Thermo-mineral springs of North-Eastern Sikhote-Alin’ Ridge, Far East of Russia

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Abstract. New data on hydrogeochemistry of thermal waters of the Russian Far East is presented in the paper. Ul’skiy, Annenskiy and Tumninskiy thermo-mineral waters belong to low-mineralized (TDS<320 mg/l), alkaline (pH~9.3), N2-rich, bicarbonate or sulfate-bicarbonate sodium type of water with elevated concentrations of silicon acid (up to 120 mg/l), fluorine (up to 4mg/l) and some trace metals (Li, Sr, As). Due to isotopic data water has a meteoric origin, as well as gas phase, lack of mantle helium points on the not deep intrusive body as a heat source. Waters are used for balneological purposes as bath treatment as well as drinking.

1. Introduction
Groundwater forms its geochemical shape interacting with host rock, borrowing numerous chemical elements. With the help of the modern high-sensitive analytical methods, more than 80 chemical elements can be studied in groundwater. However, the limited solubility of minerals that form the Earth's crust significantly reduces the number of basic elements in natural waters. The main ions are usually Na+, Ca2+, Mg2+, K+, HCO3-, Cl-, SO42-, which are the most abundant in minerals. The total content of these ions in water is over 90-95% of all dissolved solids. The content of microcomponents (Br, I, F, B, Li, Rb, Sr, Ba, As, Mo, Cu, Co, Ni, Au, and others) in waters does not exceed 10 mg/l.

The geochemical properties of N2-rich thermal waters are considered most fully by L.N. Barabanov and V.N. Disler [1]. According to their data, the general geochemical properties of N2-rich thermal waters include: the predominance of sodium in the cationic composition and often bicarbonate or sulfates in the anionic; positive correlations between Na+K and Cl, SO4, F, T ° C, HCO3, pH and negative correlations between Ca and HCO3, T ° C; Ca and pH, as well as the dependence of the concentration of components on solute products in the systems of Ca2+-CO32- and Ca2+-F. Since the data concerning the hydrochemistry of the thermal waters of this area were obsolete or incomplete, the analysis was carried out on the newest analytical equipment on the samples of thermal waters, water-bearing rocks, and also dissolved and associated gases. The purpose of the study was to determine the composition of the thermal groundwater (macro-, microcomponents, isotopic ratios), water-bearing rocks, and also the gas components.

The manifestations of thermal waters, located on the coast of the continental part of the Far East of Russia, attract a wide range of specialists [2, 3, 4, 5, 6], however, due to remoteness and inaccessibility, remain poorly understood.
The Ul’skiy thermal spring manifestation is located in the Nikolaevskiy district of the Khabarovskiy region, 6 km southeast of the settlement of Mnogovershinnoe (Figure 1), on the left side of the right tributary of the Right Tyvlinka River. Manifestation looks like a small pool (1.5x1.5x0.8m), strengthened with wooden bars. Mineral water is used by local residents to take baths, without medical indications.

Annenskiy thermal springs are located in the lower reaches of the Amur River, on its right bank, 120 km upstream from the town of Nikolaevsk-on-Amur, 6.5 km to the southwest from the Susanino pier (Figure 1). Modern balneary “Annenskie Vody” is using waters from boreholes, serving over 10000 people-in-need per year (80-120 patients in the winter and up to 200 people in the summer are treated monthly).

The Tumninskiy thermal spring is located in the Vaninskiy district of the Khabarovskiy region, 9 km from the Tumnin railway station, in the valley of the Chope Creek – the right tributary of the Tumnin River (Figure 1). Three balnearies are using groundwater from boreholes for treatment. Around 8000 people use these springs annually. The springs is very popular among the population of other regions as well.

The main purpose of this work was to study geochemistry and genesis conditions of thermal waters and gases of the thermal waters of the Okhotsk Sea coast of the Khabarovskiy region. For this purpose, the springs and boreholes were monitored for the physical parameters of groundwater (temperature, electrical conductivity, and water level), which together with isotope-geochemical data made it possible to understand the dynamics of processes that affect the genesis of thermal waters.

2. Hydrogeological setting
Features of the geological evolution of the territory, the variety of types of water-bearing rocks, the presence of diverse fault tectonics led to very complex hydrogeological, geothermal and geochemical conditions.

Water-bearing rocks within the area of the Ul’skiy manifestation of thermal waters are presented with an aquifer of quaternary alluvial deposits (aQIV) and a water-bearing zone of intrusive and metamorphic formations of the Paleocene age (γP), presented by fissured granites. Ul’skiy thermal
waters (+26°C<T<+31°C) and springs with elevated temperatures (up to +14°C) are associated with disruptive disturbances of the Paleogene intrusive formations, hosting mainly pressurized and non-pressurized fresh water. The yield of springs does not exceed 0.15 liters per second. The mineralization is 0.1–0.2 g/l. Groundwater is recharged by infiltration of atmospheric precipitations at watersheds. Discharge is carried out by springs, by bogging bottoms of decay.

Hydrogeological conditions of the Annenskiy thermal water deposit are entirely determined by tectonic factors. The manifestations of thermal water are confined to the zone of disturbance of the northeast strike, formed in interbedded tuffaceous sedimentary rocks of Middle Cretaceous age (K2t, K2bl). Within the zone with a thickness of 30–40 m, the rocks are strongly crushed and almost everywhere hydrothermally altered. Cracks and veins of the fault zone are the direct conductors of thermal waters (T=50–54° C) with mineralization of about 0.30–0.32 g/l. They are mostly confined to tuff-conglomerates and tectonic breccias.

Hydrogeological conditions of the Tumninskiy thermal water deposit are determined by the contact zone of the Paleocene granites (γР) and Miocene basalts and tufts of the Kizinskaya Formation (Nkz), which creates a fissure-vein aquifer system. The waters of the fissure-vein system within the boundaries of the site are hot with temperature of a 54°C and 42°C for reservoir and borehole heel consequently. The water is clear, odorless and tasteless [4].

3. Materials and methods

Using autonomous recorders, a thermometric survey of the Ul’skiy thermal water manifestation was carried out as well as detailed observations of the regime of groundwater and hydrogeochemical parameters for all studied thermal waters. Measurements of volumetric activity of radon (VAR) was carried out with the using the radon station SRS-05 (NTM-Protection, Russia) and portable measuring instrument Sirad.

Hydrochemical sampling was carried out according to a standard procedure. Unstable water parameters were measured at the sampling site (pH, Eh, TDS, temperature, HCO₃), the samples were filtered through 0.45 μm Advantec membrane filters. Gas samples were collected in glass vials with rubber stoppers by the displacement method. Water samples for the tritium measurements were taken into 1-liter plastic bottles. Water samples were analyzed for macro- and microelements in a certified laboratory of the Analytical Center of Far East Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (AC FEGI FEB RAS). The main cations and anions were determined by the method of liquid ion chromatography (HPLC-10AVp, SHIMADZU, by analyst G.A. Bakhareva), trace elements were determined by inductively coupled plasma (ICP-MS Agilent 7500 and 7500c, by analyst T.A. Romanova). The composition of the free gas was studied using a Shimadzu LC-20AD chromatograph. Samples for analysis of stable isotopes (δ¹⁸O, δ²H) were not filtered and sampled in a glass bottles, then performed on a high-temperature pyrolyzer TC/EA (ThermoQuest) connected to an isotope mass spectrometer model MAT 253 (ThermoQuest) via the ConFlo-IV interface (ThermoQuest). To calibrate the analytical system, isotope standards distributed by the International Atomic Energy Agency (Vienna): VSMOW (Vienna Standard Mean Ocean Water) δ¹⁸O = 0.0 ‰; δD = 0.0 %. The results of the δD and δ¹⁸O analyzes are given in relation to the international standard VSMOW. The reproducibility of the results in the analysis of this series of samples was monitored by repeated measurements of the laboratory standard. The reproducibility of the results averaged ± 0.1 ‰ and ± 0.3 ‰ for δ¹⁸O and δD, respectively.

4. Hydrogeochemistry

Some chemical and isotope analyses of the thermal waters of Sikhote-Alin’ ridge were published earlier [2, 3, 4, 5, 6]. According to the basic ionic composition, the subterranean thermal waters refer to sulfate-bicarbonate or bicarbonate sodium fresh waters with an increased content of silicon acid (up to 120 mg/l). The water is alkaline (9.1<pH<9.3). Geochemical conditions are reductive gley (Eh ~ 0). The water temperature, measured at the borehole heel varies from 31.8 to 49 °C. Waters are weakly gasified, nitrogen predominates in the gas component (up to 72.5–97.2 vol. %).
Among the main ions of thermal waters, there is a direct relationship between sodium and sulfate ion, while the correlation of sodium with the bicarbonate ion is much weaker. Genetically Na₂SO₄ is a typical continental salt and is considered in water as a sign of a continental environment for the formation of the chemical composition of water. In contrast to calcium and magnesium sulfates, which are part of the marine salt complex and can be an indirect indicators of marine genesis. So fresh groundwater on the watersheds reflects the dependence of calcium and magnesium on the content of sulfate, as well as sodium from chlorine, which is most likely caused by the atmospheric precipitation of the Okhotsk Sea coast.

The main part of the total dissolved solids (TDS) in studied water are sodium, bicarbonate ion and silicon, depending on water temperature. Since the temperature increases from south to north of Sikhote-Alin’, the TDS, therefore, grows consequently. It should also be noted that the increase in the content of sulfate ion is found in areas where water supply goes through sedimentary rocks rich with sulfides. The inverse relationship between the content of sodium and calcium is explained by the fact that during the formation of the chemical composition of water, sodium outruns calcium by leaching from rock-forming plagioclases. In turn, the content of calcium in waters is limited by the carbonate barrier, because of which all excessively released calcium precipitates in the form of secondary calcite.

Relatively high concentrations of microelements in the thermal springs have been found for strontium (29.3–78.6 μg/l), lithium (1.9–56.4 μg/l) and fluorine (0.8–2.7 mg/l). However, these concentrations of fluorine is two to three times lower than in same N₂-rich thermal waters located in Southern Sikhote-Alin’ ridge or Baikal rift [4, 5, 7]. Fluorine is well correlated with HCO₃ and SiO₂, and less with SO₄, indicating association of it’s source with weathering (hydrolysis) of aluminosilicates. Low calcium activity also creates conditions for increased activity of fluorine and its accumulation in water. Geochemical background of fluorine is also very low in fresh groundwater. It is possible that the difference in the content of fluorine in different thermal springs of the Russian Far East is due to the time of interaction in the water-rock system [6].

The examined geochemical features allow drawing a conclusion about the genesis of thermal waters, estimating the depths of circulation and temperature of water reservoir. Bicarbonate composition, low mineralization and surface temperature, nonequilibrium with water-bearing rocks indicate the formation conditions in the upper hydrogeochemical zone, and, therefore, at relatively shallow depths - the first kilometers from the surface. The obtained results on the thermal waters of the Okhotsk Sea coast of the Khabarovsk Territory fit well into the overall picture of the N₂-rich thermal waters of the south of the Russian Far East and Baikal rift zone [2, 3, 4, 5, 6, 8], whose characteristic features are: low mineralization (up to 0.5 g / l) , almost exclusively the sodium composition of the cations, the alkaline reaction, the predominance of nitrogen in the gas composition, significant concentrations of silicon acid, fluorine, and a number of microelements. A distinctive feature of some thermal waters is the presence of sulfates in the ionic composition, due to sedimentary host-rocks and oxidation of pyrite. To establish the genesis of waters and possible processes that affect the changes in their composition, isotope studies were carried out.

5. Stable water isotopes and gas composition
The obtained values of oxygen and hydrogen isotopes for the studied waters correspond to the infiltration genesis (Figure 2). A comparison with the available data shows that the isotopic compositions of the thermal springs reflect latitudinal dependence [7]. The calculated facilitation factor for this type of groundwater is 4.84 % for 10 ° of latitude for deuterium and 0.59 % for 10 ° of latitude for δ18O. Along with the Annenskiy and Tuminskiy, the Ul’skiy spring is characterized by the most isotopically light composition among the thermal waters of the Southern Far East. The isotopic differences within this group of thermal waters can be related to the location of their feeding areas: Ul’skiy spring is 550 m a.s.l., while Annenskiy and Tuminskiy are in the valley of Amur and Tummin Rivers respectively. Thus, the differences between the recharge and discharge areas reach large values. It is well known that with an increase in the elevation of the recharge area, the gradients ΔδD/Δh and Δδ18O/Δh are 1.5–4 % and 0.15-0.5 %o, respectively [7].
Interaction with host rocks can cause fractionation of water isotopes. Usually, the value of $\delta^D$ behaves more conservatively, since the amount of oxygen sharply prevails over hydrogen in rocks. This is expressed in the deviation of the figurative points from the meteoric water line on the Craig diagram. The magnitude of the deviation of the isotope composition of oxygen ($\Delta \delta^{18}O$) from the meteoric water line is calculated using the Craig equation [9]:

$$\Delta \delta^{18}O = \delta^{18}O \text{ (change)} - \delta^{18}O \text{ (calc.)},$$

where $\delta^{18}O \text{ (change)}$ is the value measured in water, and $\delta^{18}O \text{ (calc.)} = (\delta^D-10)/8$ – isotope composition of oxygen, calculated by Craig equation. The calculated value of the “oxygen shift” of all the studied waters in most cases does not exceed $\pm 1.5 \text{‰}$. The data show that isotopic shifts, indicating long-time interactions of thermal waters with water-bearing rocks, are not observed. The isotopic ratios of surface waters and waters of watersheds are also very close to the ratios obtained for the thermal waters.

The chemical composition of gases on the Ul’skiy mineral springs was investigated in 1986 during exploration work. During our testing, there was no release in the basin of free gases. According to the analyses of 1986, the accompanying gases were characterized by a predominance of nitrogen ($N_2 = 91–94 \text{ vol.} \%$) and oxygen ($2.5-6.5 \text{ vol.} \%$). Our previous data on the gas composition in Annenskiy and Tuminskiy thermo-mineral waters show the variation of nitrogen (82 and 85%) and oxygen (17.8 and 14.2%) respectively. The content of methane and homologs is low (0.00001-0.003 vol. %), which is close to the values of atmospheric air and does not exceed it. To obtain reliable data on the content, composition of the accompanying gases and their isotopes additional work is necessary.

6. Conclusions
Observations were carried out on the physical (temperature, electrical conductivity, VAR) and isotope-geochemical parameters of thermo-mineral waters of the Ul’skiy, Annenskiy and Tuminskiy springs, which made it possible to determine its hydrogeological regime during the summer period. It is established that water is being heated in the depth of water-bearing rocks, presented by fissured rocks and does not undergo significant seasonal temperature fluctuations and changes in its chemical composition only under the influence of endogenous processes (interactions with water-bearing rocks).
The characteristic features of the thermo-mineral waters of Northeastern Sikhote-Alin’ are following: low mineralization (up to 0.35 g/l), almost exclusively sodium cation composition, alkaline reaction, low organic content, predominance of nitrogen in the gas composition, significant concentrations of silicon acid, fluorine, atmospheric recharge. A distinctive feature of thermal waters of this area from its southern part is the presence of sulfates in the ionic composition.

The low values of TDS of studied waters are caused by slower processes of transition of elements to the solution because of the absence of readily soluble rock minerals and the influence of corrosive gases (CO$_2$, Cl$_2$, HCl, H$_2$S and others). Under these hydrogeological conditions groundwaters remain unsaturated with respect to main minerals of the water-bearing rocks. From the point of view of balneology, the expansion of the use of the Ul’skiy thermal water is possible, because therapeutic bicarbonate (sulfate-bicarbonate) sodium waters are almost the same with the thermal water of the Annenskiy and Tumninskiy spas. The obtained isotope-geochemical data fit well into the general picture of the N$_2$-rich waters of the Russian Far East and Baikal rift zone.

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