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Hydrothermal Vapours of the Koshelevsky Volcanic Massif (South Kamchatka): Composition and Origin Conditions

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ABSTRACT

The Koshelevsky volcanic massif is one of the most promising sites for the development of geothermal power industry in Russia's Kamchatka Krai. There are two well-known modern thermal anomalies – Verkhne (Upper)-Koshelevsky and Nizhne (Lower)-Koshelevsky, with a total heat output of 75 GW which is comparable to the heat efflux of the famous Kamchatka's Valley of Geysers (Vakin et al., 1976). The Nizhne (Lower)-Koshelevsky vapour-dominated geothermal deposit whose capacity equated to electric power amounts to 90 MW (Pisareva, 1987) was identified by 1,500-meter-deep drilling on the western slope of the massif. Hydrothermal discharge at the surface is manifested by gas-vapour jets, condensate waters and separate springs which are probably sourced from the depth. Studies in the 1960s-80s did not resolve all issues related to the composition and source of thermal waters of the Koshelevsky volcanic massif. Besides, the last decades have been marked by significant changes in the morphology of the thermal fields, in the distribution of discharge areas of hydrothermal fluids, etc. All mentioned above has predetermined the timeliness of our work.

The waters being discharged within thermal anomalies have a temperature of up to 98 ^oC and are referred to as acid or low acid (pH=3-5.8) sulphate ones, less frequently there are hydrocarbonate-sulphate ammonium or Ca(Na)-ammonium ones with an elevated content of silicic acid (95-175 mg/l). The total mineral content typically amounts to 0.6-0.8 g/l and can reach levels of 2.5 g/l (in water-mud pots). The gas content is dominated by CO_2, which is typical for many other Kamchatka's and systems elsewhere in the world, H_2S, CH_4, and N_2 are also always present. Verkhne-Koshelevsky hydrothermal vapours have a higher content of sulphur gases whereas the Nizhne-Koshelevsky ones have an elevated content of methane (up to 67% in some drill holes), nitrogen (up to 50%), and presence of a variety of heavy hydrocarbons and presence of oil in vapour condensate (Pozdeev, Nazhalova, 2008). Previously, it was mainly assumed that the hydrothermal vapours of the Koshelevsky deposit were formed under an impact of deep (magma-penetrating or mantle-derived) fluids which was confirmed by geodynamic, geological-structural and isotope-geochemical data. Most likely, this hypothesis is relevant and a deep (a mantle-derived one?) fluid influences the geothermal systems of the Koshelevsky massif. At the same time we focus on the fact that the composition of hydrothermal vapours may be connected with the Neogene volcanogenic-sedimentary rocks of the massif basement. The rocks contain a large amount of organic remains with observed presence of petroleum products.Probably, thermal decomposition of the organic matter under high P-T parameters of the environment causes a release of methane, ammonium and boric acid and transition of these components to the solution and to the gaseous state. We estimate that the level of thermal waters in this region may occur at an approximate depth of 2 km below the surface of the Sea of Okhotsk. The formation of a solution boiling zone is accompanied by a release of CO_2 in the steam phase, other volatiles, including hydrocarbons, boric and naphthenic acid. A gas-vapour mixture ascends to the earth surface without significant heat losses: a temperature decrease probably occurs only due to adiabatic expansion and therefore the temperature of vapour at the thermal fields reaches 120-150 ^oC. It is still unclear whether there is a modern hydrothermal system in the interior of the Koshelevsky volcanic massif or whether each large thermal anomaly is formed as a standalone one. This issue is also discussed in the present report.

1. INTRODUCTION

The Koshelevsky volcanic massif is situated on the southern end of Kamchatka peninsula at the zone of junction of the volcanic belts and at the interface of the regional Kamchatka and Kuril geological structures (Dolgozhivuschii…, 1980). It is assumed that a sublatitudinal deep-seated fault governs a long-lasting magmatic and fluid feed into this volcano-tectonic structure (Polyak et al., 1979; Lebedev, Dekusar, 1980). Large high-temperature geothermal anomalies of Verkhne- and Nizhne-Koshelevsky geothermal anomalies whose total heat efflux is comparable to the heat capacity of the Valley of Geysers and active Mutnovsky and Shiveluch volcanoes (Vakin et al., 1976) are confined to the massif. There are warm (20-40 ^oC) outflows of hydrothermal waters of various compositions in the central part and along the periphery (Calderniye, Sivuchinskiye and other springs). Based on detailed studies, water-bearing layers occurring in the base and within the structure of the Koshelevsky volcanic massif were identified, chemical types of hydrothermal fluids were defined, main thermal anomalies (t/a) were described in detail and their heat capacity was estimated. Drilling penetrated a geological cross-section down to a depth of 1.5 km and the largest on Kamchatka Nizhne-Koshelevsky vapour-dominated geothermal deposit was identified (Pisareva, 1987). At the same time, many questions related to the position and type of heat sources, conditions of formation, mixing and discharge of hydrothermal solutions and a gas-vapour mixture have remained outstanding. Relying on the complete hydrochemical sampling of the Koshelevsky volcanic massif implemented throughout a number of summer field seasons, this paper reports on new data on general chemical composition of hydrothermal fluids. For the first time ever, we discuss behaviour of micro elements in thermal waters including strontium isotopes and rare earth elements. Here we discuss conditions of formation of hydrothermal vapours in the zone of hypergenesis of Verkhne- and Nizhne-Koshelevsky geothermal system and a possible impact of a deep-seated fluid on this zone.

2. RESEARCH METHOD

Physical-chemical parameters of waters in thermal springs and river waters (pH, Eh, quantity of dissolved salts and temperature, ^oC) were determined directly at sampling points by means of portable analysers WATER TEST and Multi 340i/SET manufactured by a German company WTW. The water samples were filtered through a 0.45 µ membrane filter right on the sampling site to separate a dissolved part and fine colloids from suspended solids. The samples were then placed in a 0.5 l plastic bowl for chemical analysis and in a 0.2 l bowl for detection of micro components. The micro component samples were additionally acidified with ultra-pure HNO_3 up to pH=2. A general chemical analysis including detection of ions NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, F^-, SO_4^{2-}, H_3BO_3, H_4SiO_4 was performed in the analytical centre of Institute of Volcanology and Seismology FED RAS using volumetric, colorimetric and flame-photometric techniques. The analysis of micro element composition was performed in the analytical centre of Institute of Geochemistry SB RAS using the inductively coupled plasma mass spectrometry (ICP-MS) technique with a Plasma Quad device. AQUACHEM 5.1 (AquaChim …, 2006) software was used for processing hydrogeochemical data, cation-geothermometer-based calculation of temperatures at depth and a graphic representation of chemical composition of the thermal waters.

3. GEOLOGICAL-HYDROGEOLOGICAL CHARACTERISTICS OF THE STUDY AREA

The Koshelevsky volcanic massif is a part of the structure of the Pauzhetsky-Kambalny-Koshelevsky geothermal (ore) region. The region is a long-lived (from early Oligocene to Holocene) volcanogenic-ore centre (Dolgozhivuschii…, 1980). Rocks of the region are typical for an island arc complex and constitute three structural stages: Oligocene-middle-Miocene, Miocene-Pliocene and Pleistocene-Holocene. The Koshelevsky volcanic massif belongs in the upper structural stage and is composed of lavas, tuffs, agglutinates, extrusions and subvolcanic intrusions from andesidacites to basalts (medium composition rocks prevail). The rocks are highly permeable for meteoric waters and compose the hydrogeological basin of the volcanogenic type. The massif is underlain by rocks of the middle structural stage within the limits of which secondary quartzites, monoquartzites and argillizites enclosing quartz-carbonate-sulphide veins and dissipated ore mineralization widely occur. These rocks are characterized by a high density and enclose water-bearing complexes which mainly feature fracture-vein circulation of thermal waters. Atmospheric precipitations and probably inflows of sea waters are feeding sources for the water-bearing complexes. Discharge of underground waters of the upper horizons takes place above the drain basis at contacts of heterochronous rocks and in the zones of discontinuous faults. A vapour-dominated geothermal deposit whose capacity equated to electric power amounts to 90 MW (Pisareva, 1987) with estimated inferred resources of 210 kg/s of dry vapour was identified by 1,500-meter-deep drilling in the area of the Nizhne-Koshelevsky thermal anomaly. Based on hydrodynamic testing of wells, a dry steam section in the form of an upturned cone which widens to a depth of 1.5 km and wedges out at the surface of the Nizhne-Koshelevsky t/a was identified. Probably, a great role in localization of this region is played by a multi-phase intrusive body of diorites – diorite porphyrites in whose apical part a zone of megabreccias of intrusive and host rocks with an average thickness of 150-200 meters had penetrated. The rocks of this zone may have a higher permeability and, subsequently, maintain circulation of overheated solutions. In addition, the most recent geological-geophysical data indicate that there is a 5 km deep vertical zone featuring high permeability for a gas-vapour mixture and high-temperature hydrothermal fluids (See a report of S. Rychagov in the proceedings of WGC-2015). Identification of such a zone conforms to the previously published data stating that Nizhne-Koshelevsky t/a and the cognominal geothermal deposit are confined to a deep-seated fault (Polyak et al., 1979; Lebedev, Dekusar, 1980; Pozdeev, Nazhalova, 2008). The near-surface part of the zone (near the thermal anomaly) is a dish-shaped section of loosened and argillized rocks, where meteoric waters and ascending hydrothermal vapours are intensively mixed. A principally similar hydrogeological setting may take place in the area of the Verkhne-Koshelevsky t/a. It is assumed that there is a hydrodynamic link between the structures of the Verkhne-Koshelevsky and Nizhne-Koshelevsky t/a (Vakin et al., 1976, Pozdeev, Nazhalova, 2008), and therefore a single modern hydrothermal system may exist within the interior of the Koshelevsky volcanic massif. However, this thesis has not been underpinned yet.

4. CHARACTERISTICS OF MAIN THERMAL ANOMALIES

4.1 The Verkhne-Koshelevsky t/a

The Verkhne-Koshelevsky t/a is situated in the central part of the Koshelevsk volcanic massif in the erosion crater of Valentin volcano at absolute elevations of 1,200-1,250 m. The thermal anomaly has an estimated area of 303,000 m^2 by an isotherm of 20 ^oC at a depth of 0.5 m (Vakin et al., 1976). Surface thermal outflows are concentrated at an area of 120-130 thous. m^2. The hydrographical network consists of three main streams (Vostochny, Zapadny, Dalny) which flow from under a snow patch and merge into a single stream (the head of the Shumnaya river) beyond the t/a (Figure 1). Thermal outflows are in the form of gas-vapour jets, mud-water pots, hot lakes, steaming grounds and separate water springs. The gas-vapour activity is mainly confined to the valley of the Vostochny stream (Tartarari area). Temperatures at orifices of the jets are within 98 to 150 ^oC. The discharge of the jets is 0.1-0.4 kg/s, the flow velocity is above 100 m/s (Vakin et al., 1976). Some gas-vapour jets are discharged directly in the stream bed thus forming 2-3 meter high fountains and heating the stream water up to 95.4 ^oC near the vapour vents. This causes heating of the whole stream: the water is heated to a temperature of 8.1 ^oC at the head and the water temperature increases up to 77.3 ^oC at the point of exit from the t/a. Values of pH and Eh are not significantly influenced. The stream has a water flow of 32-35 l/s which does not vary significantly from the head to the point of exit from the t/a. A group of large boiling water pots with diameters up to 5-7 m in the upper part of the stream apparently do not contribute to the flow rate. They have been formed in erosion craters where the vents of the most powerful gas-vapour jets are located. The Polygon area is located on a relatively flat ground about 60 by 60 meters. The most typical features of this area are boiling pools (two communicating lakes sized 10 meters across). The temperature of water in vigorously boiling points is 82-90 ^oC, pH = 4.3 – 5.1, Eh = +120 - +170 mV. The amount of salts (TDS) in the solution is within a range of 0.7 – 0.8 g/l to 2.3 – 2.9 g/l. The Kisly area occupies a significant area of the t/a and is characterized by all types of thermal manifestations. Gas-vapour mixtures with temperatures up to 120 ^oC are discharged among landslide deposits, along banks and in the stream beds. In some spots there are mud-water pots and thermal water springs. In the northern end of the site we found a previously unknown group of thermal water springs which gave rise to the Khaltsedonovy ('Chalcedony') stream (See Figure 1).The water temperature in the springs ranges from 70 to 58 ^oC, values of pH remain unchanged

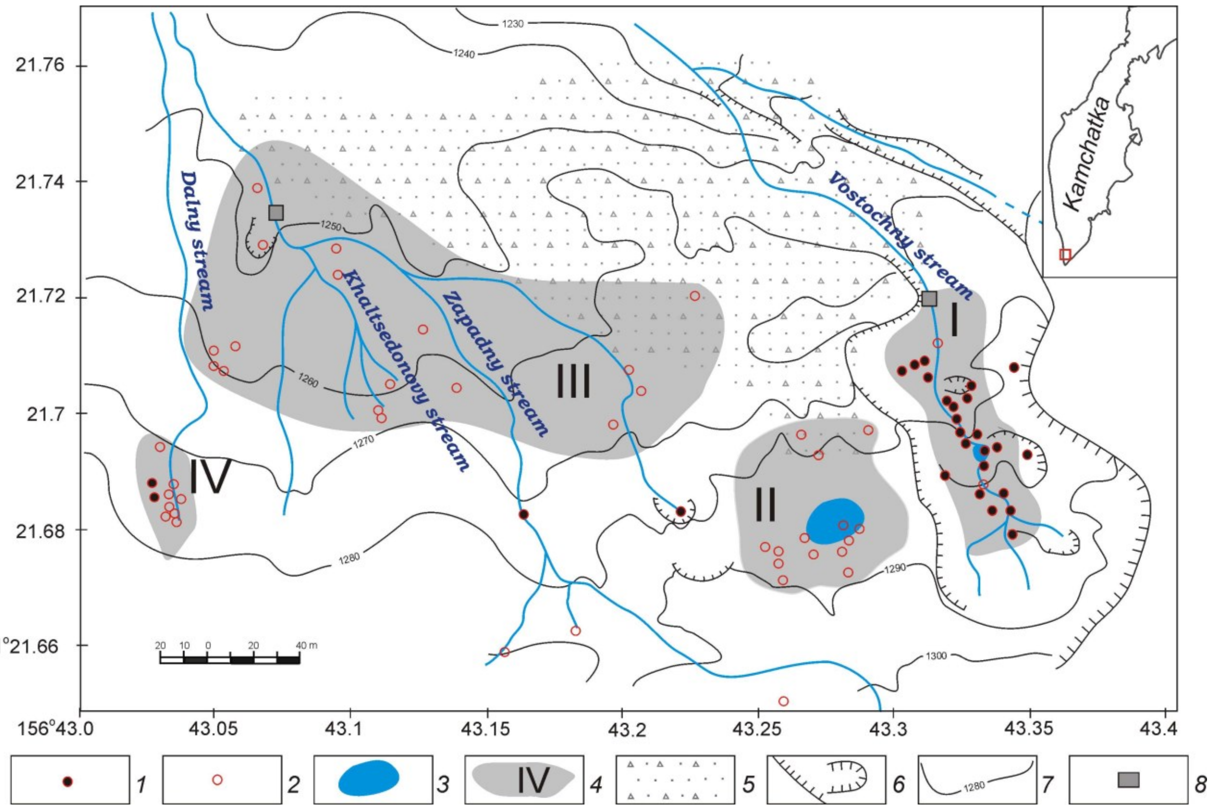

Figure 1: Map of the Verkhne-Koshelevsky t/a. (1) gas-vapour jets, (2) mud-water pots, (3) hot lake, (4) sections, (5) coarse deposits, (6) erosional banks, (7) isoline, (8) hydrologic section.

in all outflows along the stream and amount to 3.0 – 3.15, Eh = +245 mV. Rock fragments on the bed of the stream are covered with silica brushes with crystals up to 5 mm in diameter. Two more local springs with similar physical-chemical parameters and silica incrustations (tridymite-cristobalite-chalcedony) were found on the bottom of water pots of this site. Physical-chemical parameters of the water in the Zapadny stream which intersects the Verkhne-Koshelevsky t/a stay almost unchanged along all its length. We also found a previously unknown and different from the others area called Dalny. The upper group of thermal manifestations is confined to deluvial deposits on the crown of a steep slope. Drainless mud-water pots have a temperature of 90-94 ^oC, pH = 4.6 – 4.9, a general mineralization of 0.6 – 0.8 g/l. Some pots are intensively diluted by waters coming down from the snow patch. There are over ten weak gas-vapour jets with temperatures up to 98 ^oC at orifices. The lower (northern) group of thermal outflows on this site consists of drainless mud-water pots. A characteristic feature of the Dalny area is a low level of the plane position of thermal waters with reference to the water edge of the Dalny stream.

4.2 The Nizhne-Koshelevsky t/a

The Nizhne-Koshelevsky t/a is situated on the western slope of the Koshelevsky volcanic massif in at absolute elevations of 770-850 m and is confined to Zapadny volcano. The thermal anomaly is located in an oval-circumferential geomorphologic structure elongated to 500 m along the deep-cut ravine of the Gremutchiy ('Rattling') stream (Figure 2). The most typical thermal outflows are water and mud-water pots, thermal lakes, pulsating water springs, gas-vapour jets, steaming grounds. The temperatures of the grounds do not exceed 105 ^oC at a depth of 0.8 – 3.0 m, the temperatures of vapour at orifices of the jets may reach 115-120 ^oC, but mainly amount to 90-98 ^oC. The most active part of the thermal anomaly occupies an area of 100 x 250 m. The site has an estimated total heat efflux of 25 GCal/s (Vakin et al., 1976). The thermal anomaly has three distinguishable areas. A small Verkhny ('Upper') area has about 10 mud-water pots 30 cm in diameter and the same number of weak capacity gas-vapour jets. The long-lived snow patch which occupies a 70 x 120 circus is the main source of its feed water. Temperature of the water pots ranges from 80 to 101 ^oC (85-90 ^oC on the average), pH varies from 4.5 to 5.5, Eh = +100 - +190 mV. Warm lakes (30-35 ^oC) are formed in the centre of the area where the stream valley widens. The flow rate of the stream equals 3.0 l/s. The water temperature in this point is 23 ^oC, pH = 5.4, Eh = 88 mV (as of August 2009). A barrier lake called Bannoye is identified as a separate area. A thermal 1.0 x 1.5 m site featuring a multi-vented water spring is located near the eastern coast of the lake. This spring features a neutral pH (7.0 – 7.4), a relatively high general mineralization (1.0 – 1.1 g/l according to field measurements); through the years, temperatures ranged from 56 to 72 ^oC, Eh = +280 - +295 mV. Thermal waters also discharge directly in the lake and on account of this the water mass is heated up to 35 ^oC, threads of gas bubbles are rising from the bottom. The most powerful part of the t/a is a single thermal field where we can conditionally distinguish (due to geomorphologic boundaries) three areas: Bolshaya Sukhaya Voronka (BSV) ('Large Dry Crater'), Tsentralniy ('Central') and Zapadniy ('Western') (See Figure 2). BSV is a 50 x 60 m wide crater of an irregular-isometric shape with a steep eastern bank, a flat bottom, thermal knobs and several small (up to 5 m in diameter) erosion craters near the western boundary. The pH range for all thermal outflows of BSV is 4.1 – 4.5, Eh = +175 - +195 mV, temperatures vary from 41 to 94 ^oC. The western end of BSV is a starting point for a linear zone delineated by a small brook on the bed and banks of which around 10 gas-vapour jets and several small mud-water pots 25-30 cm in size occur. The temperature of the gas-vapour mixture amounts to 113 ^oC, the temperature of the water in the pots is 98 ^oC, pH ranges from 5.3 to 8.0, Eh = +111 - +225 mV. The zone is distinctive due to presence of an intensive underground run-off of thermal waters. Prospecting pits and boreholes

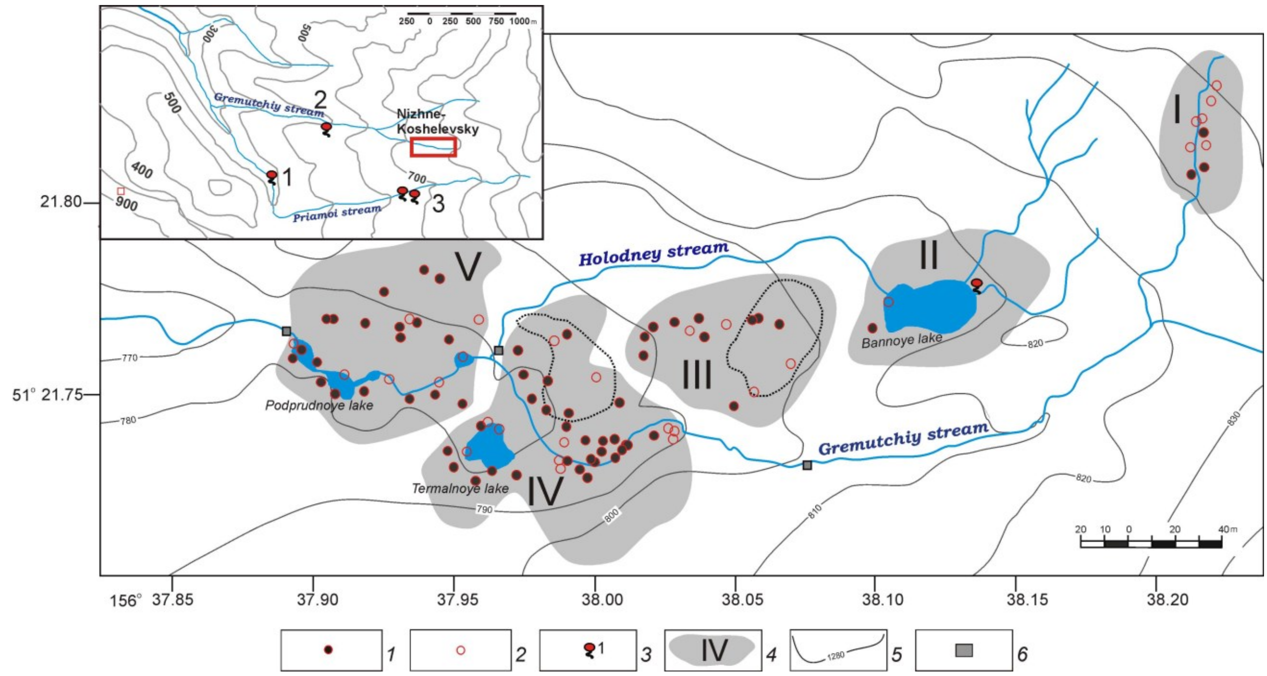

Figure 2: Map of the Nizhne-Koshelevsky t/a. (1) gas-vapour jets, (2) mud-water pots, (3) thermal springs, (4) sections, (5) isoline, (8) hydrologic section.

in this area penetrated open fractures with vapour outflows and large cavities (up to 1.0 m) into which drilling bits sank. The Tsentralny area of the t/a is located in the widest part of the Gremutchiy stream. The shape of the area which is isometric in plan (a circumferential structure 100 m in diameter) has been largely formed due to activity of geothermal processes and intensive erosion of argillized sediments on the banks of the valley. The area features a majority of gas-vapour jets including the most powerful ones comparable to those of the Verkhne-Koshelevsky t/a. The gas-vapour jets trace the stream bed and also come out along all thermal small uplifts and on the slopes of the erosion craters. In the upper part of the area below the cluster of the gas-vapour jets confined to the Gremutchiy stream (See Figure 2), there was formed a boiling water pot with a flat bottom 2 m in diameter and several small pots around it among bulks of stones. The temperature of water in different years was 85-90 ^oC, pH = 6.0 – 6.4, Eh = +250 - +295 mV. In fact, this pot gives rise to a thermal stream. There is a lake called Termalnoye (‘Thermal’) in a large erosion crater along the left bank of the Gremutchiy stream. Gas is discharged at the bottom of the lake; the water has a yellowish-grey colour due to abundance of suspended native and sulphate sulphur. Along the coast line, there are small (up to 1.0 m in diameter) boiling water pots with different physical-chemical parameters (up to contrast ones): temperature is 67 - 94 ^oC, pH = 1.7 – 6.2, Eh = +92 - +256 mV. A round 3-meter deep crater 7-8 m in diameter was formed in the lower part of the stream bed. The water is vigorously boiling in the centre and in different parts of the crater, the temperature was stable in different years (82-84 ^oC), pH = 5.5 – 6.2, Eh = +85 - +235 mV. The western part of the main thermal field is marked by presence of three large pulsating water springs located in the bed of the Gremutchiy stream. The pulsating middle spring has a lower pH (from 3.5 to 5.3 in different years).The springs were formed owing to outflows of powerful gas-vapour jets in the stream bed. A 25 x 30 m lake spreads out at the western boundary of the Gremutchiy stream t/a; it is boiling all over the surface.

4.3 Some Other Thermal Springs Of The Koshelevsk Volcanic Massif

A spring called Promezhutochny (‘Intermediate’) is located in the lower end of the Priamoi (‘Straight’) stream valley on the right bank (See Figure 2, inset). The water temperature is 18 -20 ^oC, pH = 7.9, Eh = +37 mV. The spring forms a short stream with a discharge rate of 12-15 l/s emptying into the Priamoi stream. Skazka springs (‘Fairy Tale’) flow out onto the surface on the left bank of the Gremutchiy stream 3 km below the Nizhne-Koshelevsky thermal anomaly. The springs include some outflows with a discharge rate of 1.0 l/s, the water temperature does not exceed a value of 23 ^oC, pH = 6.1, Eh = +49 mV (as of August 2009). Previously unknown hydrothermal springs were discovered in the middle current of Priamoi stream on its left bank at an absolute elevation of 675 m. Thermal waters are discharged thus forming chains of local outflows stretching along one relief isometric line and trace the footing of andesidacite lava flow. Physical-chemical parameters of the waters have gradually changed in the monitoring period since 2006. At the turn of 2008-2009, the temperature drastically dropped (by 20 ^oC) and water mineralization dropped as well. Hydrothermal outlets cause to form travertine deposits consisting of calcite and aragonite which reflects a hydrocarbonate composition of water.

5. CHEMICAL COMPOSITION OF THERMAL WATERS

Chemical composition of thermal and other natural waters is shown in Figure 3 and Figure 4. The cations of mud-water pots in the Verkhne-Koshelevsky t/a propagate in the sector stretching along the axis (Ca+Mg) - NH_4 (See Figure 3), the content of NH_4 is significantly higher than Na and K. However, some points are prone to waters of a mixed Ca-NH_4 composition.

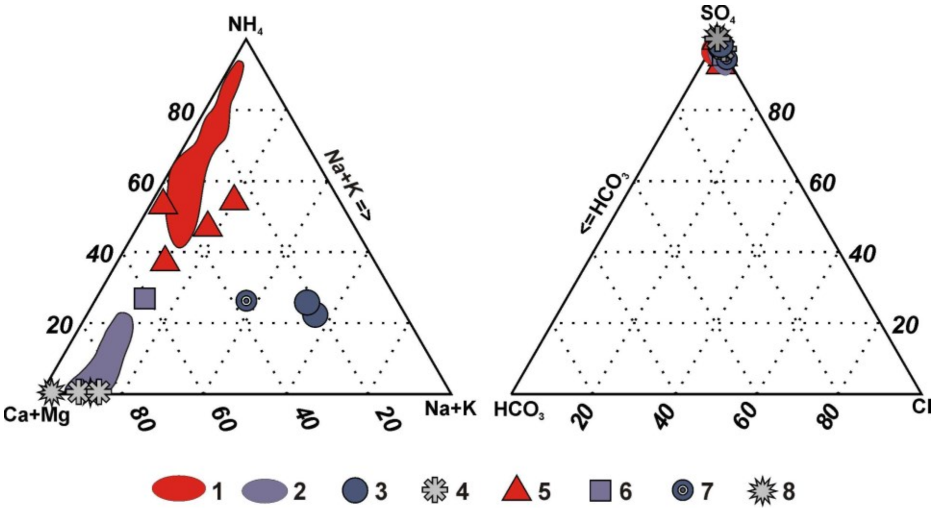

Figure 3: Chemical composition of thermal and other natural waters in the Verkhne-Koshelevsky t/a. (1) mud-water pots, (2) the Vostochny stream, (3) thermal springs, (4) background waters, (5) mud-water pots (from Vakin et al., 1976), (6) the Vostochny stream (from Vakin et al., 1976), (7) thermal springs (from Vakin et al., 1976), (8) background waters (from Vakin et al., 1976).

The prevalence of sodium and potassium ions is observed only in the waters of thermal springs which give rise to the Khaltsedonovy stream (See Figure 3). High concentrations of Al^{+3} (over 120 mg/l) were detected in the two drainless pots. High contents of dissolved H_3BO_3 are typical for mud-water pots. The maximum concentration of H_3BO_3 (966 mg/l) was recorded at the Polygon area. The waters of the Vostochny stream do not change the composition as they pass the Tartarari area and belong to Ca-Mg type where Mg^{2+} has a subordinate significance. Numerous gas-vapour jets the discharge directly in the stream channel do not contribute considerably to the water composition. Background waters typical for the stream heads are also present in Ca-Mg sector of waters without presence of ammonium ions. All waters of the Verkhne-Koshelevsky t/a in the anion part are in the sector of sulphate waters and run into one point. A comparative analysis against the acquired data with findings of the previous studies (Vakin et al., 1976) has demonstrated that the macro component composition of natural waters in the Verkhne-Koshelevsky t/a practically has not been changing in the last 40 years. Distribution and concentration of micro elements in the thermal waters is governed by distribution of certain macro components, pH values, mineralization and an extent of interaction of the waters with host rocks. For instance, the maximum values of some certain micro components have been detected in the drainless mud-water pots. Mainly, these are the elements which belong in the iron group (Ti, V, Cr, Mn, Co, Ni), and Zn, P, rare alkalis. A different environment is characteristic of the thermal waters of the Nizhne-Koshelevsky thermal anomaly (See Figure 4). Among anions, the sulphate ion is prevalent (up to 1.3 g/l). Among the waters of the Bannoye lake spring, the hydrocarbonate ion is prevalent. Chlorine is present in all the thermal manifestations in an amount of 1-4 mg/l. Fluorine has been found only in two springs in the Zapadny area. Cation composition of thermal waters is uniform. The waters are of ammonia or ammonia-calcium type. The waters of the Bannoye lake spring where Na^{+} is prevalent are excluded. The maximum mineralization of the Nizhne-Koshelevsky thermal

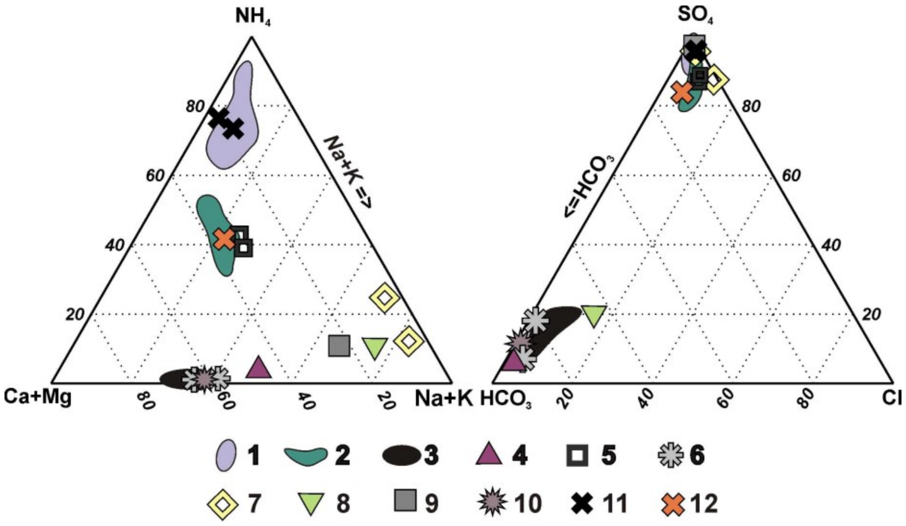

Figure 4: Chemical composition of thermal and other natural waters in the Nizhne-Koshelevsky t/a. (1) mud-water pots, (2) thermal lakes, (3) the Priamoi stream thermal sptings, (4) the Bannoye lake thermal spring, (5) the Gremutchiy stream, (6) background waters, (7) mud-water pots (from Vakin et al., 1976), (8) the Bannoye lake thermal spring (from Vakin et al., 1976), (9) the Gremutchiy stream (from Vakin et al., 1976), (10) background waters (from Vakin et al., 1976), (11) mud-water pots (from Serezhnikov, 1976), (12) thermal lake (from Serezhnikov, 1976).

anomaly is 2.2g/l. The chemical composition of the Gremutchiy stream waters, as they pass the thermal field, goes through significant changes. Before the discharge, the waters fall into the hydrocarbonate type with a mineralization of 0.1 g/l, near-neutral pH and a temperature of 10 ^{o}C. When they outflow at the thermal field they conform to the ammonia-calcium type with a low-acid reaction (pH = 5.2), a temperature of 85 ^{o}C and a general mineralization of 0.2 g/l which is mostly typical for surface outflows. Concentrations of micro elements in the thermal waters of the Nizhne-Koshelevsky thermal anomaly are averagely low. Chemical composition of the springs that discharge beyond the limits of the Nizhne-Koshelevsky falls into the hydrocarbonate calcium-sodium type with a mineralization of 200-300 mg/l. The anion part features a low-concentration presence of Cl^- and SO_4^{2-}.

6. EFFECTS OF FORMATION CONDITIONS ON THE CHEMICAL COMPOSITION OF THERMAL WATERS

Despite the fact that the hydrothermal vapours of the Koshelevsky massif has been in focus of scientists for a long time, the question about the origin of the main components included in the chemical composition has not been resolved. All the researchers share an opinion that NH_4, CO_2, H_2S, H_3BO_3, Cl and some other micro components are of a deep-seated, probably mantle origin (Vakin et al., 1976; Pozdeev Nazhalova, 2008; Serezhnikov, 1977): the components come to the hydrothermal system as a part of a magmatic fluid. However, studies by many authors have demonstrated that host rocks may have acted as the main source of matter transported by hydrothermal vapours to the daylight surface (Shvets, 1973; Eliss, 1975; Pampura, 1985). To estimate hydrogeochemical formation conditions of hydrothermal vapours of the Koshelevsky massif we have performed a comparative geochemical analysis of the waters. The previous findings (Serezhnikov, 1977; Vakin et al., 1976) and our data demonstrate that sulphur compounds, ammonia ions and dissolved boric acid are dominating in thermal waters. Figure 5 shows ratios of NH_4

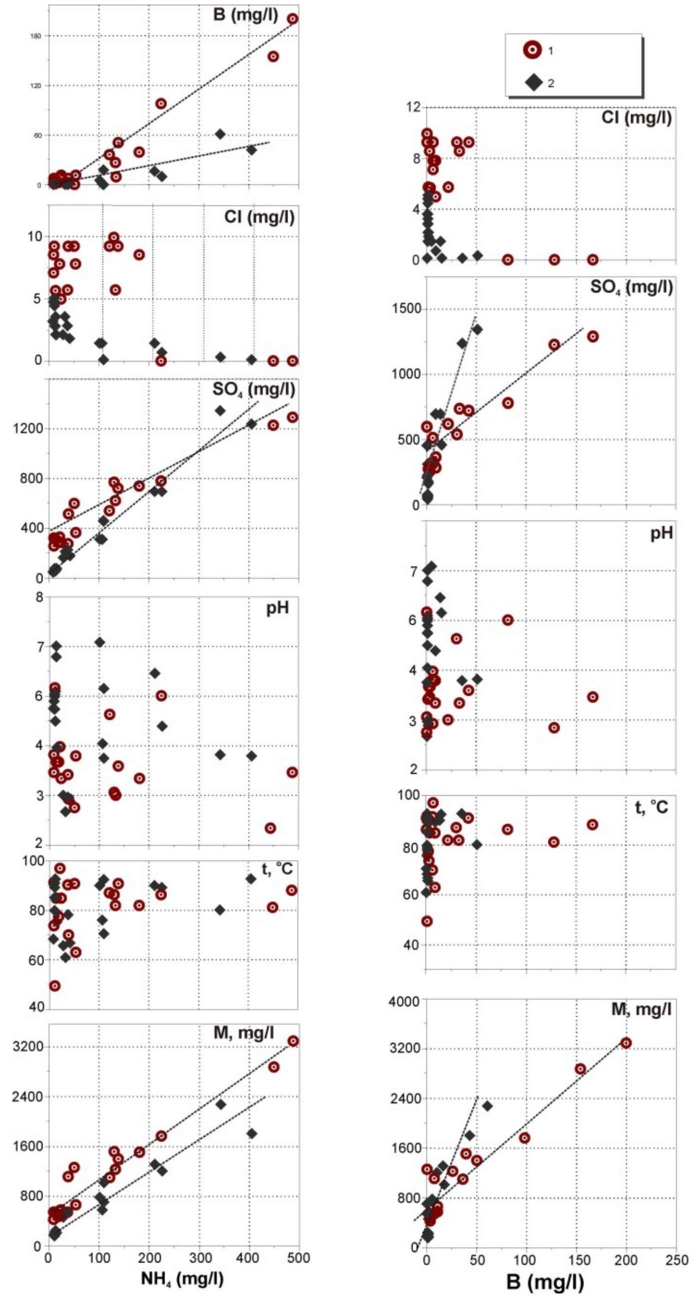

Figure 5. Ratios of NH_4 and B with respect to each other, to anions and physical-chemical parameters in thermal waters. (1) Verkhne-Koshelevsky t/a, (2) Nizhne-Koshelevsky.

and H_3BO_3 concentrations in terms of B with respect to each other, to anions and physical-chemical parameters. The comparative geochemical analysis of Verkhne- and Nizhne-Koshelevsky hydrothermal vapours has revealed high correlation dependence between ammonia and boron ions in the thermal waters, which is indicative of their common formation conditions. NH_4 and B are also closely connected with SO_4 and water mineralization which is consistent because the concentrations of these components comprise the most part of the total amount of the matter dissolved in the water. Cl/B ratio is usually used for estimation of hydrogeochemical formation conditions of thermal waters. As for the Verkhne-and Nizhne-Koshelevsky t/a, a wide range of values is typical which reflects a change in concentration of B while Cl-ion contents are steadily low. No direct dependence between these components has been established, quantity of Cl-ions in the points with maximum values of H_3BO_3 in terms of boron is below the limit of detection. As demonstrated in works (Ellis, 1975; Ellis, Mahon, 1977), low ratios of Cl/B, caused by high concentrations of B, are typical for thermal waters of sedimentary rocks enriched with organic matter, ammonia and carbon dioxide. The study of isotope composition of boron in hydrothermal fluids of the Ngawha geothermal deposit (New Zealand) demonstrated that high concentrations of B are a result of interaction of underground waters with the enclosing greywacke-argillaceous stratum (Aggarwal et al., 2003).

Sedimentary rocks in the region of the Nizhne-Koshelevsky t/a have not been penetrated, probably due to an insufficient depth of wells. However, the basement of the Koshelevsky volcanic massif has been penetrated at a depth of 1 km on the coast of the Okhotsk Sea. The basement is composed of greatly altered volcano-terrigenous sandstones of the Berezovskaya formation of middle-Miocene age (Figure 6) with a rich variety of organic remains and presence of bitumen. Also, significant contents of

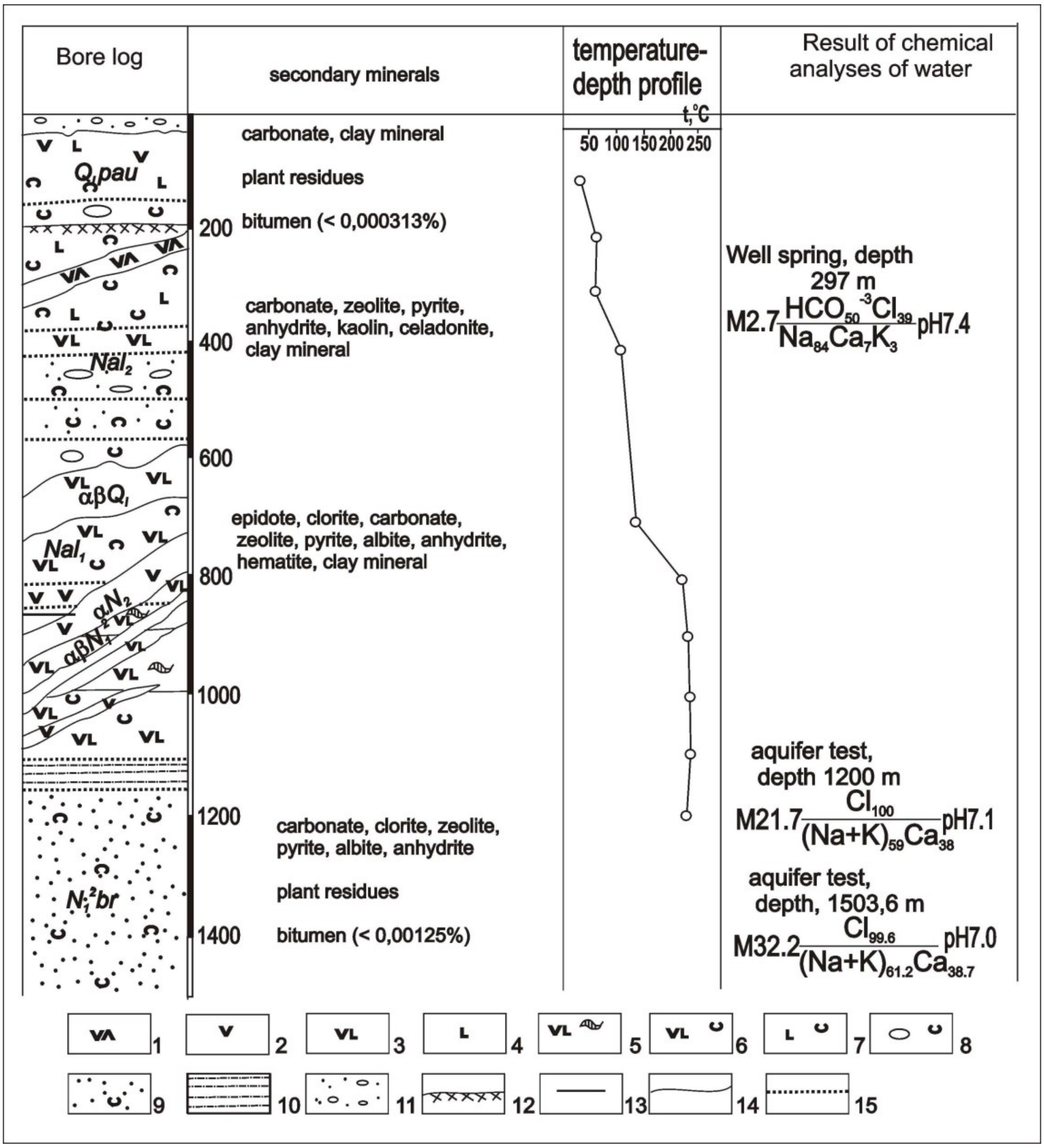

Figure 6: Well data on the coast of the Okhotsk Sea. (1) dacitic andesite; (2) andesite; (3) basaltic andesite; (4) basalt and dolerite; (5) lava breccia; (6) basaltic andesite tuff; (7) basaltic tuff; (8) tuffconglomerate; (9) volcanosedimentary sandstone; (10) volcanosedimentary siltstone; (11) loose sediments; (12) residual soil; (13) producing zone; (14) multiple-aged deposits boundary; (15) facies species boundary. Rock age: (*$Q_I$pau*) Payzhetskay suite; (*Nal_2*) Alneiskaya series, middle segment; (*Nal_1*) Alneiskaya series, bottom; (*N_1^2br*) Berezovskaya formation; (*abN_1^2*) buried igneous intrusion and dykes of middle-Miocene age; (*aN_2*) dykes of Pliocene; (*abQ_I*) dyke of bottom-Pleistocene.

naphthenic acids in the thermal waters of the Nizhne-Koshelevsky t/a and in condensate from the wells indicate the presence of petroleum products at depth. The underground waters that circulate in Neogene sediments pertain to superheated chloride sodium brines (See Figure 6). Experiments showed that at a temperature of 200 ^{o}C waters of chloride-sodium composition actively extract organics from sedimentary rocks, first of all, nitrogen-containing substances, neutral resins and naphthenic acids (Shvets, 1973). Perhaps, due to thermal decomposition of organic remains, ammonia is released from the rocks and liquates in the form of ammonia ions. The emergence of boric acid in hydrothermal fluids may be related to the presence of petroleum products in these rocks. Boron can be additionally sourced from anhydrite which occurs extensively in the sediments of the Berezovskaya formation. It is known that anhydrite contained in sedimentary rocks is usually characterized by a high content of water-soluble boron (Ozol, 1983). Therefore, active leaching of anhydrite from volcanogenic-sedimentary rocks of the Berezovskaya formation in the zone of deep circulation of hydrothermal fluids will cause the transition of boron compounds from the mineral forms to the water-soluble ones.

In the last decade, geochemistry data on rare earth elements (REE) have been extensively used for determination of processes causing the origin and evolution of natural waters including thermal ones. Figures 7 and 8 display the profiles of REE concentration distribution in the vapour-dominated hydrothermal fluids of the Koshelevsky massif with respect to North American shale rock. The highest positions of profiles in the chart are typical for the thermal waters of the Verkhne-Koshelevsky t/a (see Figure 7), whereas the lowest ones are typical for the thermal waters that are discharged downstream the Nizhne-Koshelevsky t/a (see Figure 8). All types of the Verkhne-Koshelevsky t/a waters are enriched with heavy REE with general depletion of light REE, the profiles are flattened. The REE distribution profiles for various types of the Nizhne-Koshelevsky thermal anomaly waters differ from one another: it is characteristic for the waters of drainless mud-water pots with low pH values that values of REE grow from the light ones to the heavy ones, as for the waters of the Gremutchiy stream and boiling pots it is characteristic to have a practically even distribution of values with a small positive Eu-anomaly. A similar profile has been also determined for the thermal waters discharging beyond the limits of the Nizhne-Koshelevsky t/a. The positive Eu-anomaly in the water is mainly a sequence of the presence of mineral phases in hydrophilic rocks enriched with this element or indicates a more reducing environment for the formation of these waters (Chelnokov, Kharitonova, 2008).

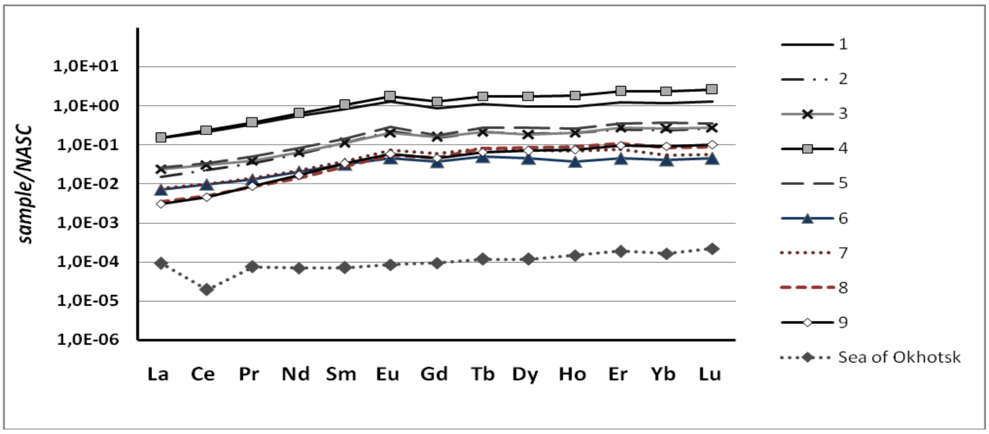

Figure 7: The profiles of REE concentrations distribution in the waters of the Verkhne-Koshelevsky t/a. (1-5) mud-water pots, (6) thermal spring, (7-8) the Vostochny stream, (9) background waters.

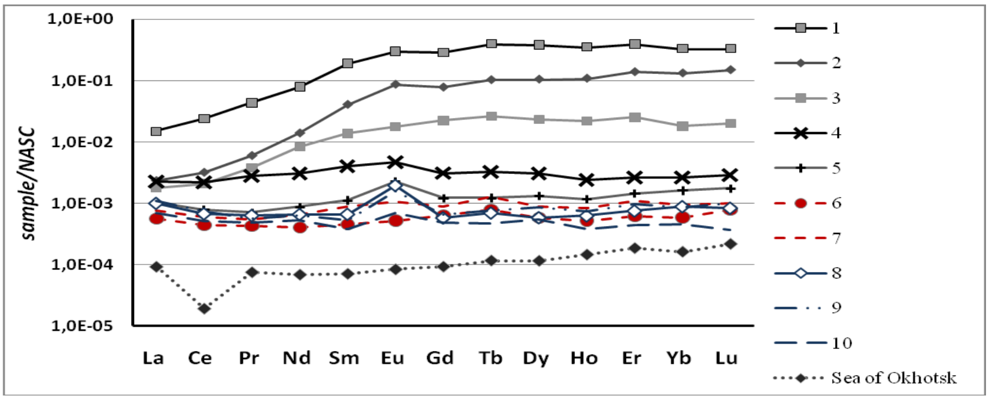

Figure 8: The profiles of REE concentrations distribution in the waters of the Hizhne-Koshelevsky t/a. (1-5) mud-water pots, (6-7) the Gremutchiy stream, (8-10) the other thermal springs.

To study the origin of the thermal waters we have also analysed an isotope composition of strontium. The spread in values of $^{87}Sr/^{86}Sr$ ratios in the thermal waters of the Verkhne- and Nizhne-Koshelevsky t/a is on the average of 0.7032-0.7034. Higher values have been recorded in one of the boiling pots of the Termalnoye Lake and in the springs which give rise to the Khaltsedonovy stream (Figure 9). A low ratio of strontium isotopes is typical for gas-vapour condensate and host rocks. The value of $^{87}Sr/^{86}Sr$ for non-altered andesibasalts is 0.7030, and 0.7032 for dacites. According to paper (*Structura*…, 1993), thermal manifestations with low values of strontium isotope ratios being close to those in the parental rocks reflect a level of deep-seated (to several kilometres) circulation of hydrothermal fluids where strontium is actively leached from host rocks to form the isotope composition of hydrothermal fluids. The waters of the Gremutchiy stream upstream of the thermal anomaly and snow waters that feed it are characterized with higher strontium isotope ratios being close to the seawater ones. It was demonstrated earlier that the snow and melt waters of the Pauzhetka volcano-tectonic depression are contaminated with Sr with a “sea” isotope ratio (0.7095-0.7093) on account of impact from the nearby marine area (Pampura, 1985). High $^{87}Sr/^{86}Sr$ values found in some springs on the thermal fields are explained by intensive mixing of these waters with cold meteoric waters.

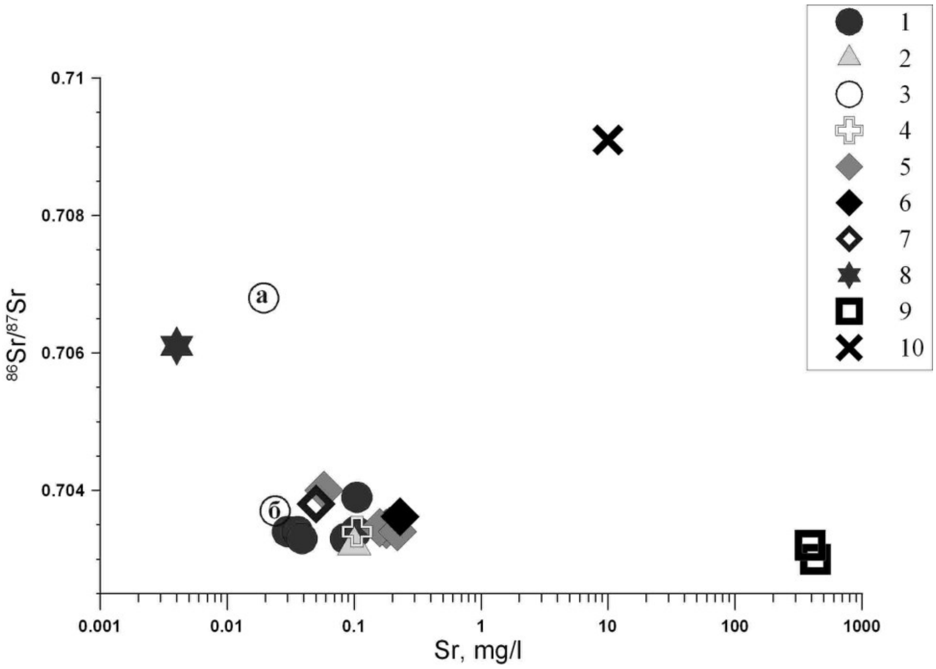

Figure 9: $^{87}Sr/^{86}Sr$ ratios in the thermal waters. Hizhne-Koshelevsky t/a: (1) mud-water pots, (2) steam condensate from well, (3) the Gremutchiy stream: in front of the thermal field (a) outside of the thermal field, (4)) the Priamoi stream thermal sptings; Verkhne-Koshelevsky t/a: (5) mud-water pots, (6) the Vostochny stream, (7) the Shymnaya river, (8) snow, (9) country rocks, (10) Sea of Okhotsk.

7. CONCLUSION

The waters being discharged within thermal anomalies have a temperature of up to 98 ^{o}C and are referred to as acid or low acid (pH=3-5.8) sulphate, less often to hydrocarbonate-sulphate ammonium or Ca(Na)-ammonium ones with an elevated content of silicic acid (95-175 mg/l). The total mineral content averagely amounts to 0.6-0.8 g/l and can reach an amount of 2.5 g/l (in water-mud pots). The gas content is dominated by CO_2, which is typical for many other Kamchatka's and world systems, H_2S, CH_4, N_2 are always present. Verkhne (Upper)-Koshelevsky hydrothermal vapours have a higher content of sulphur gases whereas the Nizhne (Lower)-Koshelevsky ones have an elevated content of methane (up to 67% in some drill holes), nitrogen (up to 50%), and presence of a variety of heavy hydrocarbons and presence of oil in vapour condensate. Previously, a viewpoint prevailed that the hydrothermal vapours of the Koshelevsky deposit were formed under impact of deep-seated (magma-penetrating or mantle ones) fluids which was confirmed by geodynamic, geological-structural and isotope-geochemical data. Most likely, this hypothesis is relevant and a deep (a mantle one ?) fluid influences the geothermal systems of the Koshelevsky massif. At the same time we focus on the fact that the formation of the composition of hydrothermal vapours may be connected with the Neogene volcanogenic-sedimentary rocks comprising the massif basement. The rocks contain a large amount of organic remains with an observed presence of petroleum products. Probably, thermal decomposition of the organic matter under high P-T parameters of the environment causes a release of methane, ammonium and boric acid and transition of these components to the solution and to the gaseous state. We estimate that the level of thermal waters in this region may occur at an approximate depth of 2 km below the surface of the Sea of Okhotsk. The formation of a solution boiling zone is accompanied by a release of CO_2 in the steam phase, other volatiles, including hydrocarbons, boric and naphthenic acid. A gas-vapour mixture ascends to the earth surface without significant heat losses: a temperature decrease probably takes place only due to adiabatic expansion and therefore the temperature of vapour at the thermal fields reaches 120-150 ^{o}C. Such conditions foster the formation of thick zones of superheated vapour which are apparently confined to the apical parts of subvolcanic intrusions of base and medium composition. The waters that discharge beyond the limits of the thermal anomalies and along the periphery of the Koshelevsky volcanic massif pertain to hydrocarbonate calcium-sodium weakly mineralized ones. They form a zone of lateral spread, which, apparently, characterizes the one whole Koshelevsky hydrothermal system.

8. ACKNOWLEDGEMENTS

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