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Thermodynamic calculations of uranium accumulation in saline lakes of West Mongolia.

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Abstract

The saline lakes are a unique geochemical barrier for the migration of uranium which forms oxides, hydroxides, carbonates, phosphates, fluorides and other minerals in lakes sediment. This article presents data of chemical composition of some salt lakes in Western Mongolia. The concentration U-238 in some lake waters up to 3 mg/l. Uranium, in turn, forms complexes with carbonate-ions and migrate to the lakes, and precipitates in lake sediments by influence of evaporation and water-rock interaction time. There is shown that accumulation of uranium in lake water due to two main factors: first, localization of the lakes and their watersheds in potential provinces of U-bearing rocks and, second, uranium complexing with carbonate (bicarbonate) anions.

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1. Introduction

Despite the aqueous migration and precipitation of uranium have been studied for decades [1-3], their mechanisms are still poorly investigated. We definitely know that uranium in natural waters occurs in quadri- and hexavalent forms and that reduction serves as a geochemical barrier for its precipitation.

Natural lakes with high concentrations of uranium are widespread, for example, Van in Turkey (110 μgL^{-1}) [4], Issyk-Kul in Kyrgyzstan (30 μgL^{-1}), Mono in the USA, California (300 μgL^{-1}), Shar Burdiin in Eastern Mongolia (15000 μgL^{-1}) [5]. In Western Mongolia, we have also discovered lakes with concentrations of uranium as high as 3000 μgL^{-1} (fig. 1). Because of their ecological pureness, these lakes present opportunities for investigating truly natural processes of water-rock interaction, for instance, migration and precipitation of uranium and its chemical compounds.

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The uranium content in the cores of sediments varies from $5.2 \cdot 10^{-5} \text{ g/g}$ (0-5 cm) up to $10.4 \cdot 10^{-5} \text{ g/g}$ (5-10 cm), which is 50 to 100 times higher than the concentration of uranium in lake water [7]. This fact explains our interest to investigate forms of precipitated uranium in detail.

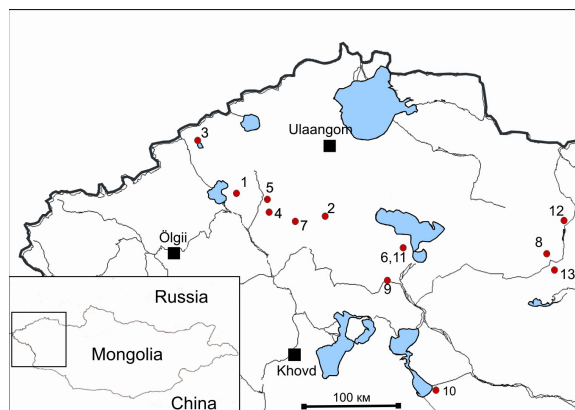


Fig. 1. Location of studied lakes. Square boxes – cities. Red dots – lakes (1-13): 1 - Baga1, 2 - Ulgin, 3 - Shaazgai, 4 - Ih-Gashun, 5 - Bor-Hag, 6 - Sangiin-Dalay, 7 - Tsohor, 8 - Unnamed, 9 - Tsagan, 10 - Baga2, 11 - Baga-Gashun, 12 - Tsavdan, 13 - Devteriyn-Davst.

2. Methods

Water samples were collected in 13 lakes (Fig. 1) annually during 2008-2011 in the same month (June). The samples have been treated immediately by filtering through $0.45 \mu\text{m}$ membrane filters and by acidification with ultra-pure HNO_3 . Physical properties of waters (specific conductivity, pH, oxidation-reduction potential, bicarbonate) were measured at each locality. Major cations and anions were determined by titration method in the "Water" Research and Training Center of the Tomsk Polytechnic University. Uranium was analyzed by ICP-MS (Agilent 7500) in the Institute of Solid State Chemistry and Mechanochemistry SB RAS. The computer modeling and calculation of the equilibrium reactions were done using the PHREEQC software package [6] and Pitzer database for lake waters with the highest ion strength.

3. Results and discussion

Saline lakes are widespread in Western Mongolia due to its arid climate and wide distribution of closed basins. They present different geochemical types: carbonate (soda), chloride and sulfate. Table 1 shows the variety of their physical and chemical properties.

Lake waters pH is near neutral to very strongly alkaline (7.1–9.8), total salinity ranges between 4 and 363 gL^{-1} , and oxidation-reduction potential ranges from -47 to $+132 \text{ mV}$. In all lakes, the dominant anion is HCO_3^- (up to 47%). Uranium is mobile and principally present as UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ complexes. [3].

In the arid climate of western Mongolia, where evaporation is 2-3 times higher than precipitation, evaporation concentration processes contribute much to the growth of salinity and uranium content in surface waters. However, we consider the main sources of uranium in the lakes of Western Mongolia it is a groundwater. The concentrations of uranium in it up to $0,2 - 0,3 \mu\text{gL}^{-1}$ [7].

Table 1. Physical properties, major cations, anions, silica and uranium in waters of the studied West Mongolian lakes

№	Lake	pH	TDS	(CO ₃) ²⁻	(HCO ₃) ⁻	(SO ₄) ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SiO ₂	U
				gL ⁻¹								µgL ⁻¹	
Soda lakes													
1	Baga 1	9,1	6,2	0,22	1,44	0,55	1,92	0,01	0,08	1,94	0,05	13,1	0,12
2	Ulgin	9,1	15	0,79	5,02	2,25	2,20	0,09	0,09	4,42	0,02	12,0	0,11
3	Shaazgai	9,3	15	0,77	3,37	0,75	5,00	0,01	0,02	5,13	0,10	18,2	1,01
4	Ih-Gashun	9,8	23	0,61	2,73	6,02	6,04	0,20	0,34	6,8	0,63	n.d.	0,3
5	Bor-Hag	9,2	28	1,21	7,10	4,80	6,30	0,10	0,63	8,03	0,31	n.d.	0,42
6	Sangiin-Dalay	9,5	74	0,72	3,47	19,2	23,1	0,012	0,37	22,5	4,38	4,3	0,38
7	Tsohor	9,3	100	0,76	3,97	52,2	9,41	0,02	0,27	31,5	1,54	7,5	0,25
Chloride lakes													
8	Unnamed	7,7	22	0	0,54	11,9	3,01	0,73	1,29	4,49	0,03	3,5	2,19
9	Tsagan	8,9	53	0,49	1,22	23,4	10,5	0,04	1,40	15,3	0,46	n.d.	0,28
Sulfate lakes													
10	Baga 2	8,2	4,2	0,005	0,97	0,39	1,40	0,004	0,09	1,24	0,08	13,9	0,13
11	Baga-Gashun	8,6	322	0,55	4,7	30,1	159	1,20	0,55	104	21,6	10,7	3,09
12	Tsavdan	7,1	340	0	0,93	35,3	191	0,14	26,8	84,8	1,50	4,7	0,22
13	Devteriyin-Davst	7,4	363	0	0,71	45,9	192	0,49	17,3	105	1,74	6,3	0,15

Table 2. Saturation Index for the investigated lakes calculated using PHREEQC

U minerals	Lakes (numbers are the same as in Fig. 1 and Table 1)												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Gummitte (UO ₃)	-13	-15	-13	-13	-14	-12	-11	-8,9	-11	-11	-4,6	-5,2	-5,4
Rutherfordine (UO ₂ CO ₃)	-8,6	-10	-9,1	-9,8	-9,8	-8,2	-7,5	-4,0	-7,5	-6,3	-0,3	-1,9	-1,9
Schoepite (UO ₂ (OH) ₂ :H ₂ O)	-7,6	-9,5	-8,1	-7,9	-9,2	-6,7	-6,3	-3,9	-6,5	-6,1	0,2	-0,5	-0,6
U ₃ O ₈ ©	-22	-32	-19	-23	-31	-19	-19	-2,9	-16	-20	-0,4	9,0	8,7
U ₄ O ₉ ©	-33	-55	-22	-37	-54	-30	-32	4,2	-23	-36	-9,5	22	21
UO ₃ ©	-9,9	-12	-10	-10	-12	-9,0	-8,5	-6,2	-8,8	-8,4	-1,9	-2,6	-2,7
Uraninite (UO ₂)	-9,7	-16	-6,0	-11	-16	-9,1	-9,9	1,4	-6,7	-11	-4,6	6,0	5,9
Uranophane (Ca(UO ₂) ₂ (SiO ₃ OH) ₂)	-16	-20	-17	-	-	-15	-14	-11	-15	-15	3,2	-0,8	-0,2
Coffinite© (USiO ₄)	-11	-18	-7,3	-	-	-11	-11	-0,4	-8,7	-12	-5,0	5,7	5,7

Considering the lakes of Mongolia located in the uranium-bearing provinces of Mongolia are characterized by a high content of uranium, a significant role in uranium accumulation in the waters of the upper hydrodynamic zone is provided by wide distribution of water-bearing rocks in lake catchments. The sources of uranium are vast granitic massifs (e.g., Harhira, Achitnuur, Oshkinsk), which are known to have natural radioactivity (Clark concentration is 25 g/t) [2]. Amount of uranium accumulated in ground water depends mainly on the time of water–rock interaction and on the equilibrium–nonequilibrium state of the system: the longer interaction time, the more uranium will be concentrated in the water, of course, the other things being equal. Analysis of the lake waters equilibrium with respect to uranium minerals shows that only four mineral phases can precipitate (Table 2): schoepite ($\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$), uraninite (UO_2), uranophane ($\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2$) and coffinite[©] (USiO_4). Equilibrium with respect to these phases is only achieved in three lakes where salinity exceeds 300 g.L^{-1} : Baga-Gashun, Tsavdan, Devteriyn-Davst. However Lake Unnamed 1, in which salinity is much lower (22 g.L^{-1}) is also at equilibrium with uraninite.

4. Conclusion

Thus, uranium accumulation in surface groundwaters is due to their flowage through the uranium-rich rocks and their alteration. Uranium is dissolved and transported as uranyl-carbonate complexes, and then precipitates in lake sediments principally under the form of oxide or oxi-hydroxide. Amount of precipitated uranium depends on intensity of evaporation and on duration of water-rock interaction.

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