

Dissolved gas composition of groundwater in the natural spa complex «Choygan mineral waters» (East Tuva)

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Abstract. The natural spa complex «Choygan mineral waters», a unique deposit of natural carbon dioxide mineral waters in Siberia, is located in the Eastern Sayan Mountains. There are 33 springs discharge in this area. Spring waters are mainly HCO₃-Na-Ca type. TDS varies from 300 mg/L to 2600 mg/L and temperature ranges from 7 °C (in spring 33) to 39 °C (in spring 12), pH varies from 5.9 to 8.3, and the value of the oxidation-reduction potential is from -170 mV to 236 mV. All studied waters were divided into two groups according to their temperature and geochemical conditions: cold fresh water with oxidizing conditions and warm slightly brackish water with reductive conditions. The gas composition of the studied waters is represented by nitrogen (28-75 vol.%), carbon dioxide (6-65 vol.%), oxygen (7-19 vol.%), radon (4-948 Bq/l). The studied gases differ not only by the content but by the different sources.

1. Introduction

Natural carbon dioxide mineral waters are widely spread in the structures of the Alpine folded system in the western and central parts of Eurasia and constitute the natural carbon dioxide mineral waters province [1]. Natural carbon dioxide waters are rare beyond this province within more ancient geological structures. However they are found in Siberia: the Krasnoyarsk Territory (Kozhanovskoe deposit of natural carbon dioxide mineral waters), Kemerovo Oblast (Tersinskoe deposit of natural carbon dioxide waters) [1].

A.M. Ovchinnikov, V.V. Ivanov, M.I. Vroblevskiy, I.J. Panteleev, N.I. Tolstikhin, G.S. Vartanyan etc. contributed greatly to the natural carbon dioxide mineral water study in the USSR. Among them the chemical and gas composition of the Caucasian natural carbon dioxide mineral waters are well studied. The new data allow us to understand fully the mechanisms of their chemical composition formation [2, 3]. In particular, the zonal distribution of mineral waters associated with regional geological structural features is observed in the Caucasus region [3]. The area of natural carbon dioxide mineral waters is located in the axial part of the Greater Caucasus near the centers of the Pliocene-Quaternary volcano activity. The natural carbon dioxide waters originate from deep magmatic processes and carbon dioxide has magmatic and metamorphic origin. The metamorphogenic CO₂ significantly exceeds magmatogenic one in the Caucasus carbonated mineral waters.

Natural carbon dioxide mineral waters are replaced by nitrogen-methane thermal waters away from the axial zone of the Main Range. Nitrogen thermal waters are located in the areas having vertical



geological movements with high rates and young volcanic activity. These conditions provide deep meteoric waters penetration into rocks and their heating by the regional thermal field.

In recent decades, new data on the chemical elements and gases distribution in natural carbon dioxide mineral waters of the Sikhote-Alin in the Maritime region were obtained [4, 5]. Mongolian researchers presented the information on the gas composition of mineral groundwaters in Mongolia [6]. At the same time, the natural spa area «Choygan mineral waters», a unique deposit of natural carbon dioxide mineral waters in Siberia, is located in the Eastern Sayan Mountains. Its formation is related to the latitudinal fault in the area with current and recently extinct volcanic activity in the East Sayan Mountains [7]. These mineral waters were discovered many years ago, but they are not well studied.

In this regard, the aim of the study is to examine the gas composition and conditions of carbonated cold and thermal groundwater formation in the natural spa complex «Choygan mineral waters».

Numerous researchers in Siberia, I.S. Kryzhin (1858), S.V. Obruchev (1945), V.G. Tkachuk (1955), E.V. Pinneker (1966-1967), studied Choigan springs. Geology and chemical composition description of some springs are given in their works. A comprehensive study of Choygan springs has been carried out by researchers from Tuva Institute of Complex Natural Resources and Tomsk Polytechnic University under Arakchaa K.D. supervision since the 1990s [8].

Along with this, due to the territory inaccessibility and lack of road communications Choygan carbonated waters are insufficiently investigated for therapy use. The processes of the gas composition formation and its relation with the groundwater chemical composition were not well studied. It is necessary to study the gas composition of groundwater, to identify patterns of carbon dioxide and radon distribution in springs, and their association with water chemical composition, geological and hydrogeological conditions of the study area.

Carbonated waters are different in distribution and discharge conditions, water temperature, the chemical elements concentration, TDS and gas composition. V.I. Vernadsky [9] emphasized the necessity of a quantitative study of the natural water gas composition, especially in the groundwaters. According to his opinion it is significant both for understanding of the chemical composition and identification the groundwater position in relation to the earth surface level.

2. Materials and methods

The natural spa complex «Choygan mineral waters» is located 1550 m above the sea level in the north-eastern part of the Tuva region on the western slope of the Eastern Sayan Mountains. There are 33 springs having various chemical composition and temperature discharge in this small area (400*700 m) (figure 1) [10, 11].

The origin of these springs is the result of a large latitudinal fault in pre-Cambrian rocks (gneisses, marbles, slates), intruded by Palaeozoic granites and diorites. Aquifer is the Upper Proterozoic Ailygskaya suite sequence represented by marbles, stratified and marbled limestones, interbedded with shales, quartzites, conglomerates, intruded by Devonian granite intrusions of Brensky sequence [7]. The hot and cold carbonated waters discharge is accompanied by the recent travertine formation. The travertine dome is brown due to iron oxides and hydroxides.

In the summer of 2013 the study of groundwater chemical composition in the natural spa area «Choygan mineral waters» was carried out by the members of «ArzhaanLab» Ltd. and Problem Research Laboratory of Hydrogeochemistry Research-Educational Center «Water» (TPU).

Electrical conductivity, temperature and pH were measured *in situ* using a portable device Water Test. Water samples were investigated by the following methods: titrimetric (HCO_3^- , CO_2 , CO_3^{2-}), ion chromatography (SO_4^{2-} , Cl^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Na^+ , K^+). Radon content in waters was studied using radiometer RGA-01, which registers the volume activity of radon 222 nuclide in liquid samples for alpha radiation.

Gas samples were taken by the vacuum method in glass bottles of 0.2 liters using a portable syringe-degasser [12].

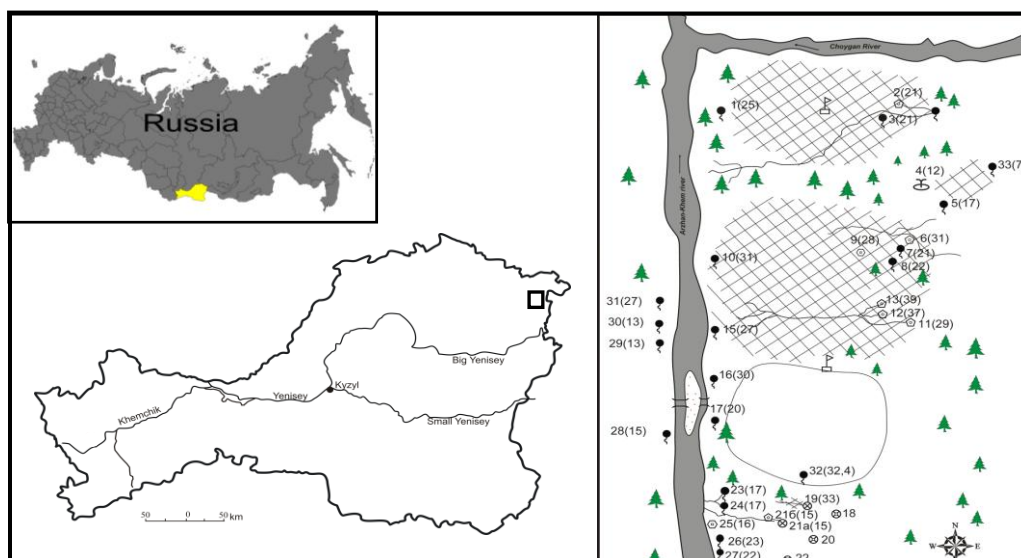


Figure 1. Scheme of the natural spa area «Choygan mineral waters» and groundwater sampling points locations (number in parentheses – water temperature)

The determination of the gas composition (nitrogen, oxygen, carbon dioxide) was performed on the Hardware and Software Complex (HSC) based on the chromatograph «Chromatec Crystal-2000M» with the software «Chromatec Analyst». The analysis of the real gas composition of water was performed by an engineer V.A. Shusharina in the accredited Problem Research Laboratory of Hydrogeochemistry Research-Educational Center «Water» (TPU).

3. Results and Discussion

Spring waters are mainly of $\text{HCO}_3\text{-Na-Ca}$ type. TDS varies from 300 mg/l to 2600 mg/l and temperatures range from 7 °C (in spring No 33) to 39 °C (in spring No12). pH varies from 5,9 to 8,3, and the value of the oxidation-reduction potential - from -170 mV and to 236 mV [5].

Choygan waters were divided into two groups according to the geochemical characteristics and temperature: cold water with temperatures up to 20 °C (springs No 2-5, 21a, 23-25, 28-29a, 30, 33) and warm water with the temperature above 20 °C (springs No 1, 6-20, 22, 26, 27, 31, 32). The gas and chemical composition of the studied springs are shown in table 1. The results in table 1 demonstrate that the gas composition does not depend on the water temperature. Although, the oxidation-reduction properties, TDS, carbon dioxide and nitrogen ratio, depending on the oxygen concentration, change with the temperature increase.

The cold spring group is situated in the northern and south-western part of the studied area. The average temperature of these waters is 13.8 °C, and they are characterized by oxidizing (Eh 201 mV) and subacidic (pH 6.6) conditions. The cold waters are fresh (TDS up to 1036 mg/L) and refer to $\text{HCO}_3\text{-Ca-Na}$ type. Most of springs discharge in the Arzhan-Khem river floodplain. There is hydraulic connection between the studied groundwater and the Arzhan-Khem River.

Table 1. Gas and chemical composition of Choygan mineral waters.

Group of waters	T, °C	Eh, mV	pH	TDS, mg/l	CO ₂ , mg/l	O ₂	N ₂	CO ₂	Rn, Bq/l
						vol. %			
Cold	<u>7.3-18.4</u>	<u>169-236</u>	<u>5.9-8.3</u>	<u>288-1545</u>	<u>41-1488</u>	<u>7-19</u>	<u>28-75</u>	<u>6-65</u>	<u>53-520</u>
	13.8	201	6.6	1036	669.2	13.7	55.3	31.0	194.3
Warm	<u>20.3-38.5</u>	<u>-170-183</u>	<u>6.1-6.9</u>	<u>1545-2646</u>	<u>277-1251</u>	<u>7-17</u>	<u>32-70</u>	<u>13-61</u>	<u>4-948</u>
	27.3	36.5	6.4	2207	728.5	13.0	54.4	32.6	180.4

The numerator indicates the minimum and maximum values of the index; the denominator shows the average value.

Dissolved gas composition of cold waters is represented by nitrogen (average content 55.3 vol.%), carbon dioxide (average content 31 vol.%) and oxygen (average content 13.7 vol.%). Other gases in these waters were not identified. In fact, the gas composition of cold waters with oxidizing conditions is mostly nitrogen one. Only when O₂ content in waters is less than 10 vol. %, N₂ and CO₂ concentrations become equal or even CO₂ prevails (table 2). The CO₂ content ranges from 6 to 65 vol.% in cold waters. The maximum CO₂ concentration at the minimum N₂ и O₂ contents of 28 and 7 vol. % respectively is observed in spring No 4 (table 2). CO₂ domination in dissolved gas composition is observed also in spring No 3 and No 21. It is worth noting the high free carbonic acid concentration of 760-1488 mg/l in these springs. On the whole in the study of Choygan mineral waters free carbonic acid concentration varies greatly from 41 mg/l in spring № 29a to 1488 mg/l in spring No 4 at the average of 670 mg/l.

The lowest CO₂ (6 vol. %) and the highest N₂ (75 vol. %), O₂ concentration (19 vol. %) occur in the fresh neutral waters of oxidizing conditions, discharging in spring No. 33. The gas composition of these waters is consistent with the atmosphere composition but with a small excess of CO₂, due to the fractured zone, providing water enrichment in free carbonic acid.

Table 2. Chemical and gas composition of cold waters of oxidizing conditions.

Number	T, °C	pH	Eh, mV	CO ₂ , mg/l	TDS, mg/l	Rn, Bq/l	O ₂ , vol. %	N ₂ , vol. %	CO ₂ , vol. %
33	7.3	8.3	224	4.4	351	-	19	75	6
30	10.9	6.7	228	188	1546	53	18	70	12
29a	13.74	6.6	216	41	-	62	15.7	65	19.3
28	12.7	6.3	180	688	1204	354	17.7	66.1	16.2
23	16.3	6.5	230	253	1100	122	14	55	31
5	13.5	6.2	200	946	1018	126	14	55.7	30.3
25	16.4	6.4	195	600	1533	93	10	51	39
3	18.4	6.3	190	760	1235	520	10.6	43	46.4
4	11.5	5.9	188	1488	607	71	7	28	65
21	13	6.2	236	872	1037	4	10.2	39	50.8

TDS and concentrations of such major ions as HCO₃⁻, Cl⁻, Ca²⁺, Mg²⁺ grow with an increase of carbon dioxide mineral water temperature. The oxidizing conditions change to the reductive ones [11].

Warm springs with the average temperature 27.3 °C are located in the central part of the studied area. These waters are characterized by the reductive (average Eh – 36.5 mV) and slightly acidic (average pH 6.4) conditions. Warm waters of the springs belong to HCO₃-Ca-Na type and a high mean value of TDS is 2200 mg/l. The TDS of warm waters is higher than TDS of cold waters (table 1). The content of dissolved free carbonic acid in waters varies from 277 mg/l (spring № 8) to 1251 mg/l (spring No. 27). Dissolved gas composition of warm waters is represented by nitrogen within 32-70 vol.%, carbon dioxide 13-61 vol. % and oxygen 7-17 vol. %.

Table 3. Chemical and gas composition of warm waters in reductive conditions

Number	T, °C	pH	Eh, mV	CO ₂ , mg/L	TDS, mg/l	Rn, Bq/L	O ₂ , о6. %	N ₂ , о6. %	CO ₂ , о6. %
1	22.6	6.2	62	1133	2288	123	-	-	-
6	29.5	6.3	-90	744	2333	95	14.6	58.4	27
7	23.8	6.4	-150	800	1863	204	16	62.2	21.8
8	25.3	6.3	-170	277	2328	360	14	58	28
9	27	6.2	-24	371	2180	948	17	65	18
12	38.5	6.3	-54	691	2525	90	15	58	27
13	36.8	6.3	0	326	2586	122	-	-	-

17	22.4	6.1	70	1074	1545	74	16	62	24
19	30.9	6.4	142	608	2140	9	14	60	26
20	28.2	6.6	142	-	-	-	17	69	14
11	31.5	6.3	29	746	2318	-	12	52	36
15	24.9	6.4	51	484	2265	106	11	43	46
9a	25	6.9	22	409	2136	84	9.6	48	42.4
10	30.2	6.5	21	460	2570	64	9	37	55
22	27.3	6.3	108	-	-	-	9	41	50
27	21.4	6.3	169	1252	2064	-	6.6	31.7	60.8

The gas composition of warm springs is characterized by N₂ predominance, but it is different in waters where the oxygen content is less than 10 vol.%. In springs No. 15, 9a, 10, 22 and 27 carbon dioxide dominates over the nitrogen and gas composition becomes oxygen-nitrogen-carbon. The gas composition formation of these springs is associated with the carbon dioxide coming along the fault zones from great depths, where the oxygen concentration is substantially lower than in the atmosphere. Nitrogen and oxygen enrichment of the studied waters occurs due to meteoric waters. According to [3], the oxygen presence in the springs in mountain areas is a characteristic feature of infiltration recharge of mineral waters. The maximum content of nitrogen and oxygen in waters of the natural spa complex «Choygan mineral waters» can reach their content in air, that is concentration of 78,09 vol.% and 20,95 vol.% respectively [13]. As for carbon dioxide, its content in the groundwaters is much higher than that in the atmosphere, containing only 0.03 vol. % of CO₂.

At the same time, the ratio between free carbonic acid and carbon dioxide gas is found in the studied waters. The free carbonic acid content in waters is typically greater than 300 mg/l, that is the concentration of carbon dioxide is more than 20 vol.%, so 15 mg/l of free carbonic acid corresponds to 1 vol.% of carbon dioxide. In the cold waters with oxidizing conditions this ratio between free carbonic acid and carbon dioxide is 30-40 mg/l per 1 vol.%. This ratio is reduced to 18 mg/l of free carbonic acid at 1 vol.% carbon dioxide in deeper cold groundwaters with oxygen concentration of less than 10 vol.%. The ratio between free carbonic acid and carbon dioxide is 24 mg/l per 1 vol.% in the warm waters with reduciive conditions. In deeper warm groundwaters having the content of oxygen less than 10 vol.%, the ratio is 13 mg/L per 1 vol.%.

Cold and warm waters of Choygan springs do not differ in the radon concentrations. In the cold waters the radon concentration varies from 53 Bq/l to 519 Bq/l (in spring No 3) and that is for warm waters from 4 Bq/l (in spring No 21) to 948 Bq/l (in spring № 9). The mean radon concentrations are similar both in cold and warm waters, whereas the maximum radon concentration is almost twice higher in warm waters than that in cold waters (Table 1). This is explained by the fact that radon is a radioactive chemical element. It is the product of alpha decay of radium-226, included in the radioactive uranium-238 series. The radon waters formation is related to granites emanation enriched by radioactive elements. In contrast to carbon dioxide, the radon source should be located near the springs, because ²²²Rn, most stable isotope, has a half life of only 3.82 days [1, 10, 14].

4. Summary and Conclusions

The study of 33 springs in the natural spa complex «Choygan mineral waters» has shown new data on the chemical and gas compositions. All the studied waters were divided into two groups according to their temperature and geochemical conditions: cold fresh water with oxidizing conditions and warm slightly brackish water with reduction conditions. The gas composition of the studied waters is represented by nitrogen (28-75 vol.%), carbon dioxide (6-65 vol.%), oxygen (7-19 vol.%), radon (4-948 Bq/l). The gas composition of all water groups is characterized by a clear predominance of nitrogen. However, in the springs, where the oxygen content is less than 10 vol.%, carbon dioxide prevails.

The studied gases differ not only in the content but in different sources. Carbon dioxide comes along the fault zones from great depths, where the oxygen concentration is substantially lower than in

the atmosphere. Nitrogen and oxygen enrichment of the studied waters occurs due to meteoric waters. The oxygen presence in the springs in mountain areas is a characteristic feature of infiltration recharge of mineral waters. The radon waters formation is related to granites emanation.

The ratio between free carbonic acid and carbon dioxide has been identified. The free carbonic acid content in waters is typically greater than 300 mg/l at concentrations of carbon dioxide more than 20 vol.%, so 15 mg/l of free carbonic acid corresponds to 1 vol.% of carbon dioxide.

The specific features of water, chemical and gas composition, its physical properties, TDS and a unique combination of carbon dioxide and radon provide an opportunity of their use for balneotherapy. Natural carbon dioxide springs in the natural spa complex "Choygan" are natural therapy resources appropriate for organizing treatment centers and resorts.

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