## GEOCHEMISTRY AND SOURCES OF THERMAL WATER CONTENT IN THE RUSSIAN PART OF THE AMUR BASIN

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Complex and diverse geological-structural conditions in the Amur basin determine the formation of different mineral ground waters [1 - 7, 9 - 11]. Although this region is weakly studied however several hundreds of mineral water springs of different types have been already discovered in the Amur basin [4, 6, 7]. The main mineral water deposit types are as follows:

- 1. nitrogen therms,
- 2. thermal radon waters,
- 3. carbonaceous cold waters,
- 4. cold waters with specific components.

There are three main provinces of mineral waters in the basin: a province of cold carbonaceous waters, a province of nitrogen thermal waters, and a province of cold ferriferous waters.

Areas of *cold carbonaceous mineral waters* [4, 6, 7] have been discovered in the western part of the Amur basin (Verkhneamurskaya or Daurskaya), in the northern part of the Amur basin between the Amgun and Gorin rivers and Mukhenskaya and Shmakovskaya groups in the Ussuri basin. Over 300 mineral springs of this type have been found. In some places, including Darasun, Molokovka, Kuka, Amarovka, Gonzha and Shmakovka spas, wells are operated.

*Nitrogen thermal mineral waters* are discovered in Chitinskaya, Amurskaya and Jewish Autonomous Oblasts and Khabarovsky Krai [1 -7].

In the Russian Far East continental part thermal mineral waters are less common (Fig.1) compared to Kamchatka and the Kuril Islands, where volcanic activity is intensive.

Thermal mineral springs are used to develop resorts and balnearies and sometimes as heat supplies (Kuldur). Spa facilities are established at the Bylyrinsky thermal radon spring (Chitinskaya Oblast), at the Byssinsky spring (Amurskaya Oblast), at the Kuldur spring (Jewish Autonomous Oblast) and the Annenskie Vody spring (Khabarovsky Krai). Some springs do not have any facilities but are often used by local population for cure.



Fig. 1. Thermal Ground water Springs in the Amur Basin

1 - areas of cold carbonaceous mineral waters, 2 - thermal springs (1 - Bylyrinsky, 2 - Byssinsky, 3 - Soloniisky, 4 - Tyrminsky, 5 - Kuldursky, 6 - Inka, 7 - Annensky, 8 - Vyazemsky), 3 - Amur basin boundaries, 4 - Russian Federation boundary.

Prospective thermal water reserves of scattered springs in the Amur basin are 5000  $\ensuremath{\,\mathrm{m^3/day}}$  .

In the upper Amur reaches there is the Ingodino-Chikoisky thermal water region (Bylyrinsky spring), which south-western part stretches into the Mongolian People's Republic [6]. This region lies within the Central Zabaikalye mountain divine, where several big rivers are originated (Chikoi, Ingoda, Kyra and Bylyra rivers). Nine thermal springs have been explored there, only two of which are ranked as very hot: Kyrinsky (45<sup>o</sup>C) and Balarinsky (41,5<sup>o</sup>C). Temperature of the other 7 springs fluctuates from 17<sup>o</sup>C to 35<sup>o</sup>C. Springs are often accompanied with gassing, in which nitrogen prevails.

Origen and functioning of a hydrothermal system on the continent within Daurskaya, Amuro-Okhotskaya and Sikhote-Alinskaya hydrogeologic folded zones are caused by other factors than volcanic activity, which depend on the structural and tectonic specifics of thermal water discharge areas within hydrogeological massifs. Water is mostly discharged at the open crossing points of long and deep regional faults and young tectonic disturbances. Disturbances are constantly extending and renewed thus creating favorable condition for thermal water discharge from the very depths. In the plan thermal water discharge [11] usually has an isometric or elongated oval shape (a funnel or a stock). Thermal water aureole area by the isotherm is  $10^{\circ}$ C and by the depth (about 10 m from the surface) is  $5000 - 40000 \text{ m}^2$  (dimensions:  $50 \times 100 \text{ up to } 150 \times 250 \text{m}$ ).

Funnel dip is steep, observed for considerable depths (first kilometers from the surface) and significantly exceeds geometrical funnel dimensions in the plan.

Enclosing rocks within this funnel underwent hydrothermal alteration, have caverns and cured fractures. Walls of caverns and fractures are covered with deposits of secondary minerals of different genesis (calcite, quartz, hydromica, etc.). Usually the rocks surrounding the funnel practically serve as a confining layer.

Thus, thermal water discharge in this area is the result of a unique combination of favorable structural and tectonic conditions (an open funnel in the crossing point of tectonic deformations) and sufficient resources of heated ground water of infiltration genesis, which due to the thermolift can rise from the depths over 3 km through the zone of open fractures of the funnel.

Hydrotherm temperature depends on the depth of infiltration water penetration. Hydrotherms are divided into three groups by their temperature [8]: 1 – water – from 20 to  $35^{\circ}$ C; 2 – hot – from 35 to 70°C; 3 – very hot – from 70 to 100°C (Table 1).

Temperature group, °C (from – to)	No Hydrotherm on the scheme	Spring Name	Water temperature, ℃	Estimated water temperature, °C
Warm (20 – 35)	3	Soloninsky	27.5	
	8	Vyazemsky	21	
Hot (35 – 70)	1	Bylyrinsky	45	
	2	Byssinsky	46	
	4	Tyrminsky	36	78
	6	Inka	37	
	7	Annensky	54	99
Very hot	5	Kuldursky	73	103
(70 - 100)				

Table 1. Priamurye Hydrotherm Ranging by Temperature

Quartz based temperature calculation showed that thermal springs have different temperature (Table 1). Although the hydrochemical type of the studied therms are the same however their physical and chemical parameters differ [9, 10].

In the Turansky hydrogeological massif of the Amur-Okhotsk hydrogeological folded zone thermal water temperature varies from  $36^{\circ}$ C to  $73^{\circ}$ C.

Quite common are hydrotherms with fresh ground waters (water mineralization  $100 - 400 \text{ mg/dm}^3$ ) of hydrocarbonate or sulphate-hydrocarbonate composition of Kuldur type, which is characterized with high concentrations of fluorine (up to  $20 \text{ mg/dm}^3$ ) and silicic acid

 $(50 - 130 \text{ mg/dm}^3)$ .

Nitrogen thermal and sub-thermal waters are of hydrocarbonate natrium or natrium-calcium composition. They usually have increased silicic acid concentrations of 50 - 100 mg/l (Kuldur, Anninskie and other springs) and increased fluorine concentrations (up to 18 mg/l).

Chemical analysis of mineral water composition in Priamurye and adjacent territories revealed that these nitrogen thermal water zones belong to the zones of young arched uplifts, predominately to its peripheral. Such areas are usually characterized with increased jointing and quite often with the flow of Quaternary basalts.

In the thermal water discharge zones Quaternary basalts are common (Kuldur spring). Waters of the Kuldur deposit [2, 5] are weakly-mineralized (0.3 g/l), siliceous (H<sub>2</sub>SiO<sub>3</sub> – 0.112 g/l), alkaline (pH – 9.3), chloride-hydrocarbonate natrium with high fluorine concentrations 0.01 - 0.02 g/l). Kuldur spring water is weakly mineralized and its hydrochemical regime remains constant for the 100-year observation period.

At the Annensky spring [1, 3] a small decrease of mineralization and a significant fluorine concentration decrease (from 7 mg/l to 2 mg/l) have been observed in the period from 1976 to 2001. Silicic acid content remained stable in those years.

Table 2 presents comparative characteristics of micro-component composition of the Annensky, Kuldursky and Tyrminsky springs.

Element	Mass	Regime	Th-09-6 (Annensky well 21)	RSD, %	Th-09-9 (Tyrma)	RSD, %	Th-09-8 (Kuldur well 1-87)	RSD, %
Li	7	#1	55.17272	1.37	28.74204	0.76	239.6588	3.8
Be	9	#1	0.019863	2.32	0.001695	30.2	0.041471	11.23
В	11	#1	60.1582	1.15	229.8522	0.8	473.0445	3.13
Na	23	#3	61605.4	1.24	56888.95	0.53	98029.39	4.8
Mg	24	#3	31.86946	2.35	44.51913	7.16	14.06394	0.68
Al	27	#2	12.56926	9.65	13.6067	12.74	30.26508	9.66
K	39	#1	1379.899	0.75	1153.993	0.97	2181.131	3.96
Ca	44	#3	208.0703	8.08	189.3947	2.92	204.0548	5.5
Sc	45	#3	0.217515	18.03	0.204835	10.19	0.283896	35.92
Ti	49	#3	0.178734	26.36	0.522762	14.7	0.263481	3.89
V	51	#3	1.487377	4.47	0.261511	7.6	0.06961	6.32
Cr	52	#3	0.115178	9.84	0.123911	3.51	0.089817	6.44
Mn	55	#3	0.822427	14.48	0.862407	5.87	0.471867	4.4
Fe	56	#3	2.295926	9.46	21.38808	5.91	0.929877	1.12
Со	59	#3	-0.00044	14.15	0.004527	5.51	-4.8E-05	9.23
Ni	60	#3	0.217566	9.24	-0.36587	20.55	-0.23561	5.39
Cu	63	#3	1.752079	8.73	-0.44035	5.06	0.241981	5.39
Zn	66	#3	2.867903	6.37	0.692166	2.05	1.10701	4.63
Ga	71	#2	4.779963	5.84	4.764327	5.77	12.02304	12.4
Ge	74	#1	3.966734	4.54	5.146786	1.01	9.783772	15.56
As	75	#2	16.74128	4.53	2.414037	8.28	86.02302	7.46
Se	77	#2	0.089746	11.96	0.082479	13.94	0.179391	17.39

Table 2. Comparative Characteristics of Micro-component Composition of Thermal Waters, mcg/l

Rb	85	#1	6.683164	1.43	6.448728	0.75	27.35219	8.64
Sr	88	#1	66.65642	0.46	34.51179	0.5	58.9111	4.18
Y	89	#1	0.002386	3.95	0.010563	5.37	0.002195	4.16
Zr	90	#1	0.022455	9.21	0.05183	3.66	0.108979	6.51
Nb	93	#1	0.001996	30.41	0.001706	43.23	0.001227	5.09
Мо	95	#1	8.736773	0.59	9.148173	1.2	23.74248	3.39
Ag	107	#1	0.000225	8.35	-0.0009	9.43	-0.00014	19.55
Cd	111	#1	0.009554	9.74	0.006043	20.55	0.016322	23.83
Sn	118	#1	-0.00119	8.7	-0.02058	10.03	0.023813	3.46
Sb	121	#1	0.184306	3.64	0.301501	2.18	1.272158	3.49
Те	125	#1	-0.01794	26.46	-0.01962	33.07	-0.01538	15.53
Cs	133	#1	3.715301	1.15	1.077161	0.39	20.87599	3.09
Ba	135	#1	40.4231	2.67	50.86746	2.46	28.96976	4.65
La	139	#1	0.002833	50.92	0.016384	2.34	0.031625	3.66
Ce	140	#1	0.007918	40.51	0.036296	11.75	0.055234	5.27
Pr	141	#1	0.000562	37.5	0.004361	9.6	0.003692	3.53
Nd	146	#1	0.002716	36.06	0.016877	12.09	0.008956	4.83
Sm	147	#1	0.001804	17.84	0.004578	10.44	0.001553	4.14
Eu	151	#1	0.000892	5.47	0.001465	2.82	0.000704	2.42
Gd	157	#1	0.00169	12.99	0.004903	8.85	0.002471	8.02
Tb	159	#1	0.00019	5.15	0.000513	13.94	0.000235	4.6
Dy	163	#1	0.000971	24.37	0.002765	2.48	0.000934	3.15
Но	165	#1	0.000222	32.04	0.000563	21.59	0.00016	6.34
Er	166	#1	0.0006	13.85	0.001868	14.6	0.000596	7.56
Tm	169	#1	0.000136	28.67	0.000284	13.73	0.000171	5.64
Yb	172	#1	0.000921	8.94	0.001603	11.92	0.000679	2.47
Lu	175	#1	0.000168	12.82	0.000254	13.02	0.000145	6.35
Hf	178	#1	0.005504	36.33	0.007319	13.48	0.015274	8.11
Та	181	#1	0.004665	9.92	0.000535	16.46	0.002594	3.09
W	184	#1	22.58606	1.44	31.63087	0.75	191.0163	5.94
Re	187	#1	0.000801	49.38	0.000442	20	0.002991	65.47
T1	205	#1	-0.05828	4.06	-0.06266	12.59	-0.051	8.64
Pb	208	#1	-0.06662	12.1	-0.02637	2.83	-0.0481	5.85
Th	232	#1	0.00429	4.52	0.018472	0.89	0.002598	2.16
U	238	#1	0.050873	2.2	0.037986	1.6	0.002903	3.08

Notes: Sample were analyzed in the analytical laboratory of the Far Eastern Geology Institute FEB RAS (Vladivostok) with mass-spectrometry and atomic emission analyses

Thermodynamic estimations showed [9, 10], that the studied thermal waters have excess concentrations of clay minerals (smectite, illite, kaolin), low-temperature zeolites (heulandite, clinoptilolite, mordenite) and albite. Petrographical and X-Ray-sonde analysis revealed all secondary minerals that were predicted. Petrographic and X-ray studies revealed all secondary minerals predicted by calculation. Calculations of forms of main ions in the solution showed that over 85% of them are in the ion form and around 15% are in the hydrocarbonate-ion complexes. In the Annensky spring an insignificant portion of sulphate-ion is observed.

Nitrogen dominates in dissolved gas content (up to 99%) [1 -7, 9, 10], and insignificant content of  $H_2S$  is registered in the Anninskie Vody spa. Ar100/N<sub>2</sub> ratio is close to that of the atmosphere, which is an evidence of the atmosphere source of nitrogen in the

studied therms.

Atmospheric precipitations, surface and ground waters are the main sources of hydrotherm natural resources. Part of meteoric waters, which enrich hydrotherm resources, joins the long-lasting cycle that involves deep zones of the earth crust. There these waters mix with upcoming water fluids and form various warm and hot springs of heterogeneous chemical composition.

Obtained thermal spring data [9, 10] on correlation of water oxygen and hydrogen isotopes show that spring water is mostly of meteoric origin. All obtained correlations of oxygen (-19.5‰ - -17.5‰) and hydrogen (-155‰ - -130‰) are along the Craig line of meteoric waters. Oxygen values from -20‰ - -5 ‰ are specific for present meteoric and surface waters of the region.

According to E.V. Pinneker et al. (1998) estimations, the age of fissure-vein waters can be from several thousands to several dozens of thousands years, i.e. present resources of fissure-vein waters were formed in time of glaciation that prevailed in this territory. It was found out [9, 10] that waters mostly depleted of heavy hydrogen and oxygen isotopes are found in high-mountainous regions, where glacier melting waters impact is significant. In some springs a noticeable deviation from the Craig line towards heavier oxygen is observed and may be interpreted with intensive exchange of isotopes with enclosing rocks. This is mostly evident in springs, which chemical composition is formed in the zones of abundant aluminosilicate intrusive and metamorphic rocks.

High sulphate-ion concentrations are specific to waters of this region. Studies of isotope composition of sulfur in sulphates [9, 10] revealed that a heavy isotope of sulfur (+25% - +30%) dominates in these therms. Sulphate concentrations in springs correlated with anomalous concentrations of radon. It is known that radon comes from sorption collectors, which are usually formed in relatively old faults. It seems possible that sulphate-ion is not the result of sulphide oxidation but results from dilution of sulphate minerals of initially sediment and magmatic rocks.

Microelement content in water (Table 2) depends on total mineralization. This regularity is well-observed in rare alkaline and alkaline-earth elements. It was found out that concentrations of some microelements depend on solution temperature (Sc, Al, W), whereas concentrations of other elements depend on the degree of water and rock interactions (Sr, Ba).

The undertaken studies widened out knowledge of metal-bearing capacity of thermal waters in areas, not connected with present volcanism. Accumulation of similar information and data on new and operated deposits of alkaline nitrogen hydrotherms of the Coastal province and other territories will allow clarifying geological understanding the genesis of present hydrothermal solutions in the zones of post-volcanic activity and probably finding new hydrogeochemical signs of seismic activity, as well as assessing the impact of trace elements on balneal water properties.

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