

The chemical and isotopic compositions of thermal waters and gases in the Republic of Buryatia, Russia

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Abstract. The chemical and isotopic compositions of waters and associated gases in the Republic of Buryatia are investigated in this report. Results show the thermal waters are predominantly enriched in N_2 . They are alkaline, low salinity and have high concentrations of HCO_3^- , SO_4^{2-} , F, Si but low values for Ca^{2+} , Mg^{2+} , K^+ . According to isotopic composition, the thermal waters are meteoric in origin. Despite the low salinity, the thermal waters are in equilibrium with calcite, magnesite, fluorite, albite, laumontite and other minerals but are not equilibrium with respect to primary aluminosilicates. This indicates that the thermal waters and water-bearing rocks represent the equilibrium-nonequilibrium system.

1 Introduction

Thermal waters are distributed around the world, especially within tectonically active areas, and attract the attention of many scientists. The most discussed issues in case of thermal waters include the processes and mechanism of their formation, depths of circulation, trace-element geochemistry, processes of their interaction with water-bearing rocks, thermodynamic equilibrium with different minerals, and genesis of secondary minerals.

The thermal waters of the studied region were considered previously [1-3]. The papers are dedicated to chemical composition peculiarities and the saturation state with different minerals of the thermal waters in the Baikal rift zone in general.

The updated data for the thermal waters, particularly in the Republic of Buryatiya, is presented in the current manuscript. The manuscript is aimed at the detailed investigation of the thermal waters' composition and equilibrium with the main minerals of water-bearing rocks for the further identification of the mechanisms and processes of their formation.

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2 Site description

The Republic of Buryatia is located in the south-central region of Siberia, Russia (Fig. 1) along the eastern shore of Lake Baikal. Geologically the territory is located within the frameworks of the Baikal Rift Zone. It is the largest zone in Eurasia and the second largest continental zone and thermal waters of different compositions are widespread. The Baikal Rift Zone is located at the boundary between the Precambrian Siberian Platform and the Transbaikalian folded area and differs from the surrounding areas in the abundance of deep faults that resulted from rifting processes. The faults, with their water penetrate to depths of 12–15 km, based on data of electrometric monitoring [4].

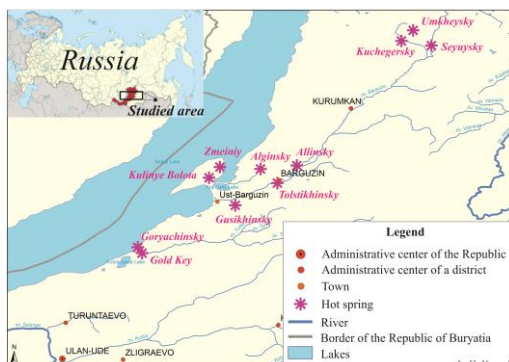


Fig. 1. Location of hot springs in the Republic of Buryatia.

The Baikal Rift Zone within the Republic of Buryatiya is composed mainly of intrusive rocks where the thermal waters' discharge zones are located. The waters occur in Barguzin complex represented by intrusive rocks of Proterozoic age. The Barguzin complex of granitoids consists of two phases: (1) medium-grained porphyritic (often, gneissoid) biotitic, biotite-hornblende, and hornblende granites, granosyenites, granodiorites, syenites, and diorites and (2) medium- and fine-grained massive and gneissoid (sometimes, porphyritic) biotitic granites [1].

3 Materials and methods

This research is based on the results of hydrogeochemical sampling that was conducted in 2016. The thermal springs were sampled for chemical, gas and isotopic compositions. The rapidly changing parameters: pH, temperature, and electrical conductivity, were determined in-situ by using an AMTAST AMT03 (USA) device. The samples were filtered in the field using a 0.45 μm membrane filter. The major chemical elements were determined by a titration method with a liquid analyzer “Anion 7-51” (Russia) and ion chromatography with a Dionex chromatograph ICS-00 (USA). The water isotopic analysis (D, ¹⁸O) was conducted by using an isotope mass spectrometer with a TC/EA-IRMS element analyzer (Finnigan MAT 253, Thermo Scientific, USA). The free gas composition was determined by gas chromatography, with chromatograph “Khromos-GKh-1000”.

Analyses were conducted in certified laboratories. The analysis for major elements composition was carried out in The Problem Research Laboratory of Hydrogeochemistry (TPU, Tomsk), the isotopic composition – in the Center for Chemical Analysis and Physical Testing (ECUT, Nanchang, China) and free gas composition – in the laboratory of Production and Geological Company “Sibgeocom” (Irkutsk, Russia).

The saturation states of the thermal waters with primary and secondary minerals were calculated using the Geochemist's Workbench software [5] at the springs' temperature. The saturation index (SI) is defined as

$$SI = \log(Q/K), \quad (1)$$

where Q is the reaction quotient (or ion activity product) and K is the equilibrium constant at a given temperature and pressure. In the case when SI=0 water is in equilibrium with the mineral and no dissolution or precipitation should take place. SI>0 indicates that

the solution is supersaturated with respect to a given mineral; $SI < 0$ indicates undersaturation.

4 The chemical and isotopic composition of water and gas

The gas data show the type of thermal waters of the Republic of Buryatia change from CH_4-N_2 to N_2 , but are predominantly enriched with nitrogen that comprises 35 to 99 vol.% (Table 1). The hot springs with N_2 exceeding 85 vol.% refer to the N_2 -rich thermal waters. However, there are two springs where CH_4 is the dominant gas comprising 61-62 vol.% and nitrogen values are below 40 vol.%. These two springs belong to the CH_4-N_2 thermal waters. The content of other gases does not exceed 1 vol.% except for O_2 and CO_2 , with values that reach 7 and 3 vol.%, respectively.

Table 1. The gas composition of the thermal (vol.%) waters in the Republic of Buryatia.

№	Hot spring	N_2	O_2	CO_2	H_2	He	CH_4
16-7	Alginsky	34.8	0.60	1.98	0.000529	0.01	62.0
16-10	Kuchigersky	37.9	0.58	0.00	0.000212	0.02	60.9
16-6	Tolstikhinsky	86.1	0.43	0.00	0.000209	0.08	12.7
16-3	Kulinye Bolota	87.7	0.55	0.00	0.000264	0.11	10.9
16-5	Gusikhinsky	89.5	7.09	2.92	0.000339	0.08	0.01
16-11	Seuisky	98.4	1.01	0.00	0.000346	0.11	0.00
16-9	Umkheysky	98.7	0.51	0.00	0.000402	0.12	0.17
16-4	Zmeiny	98.9	0.45	0.00	0.000235	0.16	0.14

The chemical composition data (Table 2) show that the salinity of the thermal waters from 453 to 858 mg/L. Despite the low TDS, the thermal waters are alkaline, with pH values of 8.19-9.66. The high pH and low salinity are typical for the N_2 -rich thermal waters but unusual for the majority of natural waters. The explanation for this is discussed in details in [1, 3, 6], but it should be briefly mentioned that this results from OH^- formed by the hydrolysis of aluminosilicate minerals and the absence of alkalinity neutralizing acids.

Table 2. The chemical composition (mg/L) of the thermal waters in the Republic of Buryatia.

№	Hot spring	T, °C	pH	Eh, mV	TDS	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	SiO ₂	F ⁻
16-1	Goryachinsky	51	9.03	-206	685	15.6	42	365	6.2	34.7	2.44	149	4.34	63	3.0
16-2	Gold Key	45	8.80	-110	526	10.0	60	210	19.6	12.9	1.22	123	4.21	78	6.9
16-3	Kulinye Bolota	51	9.40	-115	628	25.8	137	133	32.6	2.1	0.73	154	3.40	121	19.0
16-4	Zmeiny	37	9.55	-350	582	25.2	144	122	40.5	4.4	0.24	146	2.24	88	9.1
16-5	Gusikhinsky	72	8.47	38	858	9.4	106	356	33.5	17.2	0.98	211	12.00	101	10.9
16-6	Tolstikhinsky	29	9.66	-240	453	19.5	128	92	20.8	3.2	1.22	114	2.50	62	9.5
16-7	Alginsky	21	8.19	124	664	3.0	63	338	15.5	81.7	1.59	104	5.63	47	4.4
16-8	Allinsky	43	9.22	-339	556	28.5	154	88	14.3	8.6	0.73	122	4.31	125	11.5
16-9	Umkheysky	48	9.50	-275	506	42.0	134	79	12.4	1.7	0.85	125	1.90	95	14.4
16-10	Kuchegersky	38	9.51	-300	465	29.4	110	90	15.0	2.3	0.92	118	1.51	86	12.0
16-11	Seyuysky	53	9.38	-244	456	35.7	100	85	11.0	2.0	0.31	130	1.55	72	19.0

The redox (Eh) predominantly ranges from -350 to -110 mV but there are two hot springs, 16-5 and 16-7, where Eh values are respectively 38 and 124 mV. These springs are with high O_2 content in the gas. The temperature of the thermal waters varies from 21 to 72 °C. Two hot springs are located next to rivers, therefore, their temperature (21 and 29 °C) is lower, probably because of the mixing with colder waters.

The chemical composition is characterized by clear competition between SO_4^{2-} and HCO_3^- among anions. The concentration of SO_4^{2-} and alkalinity⁻ ranging respectively from

79 to 365 mg/L and from 69 to 218 mg/L. The Cl^- content is lower, 6.2-40.5 mg/L. Among cations, Na^+ is dominant except for Alginsky hot spring, where Ca^{2+} values are higher. The concentrations of Na^+ vary from 104 to 211 mg/L. The concentrations of Mg^{2+} and K^+ are low and do not exceed respectively 2.5 and 6 mg/L, excluding the Gusikhinskiy hot spring where K^+ content reaches 12 mg/L. The thermal waters of the Republic of Buryatia are significantly enriched in F^- and SiO_2 with concentrations ranging respectively from 3 to 19 mg/L and from 47 to 125 mg/L. To summarize, the thermal waters investigated change from $\text{HCO}_3\text{-SO}_4\text{-Na}$ to $\text{SO}_4\text{-Na}$ through $\text{SO}_4\text{-HCO}_3\text{-Na}$ type waters (Fig. 2).

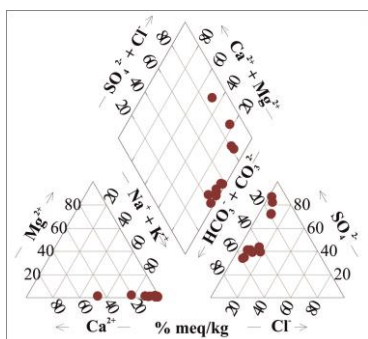


Fig. 2. The Piper diagram for the thermal waters of the Republic of Buryatia.

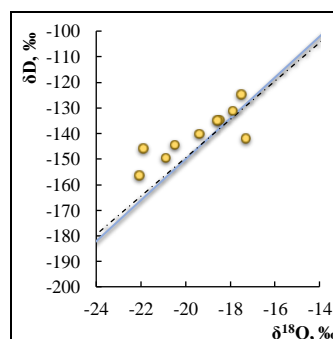


Fig. 3. Isotopic composition of the thermal waters in the Republic of Buryatia.

The isotopic composition of the thermal waters was studied to determine their genetic type. The data obtained and isotopic composition of the region's precipitation [7] show that the thermal waters plot along the local meteoric water line (Fig. 3). Therefore, the thermal waters of the Republic of Buryatia are meteoric in their origin. The isotopic composition is characterized by very low content of D and ^{18}O that respectively ranges from -156 to -124 ‰ and from -22.1 to -17.3 ‰. It can be explained by the waters originating within glacial deposits with a much lighter isotopic composition [8].

5 The thermal waters equilibrium with minerals of water-bearing rocks

Results of the thermodynamic calculation show that the thermal waters of the Republic of Buryatia are in equilibrium with some minerals and are not in equilibrium with others. To consider the saturation state of the thermal waters with carbonate minerals, it is shown in the Fig. 4 that despite low salinity and low content of Ca^{2+} and Mg^{2+} the waters are saturated with calcite (Fig. 4a) and magnesite (Fig. 4b). The equilibrium with calcite and dolomite becomes a geochemical barrier which limits the accumulation of Ca^{2+} and Mg^{2+} in these waters.

The thermal waters also achieved equilibrium with fluorite and saturation with fluorite is attained at lower temperatures than to carbonates (Fig. 4c). We will not focus on the fluorine's sources and its accumulation mechanisms in details because it was considered previously [6, 9]. But briefly mention that the high concentration of F^- in the studied thermal waters are the result of aluminosilicate hydrolysis and relatively low Ca values.

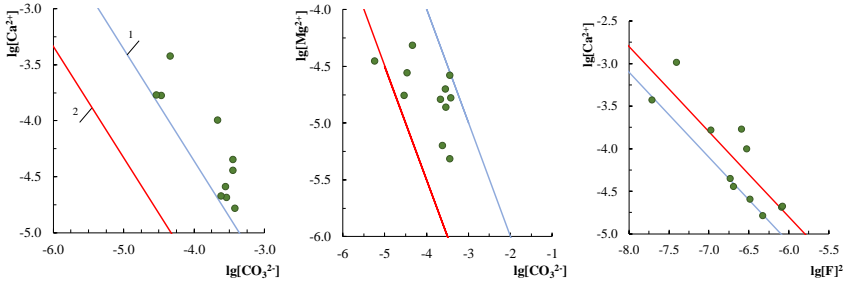


Fig. 4. The equilibrium of thermal waters with calcite (a), magnesite (b) and fluorite (c) at 25 °C (line 1) and 100 °C (line 2).

Contrary to the saturation with carbonate minerals, the thermal waters of the Republic of Buryatia exhibited more complex saturation states with respect to aluminosilicate minerals (Fig. 5). The thermal waters are saturated with albite, laumontite, microcline, glaucophane, chlorite and other minerals. But the thermal waters were not at equilibrium with primary aluminosilicate minerals, including anorthite, analcime, and forsterite.

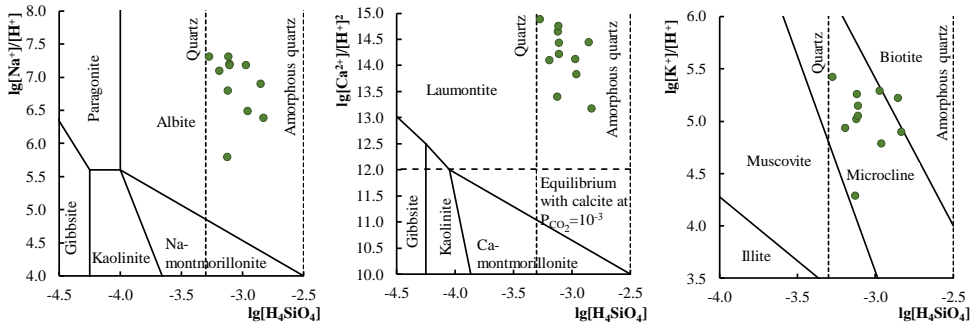


Fig. 5. Saturation states of the thermal waters with aluminosilicate minerals: (a) HCl–H₂O–Al₂O₃–Na₂O–SiO₂ system at 100°C; (b) HCl–H₂O–Al₂O₃–CaO–SiO₂ system at 100°C; (c) SiO₂–Al₂O₃–K₂O–CO₂–H₂O system at 100°C.

6 Conclusion

In the Republic of Buryatia, thermal waters are widely distributed. They are meteoric, HCO₃–SO₄–Na and SO₄–Na, predominantly enriched with N₂ gas, alkaline, with low TDS, high concentrations of HCO₃⁻, SO₄²⁻, F⁻, Si and low content of Ca²⁺, Mg²⁺, K⁺. The thermal waters and water-bearing rocks represent a unique equilibrium–nonequilibrium system. The thermal waters are undersaturated with minerals which continuously dissolve, including anorthite, analcime, and forsterite, but are at equilibrium with respect to other minerals which form at the same time, including calcite, magnesite, fluorite, albite, laumontite, microcline, glaucophane, and chlorite [9].

This study was made under the support of Russian science foundation, grant №. 17-17-01158 and was funded by RFBR according to the research project № 18-55-80015

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