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Lithium and Uranium in Closed Lakes of Western Mongolia

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Abstract

Data obtained in the investigation of the microcomponential (Li, U *etc.*) and macrocomponential (Na, Ca, K, Mg, Cl, SO_4, CO_3, HCO_3) composition of water in salt lakes of Western Mongolia are generalized. It is revealed that the majority of salt lakes in this region are characterized by an increased concentration of a number of micro components (lithium, uranium *etc.*). It is demonstrated that lithium is concentrated in chloride lakes, whereas uranium does in sodium ones. Calculations of equilibria in lake water with the basic minerals of water-enclosing rocks are presented.

Key words: chemical composition, mineralized water, lakes of Mongolia, lithium, uranium

INTRODUCTION

In recent years, there was interest grown in lakes as potential sources of Li and U [1–3]. The content of these elements in the lakes of Western Mongolia, to our knowledge, amounts up to 100 and 1 mg/L, respectively [4, 5]. In this regard, there appear problems of revealing the main distribution patterns for lithium and uranium in the lakes of Western Mongolia. Here is a brief description of the lakes under study. In the western part of Mongolia there are the largest salt lakes of this country located. They are Uvs Nuur (3350 km^2), Hyargas Nuur (1407 km^2), Thelmen Nuur (194 km^2), and others [6, 7]. Alongside with the large lakes there are also a great number of medium-sized and small lakes. The climate of the area is distinctly continental. The daily changing amplitude of atmospheric air temperature reaches 30 °C, whereas the annual changing amplitude is equal to 90 °C.

The average annual amount of atmospheric precipitations ranges within only 100–200 mm, whereas the evaporation level amounts up to 1000–1500 mm [7]. It is believed that the accumulation of salts in the internal-drainage basins could be caused by insufficient climatic humidity level, a significant deficiency of atmospheric air humidity and a high evaporation level. However, these factors cannot explain the diversity of the chemical composition of lake waters, different mineralization level and geochemical features *etc.* those are manifested under the conditions of the same climate. No sources and mechanisms inherent in uranium and lithium selective accumulation in the lakes were revealed, as well as no extent of this phenomenon was determined. Just these questions have become the subject of the present investigation.

DESCRIPTION OF THE OBJECTS UNDER INVESTIGATION

For the analysis we used partially published [4, 5] data concerning field investigations carried out by the authors in 2007–2010. The main chemical types of lakes developed in the area under investigation are presented by soda, chloride and less often by sulphate composition (Table 1). The distinctive feature of soda lakes consists in their high alkalinity (the pH value ranging within 9.0–10.3, average value being equal to pH 9.4). As far as the sulphate and chloride lakes are concerned, the average pH value therein amounts to 7.4 and 8.1, respectively. Furthermore, the soda lakes exhibit a relatively low mineralization level ranging from 4.3 to 138 g/L (average 37 g/L), but a high content of bicarbonate and carbonate ions, 4.3 and 0.6 g/L, respectively, which several times exceeds the content of these ions in chloride and sulphate waters. By the contrast, the content of sulphate

TABLE 1

Chemical composition for different types of Western Mongolia lakes

Chemical components	Hydrogeochemical type of lakes								
	Soda (n = 15)			Chloride (n = 11)			Sulphate (n = 3)		
	Content								
	min.	max.	average	min.	max.	average	min.	max.	average
pH	9.0	10.3	9.4	7.2	8.9	8.1	7.1	7.6	7.4
E_h, mV	80	132	95	50	101	83	77	203	125
HCO_3^-, g/L	0.9	29.1	4.3	0.5	4.7	1.3	0.4	1.7	0.9
CO_3^{2-}	0.1	1.4	0.6	0	0.5	0.1	0	0.2	0.1
SO_4^{2-}	0.5	52.2	8.1	0.4	86.3	19.2	0.8	117	65.3
Cl^-	0.6	43.1	7.8	0.4	190	54.5	0.2	75.6	29.1
F^-, mg/L	5.8	89.8	25.2	0.4	64.9	14.8	1.7	4.8	3.4
Br^-	1.1	110	20	0.2	1127	153	0.6	86	33
B	0.6	66.7	11.3	0.2	252	44	0.4	21.1	8.5
NO_3^-	0.2	28.6	4.5	0.1	73.7	31.6	0.5	28.5	11.8
NO_2^-	0.2	7.6	1.3	1.6	41	17.4	1.9	3.3	2.6
Ca^{2+}, g/L	0.004	0.4	0.1	0.004	2.2	0.4	0.03	0.3	0.2
Mg^{2+}	0.01	2.0	0.4	0.1	28.7	5.3	0.1	24.1	8.8
Na^+	0.6	43.0	9.6	0.4	107	32.8	0.4	58.0	33.1
K^+	0.02	4.4	0.6	0	21.6	2.8	0.05	1.6	0.6
Sr^{2+}, mg/L	0.04	23	3.1	1.4	11	4.6	1.2	6.2	3.4
NH_4^+	0.1	13.5	3.4	0.7	17.9	6.9	0.7	4.7	2.7
Li^+	0.1	3.4	0.9	0.02	97.9	9.9	0.02	2.4	0.8
U	0.02	1.0	0.2	0.01	3.1	0.05	0.02	0.08	0.04
SiO_2	2.0	78.3	20.2	0.3	94.2	19.3	13.9	17.9	15.4
Total salts, g/L	4.3	138	31	2	418	116	2.0	278	138

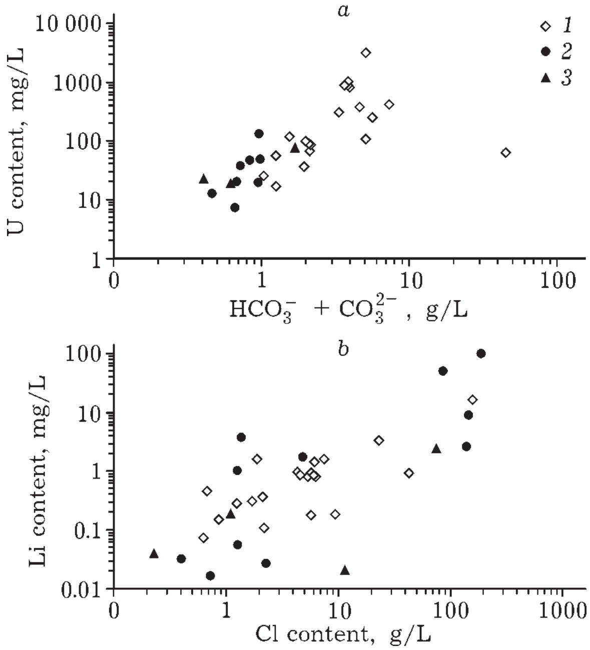

Fig. 1. Uranium content depending on the total content of hydrocarbonate and carbonate ions (*a*) and the lithium content depending on the content of chloride ions (*b*). The lake type is denoted as it follows: soda (*1*) chloride (*2*), sulphate (*3*).

and chloride ions in soda lakes is minimal comparing to all the other types of lakes (average content 8.1 and 7.8 g/L, respectively).

High pH values in the waters of the lakes under consideration determine also a high content of SiO_2 ranging from 2.0 to 78.3 mg/L (average 20.2 mg/L), which is higher to a significant extent than those inherent in the other types of lakes. The soda lakes are also characterized by the lowest content of Ca^{2+} and Mg^{2+}. In addition, the soda lakes are much richer in uranium (0.02–1.0 mg/L, average 0.2 mg/L), but they are relatively poor with lithium (Fig. 1, *a*). Some of the lakes of this type are enriched with sulphate and chloride ions. No direct correlation between the total mineralization and uranium content in the lake waters was revealed, since the mentioned correlation is manifested via the geochemical environment. Although complete analysis of water for uranium deposits are not available from the literature, it is obvious that all of the waters with a high content of uranium are alkaline and soda type (see Table 1) [9].

The intermediate values of the mineralization level (average value amounting to about 116 g/L) are inherent in chloride lakes. The saltiest lake in this series is presented by the Davsan Noor Lake, with the total salt content up to 418 g/L. The chloride lakes are also distinguished by a maximum average content of chloride and calcium ions (54.5 and 0.4 g/L, respectively). As far as the composition is concerned, among them there prevail sodium chloride type, and only a small part belongs to chloride-bicarbonate and chloride-sulphate type (13 and 3 %, respectively). Comparing to the soda lakes, the content of Ca^{2+} and Mg^{2+} in the waters of chloride type lakes is higher to amount up to 0.4 and 5.3 g/L, respectively. The water of chloride-type lakes contains the greatest amount of lithium, 98 mg/L (average 9.9 mg/L) (see Fig. 1, *b*). Alongside with lithium, chloride lakes are typically characterized by an increased content of most micro components, mg/L: Br 153, B 44, Sr 4.6, as well as that of biogenic elements, mg/L: NH_4 6.9, NO_2 17.4, NO_3 31.6.

The sulphate type of lakes is the least common in the area under investigation, but they exhibit the highest values of mineralization level (from 2 to 278 g/L, average 138 g/L) and the minimum values of pH (7.1–7.6, average pH 7.4). Sodium sulphate water type is prevailing, although in pure form such waters rarely occur, since they contain chloride ion in significant amounts. For the sulphate lakes a maximum content was revealed for Mg^{2+}, Br and B (8.8, 8.5 and 33 mg/L, respectively), but a minimum content was found out for Li, U and F (0.8, 0.04 and 3.4 mg/L, respectively).

Thus, in the territory of Western Mongolia there are widely developed different types of lakes, among those soda and chloride types are prevailing. The analysis we performed demonstrated that the latter two types differ from each other to a significant extent. So, soda-type waters are more alkaline, they concentrate uranium, whereas chloride type waters exhibit a higher mineralization level, they accumulate lithium.

RESULTS AND DISCUSSION

In order to establish the reasons for these differences, we calculated the equilibrium between lake waters and the main mineral bearing rocks. We performed calculations with the use of a HydroGeo software package [10] with real temperature values (25 °C), pH and E_h, at a pressure of 0.1 MPa.

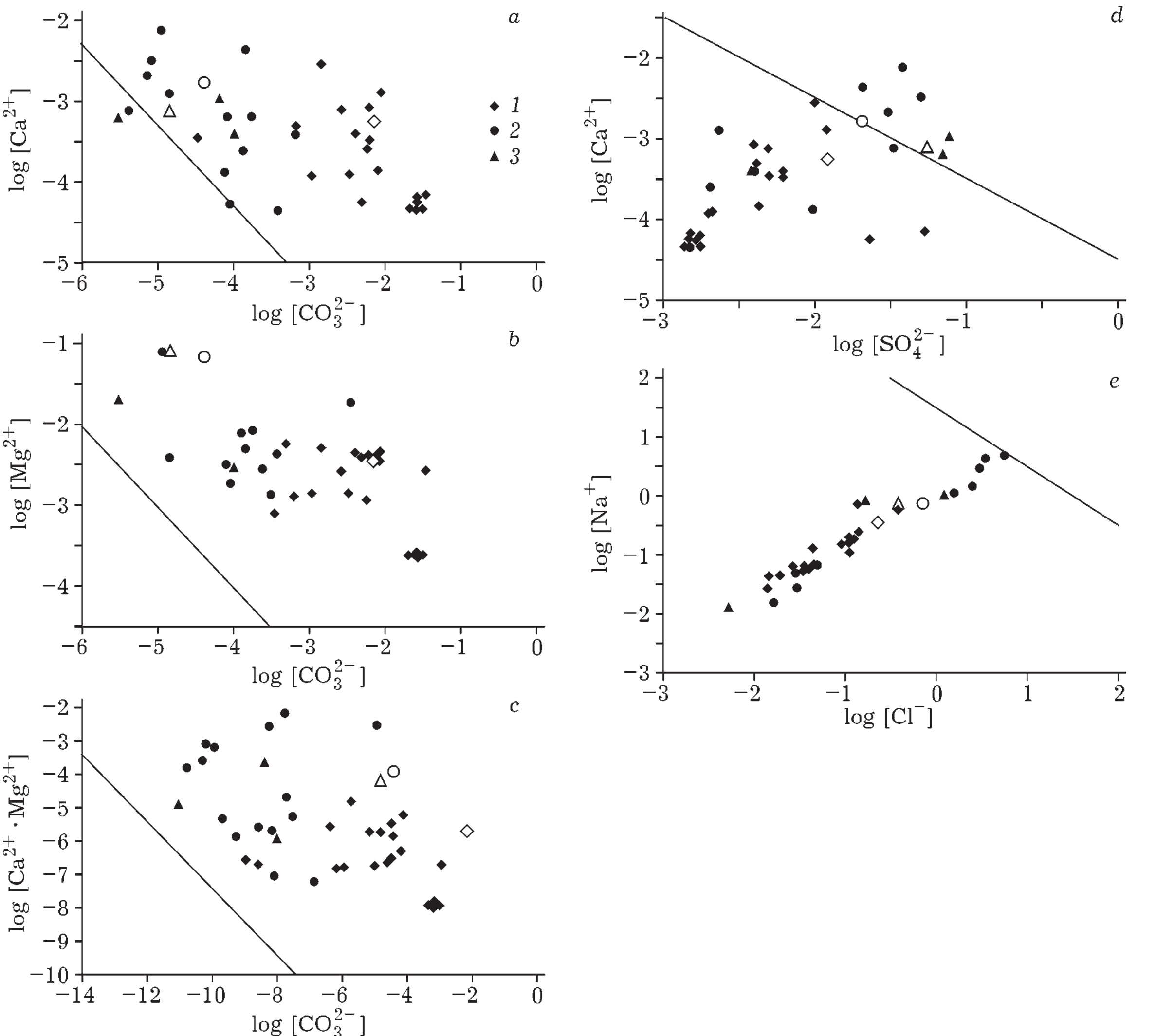

Fig. 2. Equilibrium between the lake waters of Western Mongolia and calcite (*a*), magnesite (*b*), dolomite (*a*), gypsum (*d*), halite (*e*) at the temperature of 25 °C. The lake type is denoted as it follows: soda (*1*) chloride (*2*), sulphate (*3*); open symbols show the average values for corresponding types of lakes.

The results of thermodynamic calculations demonstrated that the overwhelming majority of the Western Mongolia lake waters are saturated with respect to calcite (Fig. 2, *a*). The only exceptions are presented by the two lakes: sulphate type Ihes Nuur Lake and chloride type Hulam Nuur Lake those differ from the other in minimum pH values (6.1 and 7.2, respectively). In addition, all the lake waters exhibit equilibrium with magnesite and dolomite (see Fig. 2, *b*, *c*).

A somewhat different picture is typical for the equilibrium of the waters under investigation with gypsum and halite: the overwhelming majority of lake waters is non-equilibrium with respect to these minerals, as opposed to carbonate minerals. The equilibrium with gypsum (see Fig. 2, *d*) is inherent only in the six lakes such as Tonkha Nuur, Ihes Nuur, Sangiyn-Dalay Nuur, Uvs Nuur and Davsan Nuur Lakes, among those the former four lakes represent chloride lakes, the others are sulphate lakes. All of these lakes exhibit the sulphate ion content exceeding 30 g/L, whereas the mineralization level being greater than 150 g/L. Equilibrium with halite is observed only in the case of water in the Davsan Nuur Lake, whose mineralization level is equal to 430 g/L (see Fig. 2, *e*).

All the lake waters are saturated not only with respect to salts, but also with respect to many clay minerals, among those there are montmorillonite and illite species, sometimes kaolinite species prevailing (Fig. 3). A part of lake waters is saturated with respect to albite,

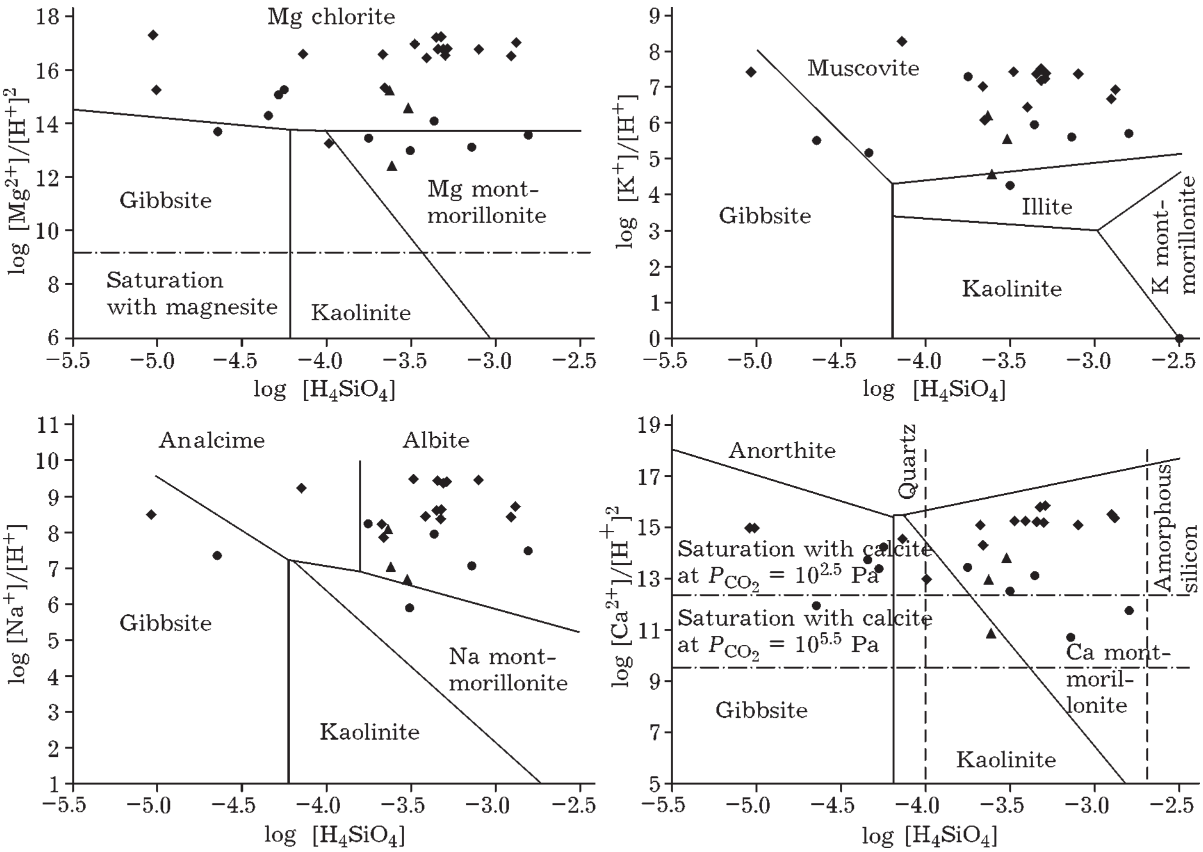

Fig. 3. Equilibrium between the lake waters of Western Mongolia and aluminosilicate minerals at the temperature of 25 °C. The lake type is denoted as it follows: soda (*1*) chloride (*2*), sulphate (*3*).

muscovite, Mg chlorite, but never with respect to anorthite and olivine.

Thus, in a similar manner with respect to underground water, the lake waters form an equilibrium-non-equilibrium system with rocks, *i. e.*, the water dissolves some minerals (mainly endogenous aluminum silicates), to form at the same time any other. Calcium and magnesium ions are bound mainly by carbonate and partly (Ca^{2+}) by sulphate minerals; SiO_2, K^+ and partly Na^+ are bound by secondary aluminosilicates, sulphate ion is partly bound by gypsum. The content of other elements those did not reached equilibrium with any secondary mineral could increase (*e. g.*, Cl^-) only until reaching the stage of saturation by either secondary mineral.

Another important factor consists in water evaporation level in the lake: the greater it is, the higher is the concentration of mobile elements in the lake water, but the lower is the content of the elements those are bound by secondary formations. In this regard, different lithium and uranium behaviour in the lakes is indicative.

Lithium entering the lakes is being concentrated mainly due to the processes of water evaporation. This fact is confirmed by a relatively high correlation level of lithium content with the content of chlorine (the correlation coefficient $r = 0.7$, see Fig. 1, *b*) which is of the same origin. Two chloride lakes (the Baga Gashun Nuur Lake and the Davsan Nuur Lake) exhibit a commercial lithium concentration level ≥10 mg/L (16 and 90 mg/L, respectively). At the same time the maximum lithium content in soda lakes amounts up to only 3.4 mg/L, whereas in sulphate ones the concentration is equal to only 2.4 mg/L.

As far as uranium is concerned, the maximum content was found out in the waters of soda lakes (up to 3 mg/L, see Table 1). Furthermore, a high correlation level of uranium content was revealed with respect to HCO_3^- ($r = 0.71$) and CO_3^{2-} ions ($r = 0.69$) (see Fig. 1, *a*), at a relatively low correlation with the mineralization level. The maximum uranium reserves in the lakes are also associated exclusively with soda lakes [4, 5].

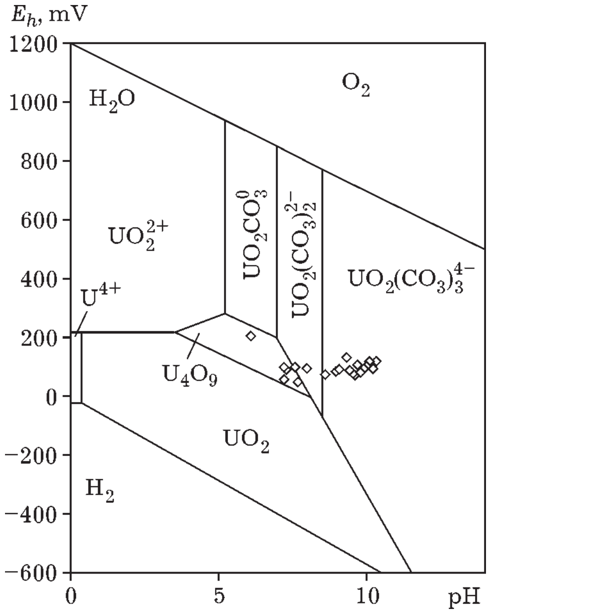

Fig. 4. pH−E_h diagram for UO_2−CO_2−H_2O (T = 25 °C, P_{CO_2} = $10^{-2.33}$ atm, the activity of UO_2^{2+} = 10^{-6} mol/L).

It is obvious that in soda lakes the uranium can form complex compounds with carbonate ions such as $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ *etc.* (Fig. 4) becomes mobile and thereby it could be accumulated in water [11]. Thus, the accumulation of uranium in lake waters is associated with the genesis of soda. However, it should be noted that the soda formation starts since water being saturated by calcite and/or magnesite. The absence of equilibrium between such water and endogenous aluminosilicates or part of them (see Fig. 3) provides dissolving them to precipitate carbonate and clay minerals with the accumulation of mobile elements in solution, especially Na and U [8]. As a consequence, the soda waters and lakes always exhibit elevated content of these elements with respect to the others. It's natural that the evaporation of water also promotes concentrating U and Na and, judging by the content of Cl, the soda lakes in Mongolia exhibit this process to take place. However, the sources of uranium, as well as that of sodium, are presented by the rocks of water collecting areas. The specific role of evaporation and rocks in the enrichment of lakes with uranium should be elucidated in the future.

CONCLUSION

Thus, over the territory of Western Mongolia, there are widespread lakes of different geochemical types. The composition of these waters is in many respects dependent both on the level of water evaporation, and on the nature of the interaction between lake water and rocks occurring over the territory of basin. It is demonstrated that lithium concentrates in chloride-containing lakes, whereas uranium concentrates in soda-containing ones. The presence of elevated uranium concentration in the soda lakes could be connected, to all appearance, with the entry of this element to the lake water in the form of carbonate complexes of uranyl ion from the rocks of uranium-ore regions wherein the catchment area of the lakes is located.

REFERENCES

1 Ariunbileg S., Isupov V. P., Vladimirov A. G., Krivonogov S. K., Shatskaya S. S., Kuybida L. V., *Mongolian Geoscientist*, 35 (2009) 115.

2 Mingkuan Qin, Current Progresses and Prospects on Uncoventional Uranium Resources (UUR) of China. Technical Meeting on Uranium from Unconventional Resources, 4−6 November 2009, IAEA Headquarters, Vienna. URL: http://www.iaea.org/OurWork/ST/NE/NEFW/ documents/ RawMaterials/TM_Vienna2009/presentations/9_QIN-CHINA.pdf.

3 Linhoff B. S., Bennett P., Puntsag T., Gerel O., *Environ. Earth Sci.*, 62 (2011) 171.

4 Isupov V. P., Vladimirov A. G., Shvartsev S. L., Lyakhov N. Z., Shatskaya S. S., Chupakhina L. E., Kuybida L. V., Kolpakova M. N., Ariunbileg S., Krivonogov S. K., *Chem. Sustain. Dev.*, 19, 2 (2011) 135.
URL: http://www.sibran.ru/English/csde.htm

5 Isupov V. P., Vladimirov A. G., Lyakhov N. Z., Shvartsev S. L., Ariunbileg S., Kolpakova M. N., Shatskaya S. S., Chupakhina L. E., Kuybida L. V., Moroz E. N., *Dokl. RAN*, 437, 1 (2011) 85.

6 Egorov A. N., *Hydrobiol.,* 267 (1993) 13.

7 Rasskazov A. A., Sevastyanov D. V., Luvsandorzh Sh., Egorov A. N., Tserensodnom Zh., Ozera MNR i Ikh Mineralnye Resursy, Nauka, Moscow, 1991.

8 Sevastyanov D. V., Shuvalov V. F., Neustrueva I. Yu., Limnologiya i Paleolimnologiya Mongolii, Nauka, St. Petersburg, 1994.

9 Shvartsev S. L., Ryzhenko B. N., Alekseev V. A., Dutova E. M., Kondratieva I. A., Kopylova Yu. G., lepokurova O. E., Geologicheskaya Evolyutsiya i Samoorganizatsiya Sistemy Voda−Poroda, vol. 2, Izd-vo SO RAN, Novosibirsk, 2007.

10 Bukaty M. B., *Razvedka i Okhrana Nedr*, 2 (1997) 37.

11 Perelman A. I, Geokhimiya, Vyssh. Shkola, Moscow, 1989.