoye (ET) deposits with the maximum permissible concentrations of substances for fishery water bodies (MPC*), domestic drinking and cultural water use (MPC**)](image-url)

Since Li, Rb and Cs are highly toxic elements and belong to the second and first hazard classes, they can have a direct Orlovskoye toxic effect on aquatic ecosystems and landscapes. It is clear that
the flow of such waters into the river network of the adjacent territory as a result of natural runoff or pumping can cause its pollution, as well as be very dangerous to human health.

4. Conclusion
As a result of the conducted research, it was found that the technogenic waters of mining facilities of rare metal deposits of Eastern Transbaikalia contain abnormally high concentrations of rare alkaline elements, in particular Li (3.74 and 3.88 mg/L). An abnormally high excess of the Li and Cs content in man-made waters in the tens, hundreds, and thousands of times relative to the standards of the MPC of chemicals for the waters of economic, drinking, cultural, and household water use and fisheries value has been determined. This creates a real environmental hazard for the population living near the territories of both existing and former mines.

The need for further study of the hydrochemical composition of technogenic waters of ore deposits, in particular, the study of the water-migration properties of rare alkali metals, seems obvious. The results obtained are important both for studying the hydrogeochemistry of technogenic systems and for developing technological measures to restore mining landscapes.

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