Hydrogeochemistry and Hydrogeological Model of CO$_2$-rich Springs on Buryatia Territory (Russia)

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Abstract. The work presents the results of isotopic-geochemical and hydrodynamic studies of CO$_2$-rich springs of the Tunka Valley, Buryatia. The waters are remarkably diverse in terms of cationic composition, although the dominant anion is hydrocarbonate. In general, the springs studied are characterized by high concentrations of microcomponents. To form these springs, the presence of active deep-seated faults is necessary. Such fractured zones serve as channels bringing gas to the upper horizons of groundwater. The 2D numerical model presented convincingly proves that the Arshan field's waters are meteoric waters of long-term water circulation (up to 220,000 years).

1. Introduction
The Tunka National Park (Buryatia, Russia) is unique in terms of the number and diversity of mineral springs with a wide range of balneological properties. We studied the largest most famous springs and resorts, which vary in temperature, chemical composition, and were localized in different water-bearing strata types. Overall, six springs (Figure 1, Table 1) were sampled and studied. The work aimed at identifying the physical and chemical conditions of the hydrocarbonate mineral groundwaters formation during the continental rifting. Another purpose was to build a 2D numerical model on the example of the Arshan spa in Tunka Valley. The main methods used included isotopic and geochemical study, as well as the 2D hydrodynamic model simulation (DHI FeFlow 7.2 Software [1]).

2. Geological setting
The geological structure of the area is extremely complex: Proterozoic, Mesozoic, and Cenozoic rocks, including magmatic, metamorphic, and sedimentary, occur here in complex structural relationships. Structurally, Tunka Valley is located within the Baikal Rift System, which is a part of the Mongol-Okhotsk Orogenic Belt [2]. The Tunka area has a network of deep-seated faults which were embedded in the Paleozoic and Mesozoic ages, but they are still active today. Spreading of the Baikal Rift followed by the Cenozoic tectonic revitalization, accompanied by basalt magmatism, which, in turn, had a significant impact on the formation of thermal waters on the area under consideration.


Figure 1. Sampling locations in the Tunka Valley National Park, Buryatia. A-1-6 - Sampling points on the Google map.

3. Hydrogeological characteristics

There are various water types on the studied territory: 1. porous waters of Quaternary sediments; 2. reservoir-fractured waters of Jurassic sediments; 3. fractured water of Paleozoic magmatic and metamorphic formations and 4. fracture-vein water of crystalline rocks.

Table 1. Physical and chemical properties of the Tunka Springs: chemical composition of their bubbled gases. "*" - no data, "*" - measured during the sampling.

| N    | Altitude | T* (°C) | pH* | Ar  | He  | H2  | O2  | N2  | CH4 | CO2 | δ¹⁸O | δD |
|------|----------|---------|-----|-----|-----|-----|-----|-----|-----|-----|------|----|
| A-1  | 850      | 36      | 6,7 | 0,99| 0,0004| 0,0001| 1,39| 4,57| 0,001| 93,05| -   | -   |
| A-2  | 900      | 40      | 6,7 | 0,92| 0,016| 8,27E-05| 7,52| 25,46| 0,003| 66,1 | -   | -   |
| A-3  | 920      | 11      | 6,1 | 0,15| -    | -    | 0,03| 20,12| -    | 79,7 | -   | -   |
| A-4  | 720      | 38      | 8,8 | 0,4 | 0,083| -    | 0,01| 17,07| 82,4 | -    | 15,7 | 118,2 |
| A-5  | 720      | 53      | 7,3 | 0,02| -    | -    | 0,61| -    | 99,37| 14,5 | 107,2 |
| A-6  | 900      | 39      | 7,1 | 0,72| 0,15 | 0,037| 14,3| 84,66| 0,004| 0,13 | -   | -   |

The table provides the physical and chemical properties of the Tunka Springs, including the chemical composition of their bubbled gases. The data indicates a variety of water types with different properties, reflecting the diverse geologic formations in the study area.
The groundwater of the Tunka area is fed mainly by the infiltration of atmospheric precipitation. Groundwater replenishment conditions are not favourable enough due to sharp relief fragmentation, steep mountain slopes, and significant surface watercourse beds. The presence of permafrost here also does not favour the direct infiltration of precipitation into aquifers.

However, when geological conditions are favourable, the infiltration waters penetrate deeper into fractured tectonic zones and saturate with CO$_2$ gas. The intense interaction of groundwater with both gas phase and host rocks leads to the formation of mineral waters containing valuable therapeutic components. Usually, the catchment area is confined to watersheds and ridge slopes.

4. Hydrogeochemistry

According to ion composition, the studied springs are hydrocarbonate waters (HCO$_3^-$ >50 %-meq/L), except for sample A-6, which refers to sulfate waters (Figure 2A). In samples A 1-3, Ca$^{2+}$ dominates (47-51 %-meq/L); contents of Na$^+$ or Mg$^{2+}$ vary from 19 to 28 and from 21 to 32 %-meq/L, respectively. As for anionic composition, the content of HCO$_3^-$ is 71-83 %-meq/L, while SO$_4^{2-}$ is 14-25 %-meq/L, accordingly. Na$^+$ prevails in A-4 and A-5, reaching 36 - 92 %-meq/L. The content of Ca$^{2+}$ and Mg$^{2+}$ changes, respectively, within the limits of 7-33 and 23-29 %-meq/L. In the A-4 sample, the values of Mg$^{2+}$ is insignificant. The K$^+$ content in the samples under study varies from 3.1 mg/L (sample A-4) to 32.4 mg/L (sample A-2).

![Figure 2](image)

Figure 2. The triangular diagram (A), the trace element distribution (B), and charts on the correlations of the altitude - $\delta$D values (C) and the altitude - $\delta^{18}$O concentrations (D). The dotted line in Figure B represents the average content of elements in the hypergenesis zone [3].

Most of the studied springs were thermal and have a rather high temperature [2], except sample A-3, which is 10.7 °C, so it could be classified as moderately cold waters (Table 1). TDS of water varies from 1.12 g/l (A-6) to 5.3 g/l (A-5). The pH values change from slightly acidic 6.12 (A-3), 6.66 (A-2), 6.73 (A-1) to neutral 7.1 (A-6), 7.3 (A-5) and, even, alkaline 8.8 (A-4) (Table 1).

The trace element contents in the Tunka springs were determined (Table 2, Figure 2 B). The F$^-$ concentrations do not exceed average values within the hypergenesis zone (Fig.2B), varying from 0.17 mg/l to 0.99 mg/l, except for A-1 and A-2, for which the F$^-$ content is 3.33 mg/l and 2.8 mg/l, respectively.

The arsenic value changes from 0.05 (minimum) in sample A-4 to 5.3 mg/l (maximum) in sample A-2. The average arsenic content for hypergenesis zone waters is 2.1 µg/l. Zinc and cooper contents in
all tested springs varied within the nearly same limits (3 -11.4 µg/l for Zn and 0.49 to 11.5 µg/l for Cu) (Figure 2 B). Mn contents changed from 13 to 104 µg/l. Molybdenum values were in the range of 0.2-16 µg/l. Waters of the hypergenesis zones had the average zinc content of 34 µg/l, copper 5.6 µg/l, and that of molybdenum 2.1 µg/l.

The silica content in Tunka groundwaters varies from 9.5 to 119 mg/l. Since the highest spring's temperature (53.7°C, sample A-5) corresponds to the high silica content (119 mg/l), the correlation between the outlet temperature and the silica content can be traced. As for the boron, the highest values (6.1 mg/l) were in sample A-5, while in other samples, it adjusted between 0.06 and 0.5 mg/l.

Table 2. The trace element contents (µg/L), Si and Sr (mg/l) in the Tunka mineral springs.

|    | Sr  | Si   | As  | Zn  | Mn  | Ba  | Rb  | Cs  | Mo  | B   | Br  | F   | Al  |
|----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| A-1| 10.2| 46.76| 4.97| 6.9 | 104 | 58  | 417 | 91  | 7   | 0.2 | 379 | 132 | 3330|
| A-2| 11.1| 48.43| 5.3 | 11.4| 98  | 40  | 452 | 100 | 7.5 | 0.29| 387 | 144 | 2800|
| A-3| 2.17| 9.55 | 0.08| 4.64| 84  | 12.6| 73  | 16  | 1.04| 0.29| 58  | 22  | 930 |
| A-4| 0.35| 19.53| 0.05| 3.04| 62  | 56  | 12.1| 3.47| 0.16| 1.6 | 71  | 217 | 430 |
| A-5| 6.04| 118.8| 0.47| 6.8 | 81  | 207 | 2340| 105 | 7.4 | 1.24| 6140| 2457| 990 |
| A-6| 2.7 | 25   | 6.3 | 14.2| 13.2| 11.5| 830 | 103 | 38  | 16.6| 510 | 34  | 900 |

The bromine content of the selected samples varies from 22 µg/l to 2.5 mg/l, with an average value of 183 µg/l in the waters of hypergenesis zones. The aluminum content of the Tunka springs does not prevail limits from 3.9 to 80 µg/l. The strontium content varies widely from 0.35 (A-4) to 11.1 mg/l (A-2), but the average strontium content is 0.19 mg/l in hypergenesis zones waters. Barium content in the waters of the Tunka district is relatively high; it varies from 11.5 to 207 mg/l. The average barium content in the waters of the hypergenesis zone is 20 µg/l. The manganese concentrations of most samples are high and range from 62 to 104 µg/l, except is sample A-6, for which the manganese content is 13.2 µg/l (Figure 2 B).

Samples A-1, A-2, A-5, and A-6 have a high content of lithium, rubidium, and cesium. The concentrations of lithium in these samples vary from 0.42 to 2.34 mg/l; rubidium contents are 0.09-0.1 mg/l, while cesium changes from 7 to 38 µg/l. For samples A-3 and A-4, the lithium content is 73 and 12 µg/l, rubidium is 16 and 3.5 µg/l, and cesium is 1 and 0.2 µg/l, respectively.

5. Gas composition

Concerning concentrations of gases, most samples (A-1, A-2, A-3, and A-4) are CO2-bearing waters with a high content of CO2 (up to 99.37 vol.%). The amount of nitrogen (N2), oxygen (O2), methane (CH4) and noble gases, such as He, Ar, Ne are small. Hydrogen (H2) presents in a subordinate quantity. Sample A-6 is nitrogen-bearing gas phases spring, where N2 values reach 84.7 vol.%, while A-4 is saturated with methane phase (up to 82.4 vol.%).

The oxygen contents of Tunka samples vary from 0.01 to 7.5 vol.%. Oxygen, apparently, has an atmospheric origin and could have been captured by spontaneous CO2 bubbles from the infiltration water flow. In the triple chart, carbon dioxide and nitrogen from samples A-3 and A-6 are located in the field, which is characteristic for volcanic and metamorphic rocks, and the most likely have a deep (mantle) origin. Gases from all other wells belong to near-surface, air-related gases.

6. Isotopic composition of the aqueous phase

In order to determine the origin of the Tunka valley springs, stable isotopes of oxygen and hydrogen were studied (Table 1). The values 6D and 818O in the waters of Tunka area vary within -13.8 to -15.7 (Figure 2C) and -101.3 to -127.9 ‰ (Figure 2D), respectively. All the waters studied have infiltration origin, since all the figurative points are located along meteor lines (signed by brown dotted line, Figure 2 C, D). All springs demonstrate distinct high-altitude zoning in terms of oxygen and hydrogen,
which let us assess high-altitude isotope effects for the Tunka Valley springs, accounting for ~ -80‰/km and -~ 1‰/km for δD and δ18O, respectively. A study of the isotopic analysis of the waters of the Tunka district sources showed that the waters of these sources had a meteoric origin, and the depth of formation was approximately 2-3.4 km.

7. Hydrodynamic groundwa ter model
The hydrodynamic filtration model was built based on the isotope and geological data. The purpose of the modelling was to clarify all the peculiarities of water formation as well as its age.

At the first stage, we estimated the age of groundwater of the Tunka area. The numerical solution of the task was carried out based on the FeFlow Software, which is based on the finite element method (FEM). The calculation section was divided into eight layers, 9468 knots, and 18634 elements. Non-orthogonal sampling makes it possible to consider the fractured zones, 10-15 m wide.

As a result of numerical modelling, the ages of groundwater sources in the Tunka area were obtained (Figures 3). The maximum observed ages (approximately 3.2 million years) are in the centre of the Tunka Basin. For the Arshan springs, the maximum age does not prevail 220,000 years. The calculated age of the Arshan's groundwater circulation is close to those quantified using the helium-argon dating method.

![Figure 3. The numerical hydrodynamic simulation of the circulation period of the Arshan’s spa mineral groundwaters. Ages indicated by colour.](image)

8. Conclusions
Thus, the study revealed that the chemical composition of studied mineral waters is the result of interaction processes in the bedrock–gas system. The initial waters are of meteoric origin, and their chemical composition depends mainly on the chemical and mineral composition of the host rocks. In general, all studied springs are enriched by the trace content, especially Li, Rb, and Ce. The transition of elements into water is caused by interphase interactions in the water–gas–rock system. Active deep-seated faults are essential for the formation of these springs since they can serve as channels carrying the gas to the upper horizons of groundwater. The modelling proved that initial water could penetrate through the tectonic faults into the Earth's depth (1-3.5 km), and, then, they heat up to 75-214 °C, and, eventually, interact with the rocks. The numerical hydrodynamic simulation showed that the mineral
groundwater within the Arshan spa is the long-term circulated groundwater. Groundwater age values obtained from the model coincide with the calculated values and range from 20,000 to 220,000 years.

9. References
[1] Diersch H J 2013 FEFLOW: finite element modeling of flow, mass, and heat transport in porous and fractured media (Heidelberg, Germany: Springer)
[2] Plyusnin A M, Chernyavskii M K, Zamana L V, Shvartsev S L, Tokarenko O G 2013 Russ. Geol. Geophys. 54 5 pp 495-508
[3] Shvartsev S L 1998 Hydrogeochemistry of Hypergenesis Zone (Moscow: Nedra) p 366

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