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4.3
Hydrogeochemical characteristics of mineral and thermal waters

title: **Geochemistry of thermal waters of Sikhote-Alin ridge, Russia**

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INTRODUCTION

Low-temperature thermal waters of the continental margin of Russian Far East are widespread along the coast of Japan and Okhotsky Seas. All thermal water systems occur in Sikhote-Alin ridge (Fig. 1). Most of them were studied from the 1930s until 1960s (Makerov, 1938). Some are now balnearies: Annensky, Tumninsky ("warm spring"), Amgunsky and Chistovodny and others are used by locals for self-treatment: Khucin and St.Helen's springs at Amgunsky and "Hot spring" at Chistovodny thermal area. Latest investigations (Bragin et al., 2007) have shown geochemical properties of waters. However information about geochemistry and REE is limited. So this paper presents new data on geochemistry, isotopes, and REE of thermal springs of the Sikhote-Alin ridge.

Figure 1. Sikhote-Alin ridge. Situation plan.

SPRING CHARACTERISTICS

Annensky spa thermal area is located on the East of Khabarovsky krai, in the lowest part of the Amur river, 80 km from the Okhotsky sea shore. According the borehole data, thermal waters occur in the contact zone between effusive and tuffaceous sedimentary rocks of upper Cretaceous of Bolbinskaya and Tatarkinskaya suites. All over the area rocks are covered with eluvial-delluvial sediments (thickness up to 5-8 m) consisting of clay, poorly sorted sand and gravel. The water is low-temperature (49.5-54.5°C), low-mineralized (TDS 0.20-0.35 g/l), alkaline (pH 8.5-9.4) and the chemical classification of the groundwater is a Na-HCO_3-SO_4 type of water with high content of silica (25-35 mg/l) and fluorine (up to 7 mg/l).

Tumninsky spa thermal area is located on SouthEast of Khabarovsky krai, 9 km from the Tumnin River, and 40 km away from the Tatarsky channel (Japan sea). The geological structure is defined by the contact- zone of granites and andesitic basalts of the Eocene Kuznecskaya suite (Sidorenko, 1971). Waters from borehole № 9 (depth 460.0 m) are low-temperature (43.0-

46.0°C), alkaline (pH= 8.65-9.7), low-mineralized (TDS 0.15-0.25 g/l) and the chemical classification of the groundwater is a Na-HCO_3-SO_4 type.

The Chistovodny geothermal area is located in Lazo area of the Primorsky krai, 70 km away from the of Japan Sea shore and is known from a group of springs and boreholes (Chudaev, 2003). Host rocks consist of crumbling granites of upper Cretaceous age, broken by Paleocene dykes of aplites and diorite porphyries. Bedrock is covered by Quaternary alluvial deposits of 3 to 7 m thickness. The geothermal field is presented by several outlets, notably “Chistovodny spa” and “Hot Spring”. Waters are low-temperature (30°C) low-mineralized (TDS= 0.14-0.16 g/l), low-alkaline (pH=7.0-8.4) of Na-HCO_3 type with high content of silica (up to 60mg/l) and fluorine (up to 4 mg/l).

The Amgunsky geothermal area is located in the Terney area of the Primorsky region, 10 km from the Japan sea shore. This geothermal field is presented by three well-known outlets: Banny, St.Helen’s, and Khucin. The geological structure is defined by the contact of granite intrusions with rhyolites, tuffs and ignimbrites of Mesozoic and Cenozoic age (Chudaev, 2003). Waters are low-mineralized (TDS=0.1-0.2 g/l), alkaline (pH=8.5-9.0) of Na-HCO_3 type with content of silica (up to 22 mg/l).

ANALYTICAL RESULTS

Moving from southern to northern thermal areas of Sikhote-Alin we can find an increase of temperature of the waters that is reflected in quartz geothermometry (Bragin et al. 2007). The temperature increase is paralleled by increases in most dissolved species (Table 1). These trends may reflect enhanced reaction rates in higher temperature waters combined with likely longer flow paths as the higher temperature waters penetrate to greater depths than do lower temperature waters.

Table 1. Spring characteristics.

	Annensky	**Tumninsky**	**Amgunsky**	**Chistovodny**
pH	9.2	9.3	9.1	8.9
		mg/l		
TDS	235	195	183	167
Na^+	61.0	32	33.4	19.62
K^+	1.17	0.35	0.7	0.33
Ca^{2+}	2.0	2.11	2.0	5.42
Mg^{2+}	0.01	0.01	0.08	0.007
HCO_3^-	112.8	78.1	70.7	63.4
SO_4^{2-}	25.4	7.1	13.6	5.7
Cl^-	4.0	1.4	3.6	2.4
F^-	2.7	0.8	0.9	3.9
SiO_2	46.8	35.2	31.1	18.6
		°C		
T, °C (surface)	49.9	44.8	34.5	27.5
T, °C quartz geothermometer (Fournier, 1977)	98.7	86.1	80.9	60.7
T, °C Na/K geothermometer (Arnorsson et al. 1983)	123.7	95.9	128.7	116.8

Oxygen and hydrogen isotope ratios were measured in thermal waters from the whole Sikhote-Alin folded area. The δD and $\delta^{18}O$ values for thermal waters in Annensky and Tumninsky areas correlate well with data of Chudaev (Chudaev, 2003) on Chistovodny, Amgunsky and for precipitations in Primorye (Southern Sikhote-Alin). On a δD vs. $\delta^{18}O$ diagram the Sikhote-Alin thermal waters lie close to the global meteoric water line (Craig, 1961) as shown in Figure2.

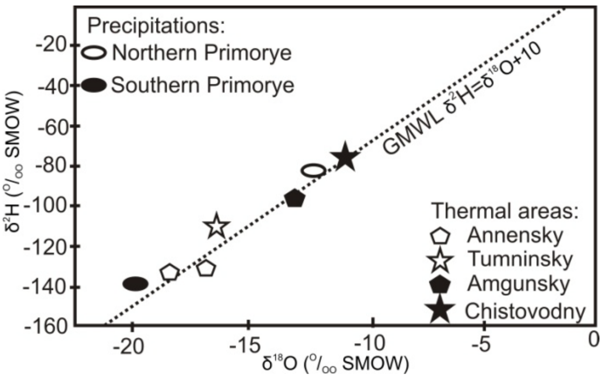

Figure 2. Deuterium and Oxygen-18 isotopes.

Rare earth elements were measured using an Agilent 7500C inductively-coupled plasma mass spectrometer (ICP MS). The REE data, normalized to North American Shale Composite (NASC), show the common rising trend caused by greater solubility of heavy REE (Figure 3).

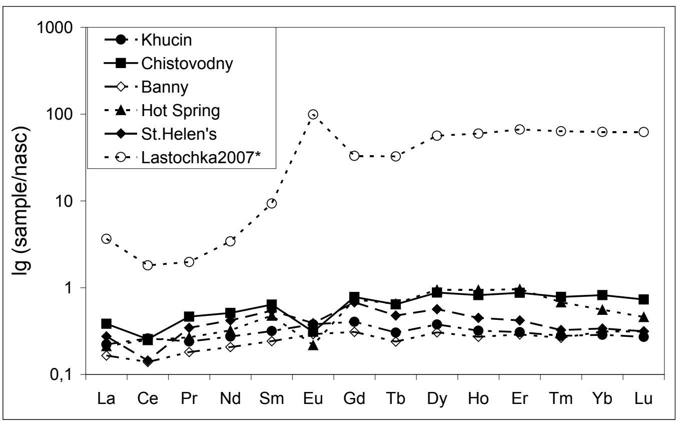

Figure 3. Concentration of REE in thermal and high pCO_2 waters (Lastochka) of Sikhote-Alin ridge normalized to NASC. * Lastochka data obtained by Tchepkaia (2007)

In contrast to the small REE concentrations in our waters ($0.02\text{-}20*10^{-9}$ g/l), the high pCO_2 Lastochka waters, also from the Sikhote-Alin region, have high REE concentrations, probably reflecting low alkalinity of studied thermal waters. Some water lines show negative anomalies on Ce and Eu. Eu anomaly may be caused by Eu-deficient plagioclase. Whereas Ce could be precipitated under oxidizing conditions.

Microprobe analyses of granite rock, which is host to the Tumninsky springs, showed the possible source of some REEs in monazite (Figure4) (La 12.49%, Ce 28.89%, Nd 12.9%, Sm 2.32%, Gd 2.14%). Other REEs are probably from plagioclase.

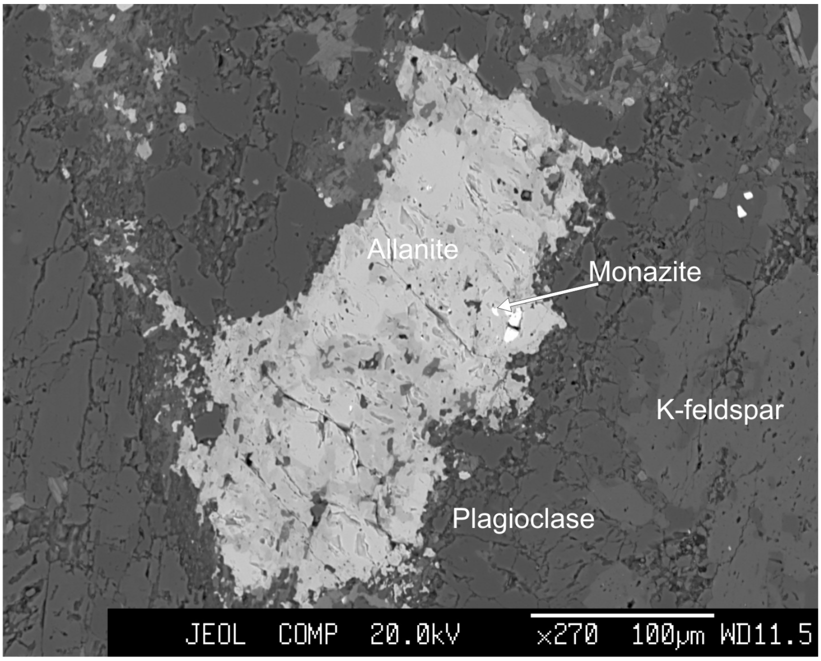

Figure 4. Monazite in granites of Tuminsky spring host rocks.

WATER-ROCK INTERATCTION MODELING

Calculations with computer code WATEQ4F (Ball & Nordstrom, 1991) show that all studied thermal waters are slightly supersaturated with calcite and chalcedony and strongly undersaturated with fluorite and albite (Bragin et al. 2007).

Temperatures calculated by quartz (Fournier, 1977) and Na-K (Arnorsson et al. 1983) geothermometers are shown in the Table 1. The Na-K geothermometer shows higher temperatures than quartz, possibly caused by admixing of fresh cold groundwater into reservoir, which lowers the quartz temperature but not Na-K geothermometer tempeature.

Based on all this data on geochemistry we propose a conceptual model (as an example) for a Tumninsky geothermal area (Figure 5) wherein meteoric groundwaters penetrate deep enough into the permeable rock to become heated to 90 to 120 C, and then rise through the contact zone or some other fissured zone. Rising water cools, and precipitates chalcedony and calcite, accounting for equilibrium with those two minerals, outflows at the surface.

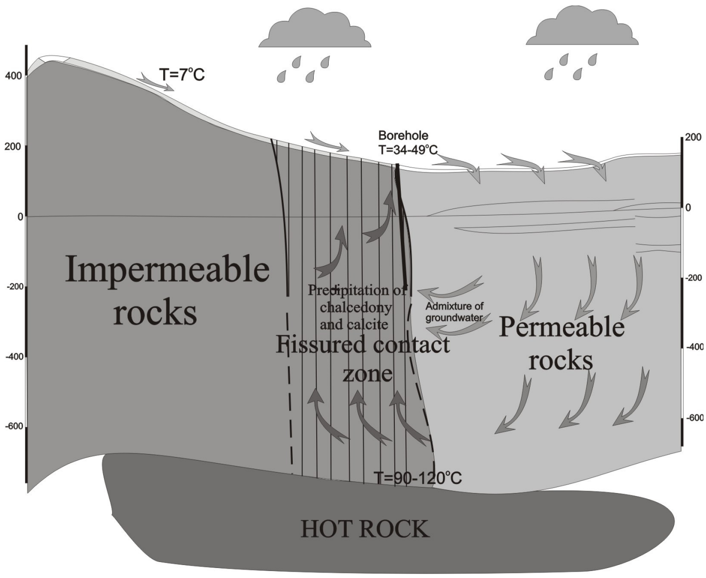

Figure 5. Conceptual model of evolution of thermal waters of Sikhote-Alin ridge.

CONCLUSIONS

The following summarizes the investigations of the thermal waters of Sikhote-Alin ridge:

- Data on stable isotope ratios ($\delta^{18}O$, $\delta^{2}H$) show that the waters are of meteoric origin (rainwater);
- REE measurement showed it's low concentrations caused by low alkalinity. Some water lines have Ce and Eu anomalies which should be studied further;
- Analytical results coupled with thermodynamic and geothermal modeling helped us to create a conceptual model of evolution of studied waters.

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