Hydrochemistry of thermal waters in crystalline rocks of the Sikhote-Alin ridge, Far East of Russia

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Abstract. Low-enthalpy thermal waters (30-50°C) of HCO3-Na and HCO3-SO4-Na types with nitrogen as a dominant associated gas discharge on the southern continental margin of the Russian Far East and traditionally are of great importance for recreation and balneology facilities. All studied thermal waters have meteoric origin and relate to Palaeocene granite intrusions. Based on the chemical characteristics and isotopic composition, thermal waters are divided onto "immature" thermal waters (3H=1.3±0.2TU), and "mature" thermal waters (3H=0.3±0.2TU) originated as a result of a longer evolution history (more than 60 years). The chemical composition of waters is largely determined by water-rock interactions, residence time and the local geothermal gradient.

1 Introduction

Low-temperature thermal waters of the continental margin of the Russian Far East are widespread along the coasts of the Sea of Japan and the Sea of Okhotsk. All geothermal manifestations occur within the Sikhote-Alin Ridge and relate to regional deep faults in crystalline rocks of different ages (Fig. 1) Most of thermal waters have been discovered as a result of drilling in 1930s - 1960s [1]. Some groups of springs (Annenisky, Tumninsky, Amgu, Chistovodny and Ulsky) are used by locals as spa for self-treatment. During the last two decades the geochemistry of these groups of springs has been studied [2-6]. Here we present the hydrochemical data for 5 groups of thermal springs of the Sikhote Alin Ridge combined with the analysis of geological and tectonic settings and discuss factors and processes controlling the origin of these waters.

2 Location and geology

The areas of thermal waters manifestations along the continental margin of the Russian Far East are similar to each other in size, chemical composition of water and associated gases,
and could be divided on three type by geomorphology and geological characteristics (Fig. 1, Tabl. 1).

The Ulsky thermal spring is located on the East of the Khabarovsky Krai, in the north end of Sikhote-Alin ridge, 25 km from the Sea of Okhotsk shore. The thermal waters circulation area is limited by the area of the Paleocene granites of the Beckcheul massif. The rocks are covered with Quaternary alluvial sediments (thickness ranges from 1m to 3 m) consisting of poorly sorted sand and gravel.

The Annensky spa thermal area is located on the East of the Khabarovsky Krai, within the Amur river estuary, 80 km from the Sea of Okhotsk shore. Thermal waters occur in the contact zone between effusive (quartz porphyry) and tuffaceous sedimentary rocks of the upper Cretaceous age in the Bolbinskaya and Tatarkinskaya suites. The granites of Palaeogene age intrude these rocks [5].

The Tumninsky thermal area is located on the South-East of the Khabarovsky Krai, 9 km from the Tumnin River, and 40 km away from the Tatarksky strait. The geological structure is defined by the contact zone of granites and andesitic basalts of the Eocene Kuznecskaya suite [5].

![Fig. 1. Low enthalpy thermal areas location and main schemes of geological conditions: A-Chistovodnoe and Ul'sky thermal areas; B-Tumnin and Amgu, C-Annensky.](image)

The Amgu thermal area is located in the Terney region of the Primorsky krai, 10 km from the Sea of Japan shore. The geological structure is defined by the contact of granite intrusions with rhyolites, tuffs and ignimbrites of Mesozoic and Cenozoic ages [3].
The Chistovodny thermal area is located in Lazo region of the Primorsky krai, 70 km away from the Sea of Japan shore [3]. Host rocks consist of Upper Cretaceous granites, broken by Paleocene dykes of aplites and diorite porphyries.

All hot springs of the Sikhote-Alin Ridge are devoid of young volcanism influence but located within Paleocene granite intrusions. The maximal temperature of water discharge from the different geological conditions is: granite - 32°C, contact "granite-basalt" is 50°C and from quartz porphyry - 50°C. Waters have low TDS (0.1-0.2 g/L) and high pH (9-9.3). Main associated gas is N₂ (98.3-99.4 vol.%) [6], volume activity of 222-radon less than 220 Bq/L.

### 3 Results and discussion

#### 3.1 Hydrogeochemistry

The hydrochemical properties of five representative waters are shown in the Table 1. The water fluid circulation mainly relates to crystalline rocks inducing two distinct groundwater types: HCO₃(CO₃)-Na and HCO₃(CO₃)-SO₄-Na.

All studied waters have low TDS (<0.3 g/L), high pH (>9) and water temperature 24-50°C. The north thermal areas have content of SO₄ more than 25 meq% (Table 1). Cl/F molar ratio range from 0.3 to 2.2.

**Table 1.** The characteristics of thermal waters and geological environment.

| Unit          | Ulsky            | Annensky         | Tumnin           | Amgu            | Chistovodnoe       |
|---------------|------------------|------------------|------------------|------------------|---------------------|
| Geograph. coordinates | E 139°59' N 53°54' | E 140°09' N 52°46' | E 139°59' N 49°38' | E 137°35' N 45°53' | E 133°53' N 43°22' |
| Type          | HCO₃(CO₃)-SO₄-Na | HCO₃(CO₃)-Na      |                  |                  |                     |
| Host rock, Age | Granite P₁       | Q-porphyry K₂    | Granite P₂       | Tuff K₂          | Granite K₂          |
| Age of granite intrusion | P₁              | P₁               | P₁               | P₁               | P₁                  |
| T, spring well °C | 32              | no springs 50    | no springs 50    | 25              | 24                  |
| TDS mg/L      | 170              | 235              | 195              | 185              | 170                 |
| pH            | 9.1              | 9.2              | 9.3              | 9.1              | 9                   |
| Eh mV         | 0                | 140              | 150              | 170              | 170                 |
| K             | 0.7              | 1.2              | 0.6              | 0.7              | 0.7                 |
| Na            | 57.3             | 61               | 34.1             | 33.4             | 32                  |
| Ca            | 2.1              | 2.2              | 1.8              | 2                | 3.37                |
| Mg            | 0.05             | 0.01             | 0.04             | 0.08             | 0.01                |
| Cl            | 4.9              | 4.8              | 2.1              | 3.6              | 4.9                 |
| SO₄ mg/L      | 26               | 37               | 10               | 8                | 10.6                |
| HCO₃          | 58               | 112              | 78               | 70               | 69                  |

**Specific minor components**

| Si   | mg/L | 24     | 41     | 34     | 25       | 20       |
| F    | mg/L | 2.7    | 3.8    | 0.5    | 0.9      | 6.1      |
| Sr   | mg/L | 0.03   | 0.7    | 0.1    | 0.5      | 0.06     |

**Water isotopes**

| δ¹⁸O | %o Ver SMOW | -15.5   | -18.8  | -16    | -11.5    | -11.2    |
| δD   | %o SMOW     | -113.4  | -136   | -117   | -83.6    | -80.1    |
| δ¹⁵N | %o T.U.     | No data | No data | 0.3    | 1.2      | 0.3      |

**Na-K-Mg** [9] Immature Part. Equilibrated Immature Part. equilibrated
The lithophile elements: Na, K, Si, F and Sr originate from hydrolysis of Al-silicate minerals, for example biotite. Albite is most likely to be the dominant source of major cations in acid rocks:

\[2\text{NaAlSi}_3\text{O}_8 + 2\text{H}_2\text{CO}_3 + 9\text{H}_2\text{O} \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4.\]

The mixing processes with cold groundwaters are absent which is indicated by low Mg concentrations in all studied thermal waters (0.007-0.01 ppm). Based on the K-Na-Mg equilibrium diagram [9] we estimate that under similar hydrogeological conditions thermal waters of Amgu and Ulsky are "immature" which means that a short residence time is required to gain temperature at depth (or more time to reach the surface). In such hydrogeological conditions it is unlikely that waters could attain chemical equilibria with host rocks. Whereas, Tumnin and Chistovodnoe waters are partially equilibrated due to longer evolution history (more than 60 years as indicated by tritium contents) (Table 1).

High fluoride concentration can also be related to long residence time of groundwater due to enhanced water-rock interaction process [10], when the tritium content indicating substantially long circulation time within the aquifers. Because we do not have $^3\text{H}$ measurements for Ul'sky and Annensky areas it is difficult to say if this is a long circulation or modern water. The dynamics of this system are not fully understood, but are be the focus of ongoing research.

### 3.2 Isotopic studies

The isotopic composition of the studied waters is presented on the $\delta\text{D}$ vs $\delta^{18}\text{O}$ diagram (Fig. 2, Table 1). Our data are similar to data reported for these springs by Chudaev [3] and Bragin [4]. It can be seen that all points are plotted close to the global meteoric water line with a significant latitude effect.

Tritium analyses have been conducted in relation to "mature" and "immature" thermal waters. The results indicate that "immature" thermal waters with $^3\text{H}=1.3\pm0.2\text{TU}$ was recharged approximately in 1960's. Whereas, "matured" thermal waters have almost no tritium $^3\text{H}=0.3\pm0.2\text{TU}$. The surface waters tritium content in 2012 was $9.5-13.3\pm0.2\text{TU}$ [6, 8].

![Fig. 2. Isotopic characteristics of Sikhote-Alin thermal waters. 1-Ulsky, 2- Annensky, 3-Tumnin, 4-Amgu, 5-Chistovodnoe.](image-url)
4 Conclusions

Geological and hydrogeological data obtained provide reliable and sufficient evidence that the thermal waters in crystalline rocks of the continental Far East of Russia are the local convective groundwaters and relate to Paleogene granite intrusions. The meteoric waters present the source of the thermal waters in fractured aquifers of granites or quartz porphyries. Based on the chemical properties and isotopic composition, thermal waters are divided into "immature" thermal waters with short residence time ($^2$H=1.3±0.2TU) and "mature" thermal waters ($^2$H=0.3±0.2TU) originated as a result of a longer evolution history (more than 60 years). The chemical composition of waters is largely determined by water-rock interactions, residence time and local geothermal conditions.

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