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Geochemistry of Thermal Waters of Pauzhetsky-Kambalny-koshelevsky Geothermal Area (Southern Kamchatka, Russia)

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ABSTRACT

The Pauzhetsky-Kambalny-Koshelev geothermal area is one of the largest areas of Kamchatka, characterized by intensive and diverse hydrothermal activity. The hydrothermal activity takes place on the surface in the form of boiling and hot springs (Pauzhetsky, Ozernovsky, Sivuchinsky, etc.). Numerous streams of steam and gas and thermal springs ("hydrosolfataras") connected with them are confined to slopes of the Kambalny ridge and Koshelev volcano. The investigated area has drawn attention of researchers for a long time. The area was most studied in the second half of the XX-th century during complex geological, geophysical, and hydrogeological studies of the Pauzhetsky hydrothermal deposit. Since 1967 on the basis of the deposit the Pauzhetsky geothermal power plant with an installed capacity of 11 MW_e has been operated. Rated operational reserves of the Nizhne-Koshelev geothermal deposit are 90 MW_e. As a result of authors' field works in 2005-2008, the new data on geochemistry of thermal waters were obtained. Three basic geochemical groups of thermal waters were identified. They differ by physical and chemical parameters and have various conditions of formation. Acidic thermal waters (pH = 2.1-5) with high content of NH_4, with a temperature of 68-98°C and total mineralization of 1 g/l are discharged on the volcanoes. In the valley of the Pauzhetka river neutral (pH = 7.2-7.4) sulphatic waters with a temperature of 75-80°C and total mineralization of 1-1.5 g/l are discharged. Deep-seated alkaline (pH = 8) chloride-sodium hydrothermae with a temperature of 92-96°C and mineralization of 3-3.4 g/l are detected by wells. The implemented thermodynamic simulation has allowed estimating the degree of saturation of thermal waters of geothermal area in relation to various minerals.

1. INTRODUCTION

The Pauzhetsky-Kambalny-Koshelev geothermal area is one of the largest ones on Kamchatka and is characterized by active and long-lived (from the lower-quaternary up to now) volcanic and hydrothermal activity (Belousov, 1978; Rychagov et al., 2006). A lot of papers were devoted to studies of the area most of which were written in the second half of the XX century. This article deals with new data on composition of thermal waters both from natural springs and from wells drilled during exploration and exploitation at Pauzhetsky and Lower-Koshelev geothermal deposits and Ozernovsky geothermal area. Water samples were taken in July-August 2005-2008. pH, Eh, total mineralization and temperatures of solutions were measured *in situ* by means of a portable multi-mode analyzer WATER TEST. A total chemical analysis including detection of the ions NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, F^-, SO_4^{2-}, H_3BO_3, H_4SiO_4, was made in Analytical Center of Institute of Volcanology and Seismology of FEB RAS using potentiometric, volumetric, colorimetric and atomic-absorption methods. The analysis of micro element composition was made in Analytical Center of Vinogradov Institute of Geochemistry of SB RAS by inductively coupled plasma mass spectrometry (ICP-MS) using Plasma Quad instrument.

2. GEOLOGICAL-HYDROGEOLOGICAL DESCRIPTION OF THE AREA UNDER STUDY

The geothermal area is located within the previously identified Pauzhetsky long-lived volcanic (volcanogenic ore) center of the southern end of the Kamchatka peninsula (Dolgozhivushiy…, 1980). The geological structure is an accumulative tectonic dome with an area of more than 1600 км^2 with volcanic-tectonic depression 20 x 25 km in size in the center. It is dominated by lavas, tuffs and intrusive rocks of intermediate to acid composition from the Miocene-Pliocene to the Holocene in age (Litasov et al., 1974). Quaternary volcanic activity is connected with resurgent tectonomagmatic uplifting of the Kambalny ridge and the evolution of the complex Koshelev massif. Koshelev and Kambalny volcanoes are active. Present-day high temperature hydrothermae are confined to the Koshelev volcanic massif (Lower – and Upper-Koshelev thermal anomalies) and the Kambalny ridge (a number of thermal fields from North- to South-Kambalny is localized along the axial zone of the ridge). Pauzhetsky hot springs and the first in USSR exploited Pauzhetsky high-temperature geothermal deposit are located on the northern slope of the Kambalny ridge **(Figure 1)**. Low-temperature hydrothermal waters are discharged in some areas in the valleys of the Ozernaya River (Perviye Goriachiye Kluchi ("First Hot Springs")) and the Shumnaya River, and in the eastern end of the geothermal area (Tyoplaya ("Warm") Bay of the Kuril Lake, etc.).

Thermal fields of the Kambalny volcanic ridge are located from 700 to 1,000 meters above sea level. Each thermal manifestation is localized in a separate geological feature such as a volcanic crater or erosion funnel 500-800 meters in diameter (Structure…, 1993). Outlets of gas-vapor jets and thermal springs are confined to psephitic andesite and andesidacite tuffs of Pliocene-Pleistocene age and probably associated with a single temperature-controlling zone of the north-west strike (Belousov, 1978). It is assumed that peripheral magmatic chambers of Kambalny volcano, cooling subintrusive bodies and small gabbro-diorite intrusions are the sources of heat.

Hydrothermae of the Koshelev volcanic massif are discharged on the day surface within the limits of two thermal anomalies. The Upper-Koshelev thermal anomaly is confined to extrusive-subvolcanic complex of Pleistocene-Holocene age from intermediate to acid

composition and is located in an erosion crater around 1.5 km in diameter at a height of 1,250-1,300 m above sea level. The Lower-Koshelev thermal anomaly is located in a deeply-cut canyon of the Gremuchiy Creek ("Rattling") 750-850 meters above sea level at the external slope of the old somma within the lower-quaternary Tretya Rechka Volcano ("Third River" Volcano) (Vakin et al., 1976). The thermal anomaly is a set of geothermal heat discharge activities in the form of gas-vapor jets, water and water-mud pots, pulsating springs ("geysers") and steaming soils on an area of 250 x 500 m. Natural heat efflux is estimated to be 50,000 kcal/sec for the Upper-Koshelev and 25,000 kcal/sec for the Lower-Koshelev thermal anomaly (Vakin et al., 1976). The thermal anomalies are topped by thick overheated steam zones occurring to a depth of more than 2 km (the zone was established based on drilling data on the Lower-Koshelev geothermal deposit (Pisareva, 1987)) and, probably, are hydrodynamically connected within the single Koshelev hydrothermal-magmatic system (Rychagov, Nuzhdayev, 2009).

The Pauzhetsky hydrothermal deposit was identified in the central part of a hydrothermal-magmatic system of the same name confined to the north-west slope of the Kambalny volcanic ridge. The deposit includes two water-bearing horizons: the lower one is composed of agglomerate tuffs (tuff-breccias) andesibasalts of Lower-Neogene age; the upper one is composed of coarse-grained and psephitic andesidacite tuffs of the Upper-Neogene – Lower-Quaternary age. Ascending fluxes of steam-water fluids and steam zones are confined to uplifted blocks of rocks and to their boundaries (Structure…, 1993). Above ascending fluxes of fluids and steam zones the following thermal fields are formed on the day surface: Upper-, East-, Lower- and South-Pauzhetsky. Discharge of Ozernovsky springs and hot springs in the valley of the Shumnaya River ("Noisy") occurs around the extrusive-subvolcanic complex of the Kluchevskaya mountain, apparently, at the contact of tuffaceous siltstones of the early-Quaternary age (the Lower-Pauzhetsky subsuite) with underlying massive and compact ignimbrites acting as the upper water-tight stratum for the lower water-bearing horizon within the structure of the Pauzhetsky hydrothermal system (Structure…, 1993).

3. RESULTS OF RESEARCHES

Field works were focused on studies of the thermal fields of the Kambalny ridge, Lower- and Upper-Koshelev hydrothermae, Ozernovsky springs, thermal fields and wells of the Pauzhetsky deposit. The results of the complete chemical analysis are as follows. Thermal waters discharged within solfataric fields of the Kambalny ridge **(Figure 2)** are acid or low acid ones (pH = 2.1-5.8) of $Ca(NH_4)$-Mg-SO_4 type with a temperature of 68-98°C. Total mineralization rarely exceeds 1g/l (only in mud pots), and, averages within 0.6-0.8 g/l. Thermal waters of the Lower-Koshelev field have different composition and distinctly fall into two groups: sulfate and hydrocarbonate waters (Figure 2). Hydrocarbonate waters are condensate of vapor-gas jets with pH 6 and a low total mineralization of 0.3-0.4 g/l. As for cations Ca^{2+} prevails. Waters of low-yield mud pots (T = 90-96°C) and thermal lakes (T = 60-70°C) are sulfate waters with pH values from 2.8 to 4.6. Cations are dominated by NH_4^+ which determines the type of these thermal waters – sulfate ammonium. Total mineralization of the waters amounts to 2-3 g/l because of higher concentrations of SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+. According to relevant publications (Vakin et al., 1976), gas composition is essentially carbon dioxide both for Upper-Koshelev and for Lower-Koshelev thermal anomalies. Gas-vapor mixture at the Lower-Koshelev thermal anomaly steadily contains methane (up to 14.3 volume %) and hydrogen sulfide (up to 9.1 volume %); hydrogen sulfide concentrations are elevated in Upper-Koshelev hydrothermal waters (up to 24.1 volume %), and a sum of acid gases may amount to 97.4 volume %. Based on data derived from drilling, vapor hydrothermae of the boiling zone of the Lower-Koshelev deposit at a depth of 1,200 m contain CH_4 up to 45.9 volume %, N_2 – up to 30.2 volume %, C_2H_6 – up to from 0.2 to 2.2 volume %, and other hydrocarbons (Pozdeev, Nazhalova, 2008).

Thermal waters channeled to the surface by the wells within the Pauzhetsky geothermal deposit are well studied and described by many researchers. They have chloride-sodium composition (Figure 2), a temperature of 92-98°C at the mouth, pH 7.6-8.2 and a total mineralization of 3-3.5 g/l. It is worth noting that during exploitation the surface thermal manifestations of the Pauzhetsky thermal anomaly have changed. Boiling springs and geysers described in the paper (Pauzhetskiye…., 1965), have disappeared, whereas boiling (T = 95°C) low-yield pools with water having chloride-hydrocarbonate sodium composition with a total mineralization of 0.5-0.7 g/l and pH 7.7-8.0 have emerged in the valley of the Bystriy Creek ("Rapid") on the Lower thermal field. Ozernovsky springs produce low-alkaline (pH 7.7-8.2) sulfate sodium-calcium waters with elevated content of Cl^- (Figure 2). A Total mineralization is 1.4-1.5 g/l. Gas composition includes methane and nitrogen (Sviatlovsky et al., 1956).

Concentration of micro components in thermal waters of the whole area varies in wide range. Among siderophile elements *Fe* has the highest concentration (0.5-4 мg/l); content of *Ni* and *Co* comprise the first tens, and *Mo* – the first unint of μg /l . In mud pots elevated concentrations of lithophilous elements are observed. Maximum content of *Al* (2.3 мg/l) was detected in the thermal manifestations of East-Pauzhetsky thermal field. Content of *Ba, Li, Rb, Cs, Ti, Cr, V* comprises tens of μg /l, and *Be, Zr* and *W* – less than one. Maximum values of *Li* (up to 10 мg/l) were detected only in thermal waters penetrated by drilling wells. Concentration of chalcophile elements in acid sulfate waters are subjected to minor variances. Contents of *Pb, As, Zn* and *Cu* constitute 5-35 μg/l. Hydrothermae of the fall into two groups by ratio of Li/Rb/Cs **(Figure 3a)**. One group includes Ozernovsky springs, waters from Pauzhetsky wells and the Lower-Pauzhetsky thermal field; the other includes water discharges of the Koshelev volcanic massif and the Kambalny ridge.

Probably, lithium domination in waters reflects a more deep-seated origin of hydrothermae. Isotope relations $^{86}Sr/^{87}Sr$ in all the types of waters are close to the values typical for enclosing rocks **(Figure 3b)**. Some thermal waters of the Kambalny ridge are exclusion since they have higher values of strontium isotope relations.

4. CONCLUSION

Hydrothermae under study fall into two large groups. Hydrothermae of Kambalny volcanic ridge and Koshelev massif belong to a special type of waters formed in the vadose zone of hydrothermal systems connected to active andesite volcanism. Depending on relief and local hydrogeological conditions on the surface they are manifested in the form of closed (i.e. without outflow) bubbling mud pots, pools, and hot springs. The cation part of waters is formed mainly due to interaction with enclosing rocks and due to efflux of some of elements by gas-vapor mixture from the interior. Concentrations of basic ions and a number of microelements are directly related to

pH and to a level of interaction with rocks. Closed mud pots discharge more minerals than springs. Such thermal manifestations are called hydrosolfataras (Naboko, 1959). Their main difference from acid fumarole hydrothermae is practically total absence of halogens (Cl, F) in water composition, a higher pH and low mineralization. At the same time, geochemistry data on strontium isotopes, relatively high concentrations of Au and other ore elements, their localization in geological features directly above peripheral magmatic chambers of, namely, Kambalny volcano (Sivorotkin, 1993), elevated content of carbon dioxide, methane and heavy hydrocarbons (the area of Lower-Koshelev deposit) witness in favor of the fact that vapor-hydrothermae of this group are influenced by deep-seated (probably, low crustal or mantle) components.

The second group is represented by vapor-hydrothermae of the lower water-bearing horizon (lateral flow) penetrated by wells at the Pauzhetsky geothermal deposit and discharged at the bottom of volcanic structures (Ozernovsky springs, Sivuchinsky springs in the vicinity of the Chetvertaya River ("Fourth") etc.). Apparently, of the same type are Pauzhetsky thermal field's springs as derivatives of thermal waters intersected by deep well.

One of the most important issues related to hydrogeochemistry and hydrodynamics of the Pauzhetsky-Kambalny-Koshelev geothermal area remains unclear: composition, formation conditions and mechanisms of interaction of thermal waters with rocks in the overheated steam boiling zones. Such zones play an important role in the structure of the Koshelev hydrothermal-magmatic system and, apparently, in the interior of the Kambalny ridge. based on mineralogical data, paleozones with a thickness of ≥ 300-500 m were identified in uplifted blocks of rocks of the Pauzhetsky deposit (Structure…, 1993). Study of these zones by means of a set of geological-geophysical, hydrogeological and geochemical methods will allow to comprehend in a greater detail mechanisms of formations of large high-temperature geothermal deposits and derive factual data for physical-chemical and quantitative hydrodynamic modeling of mixture processes for various types of waters and transport mechanisms of deep-seated metal-bearing fluid flux.

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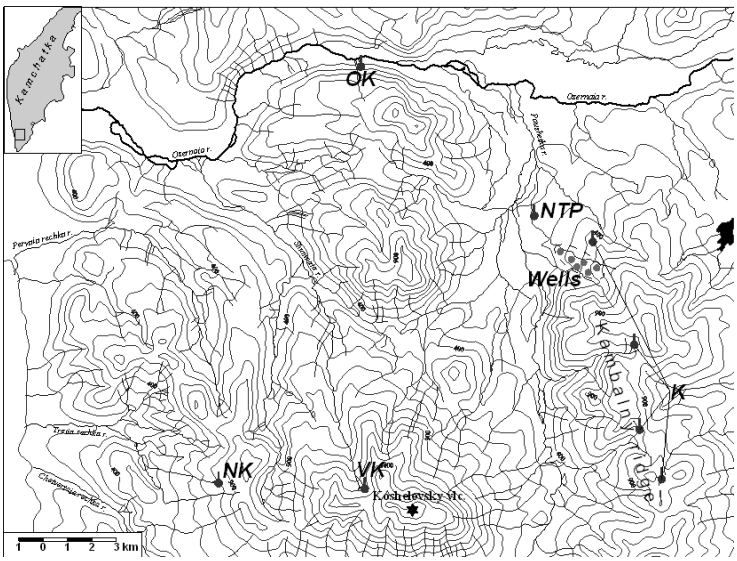


Figure 1: Plan of thermal fields in the Pauzhetsky-Kambalny-Koshelev geothermal area.

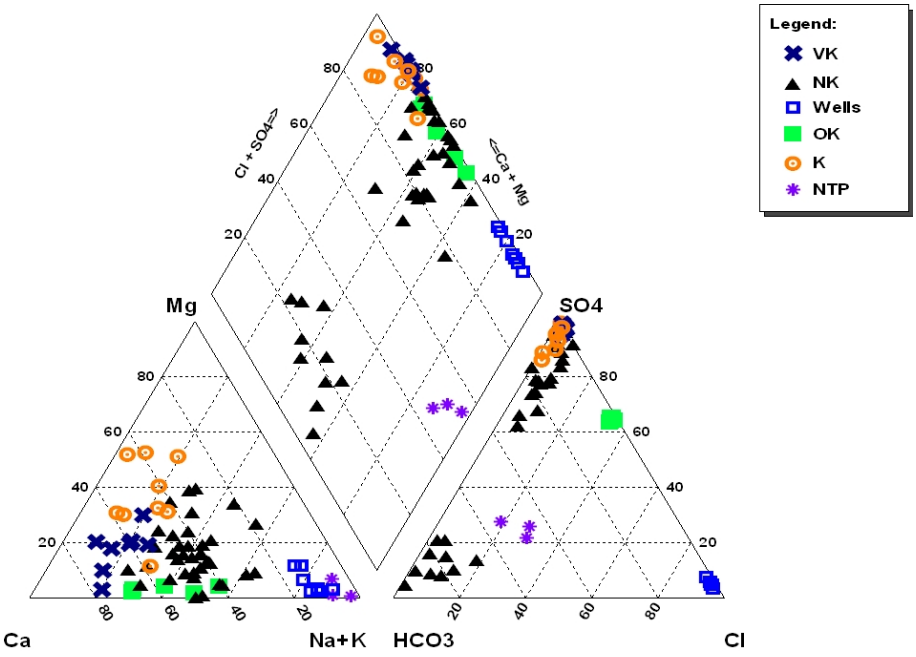


Figure 2: Chart of chemical composition of thermal waters in the area.

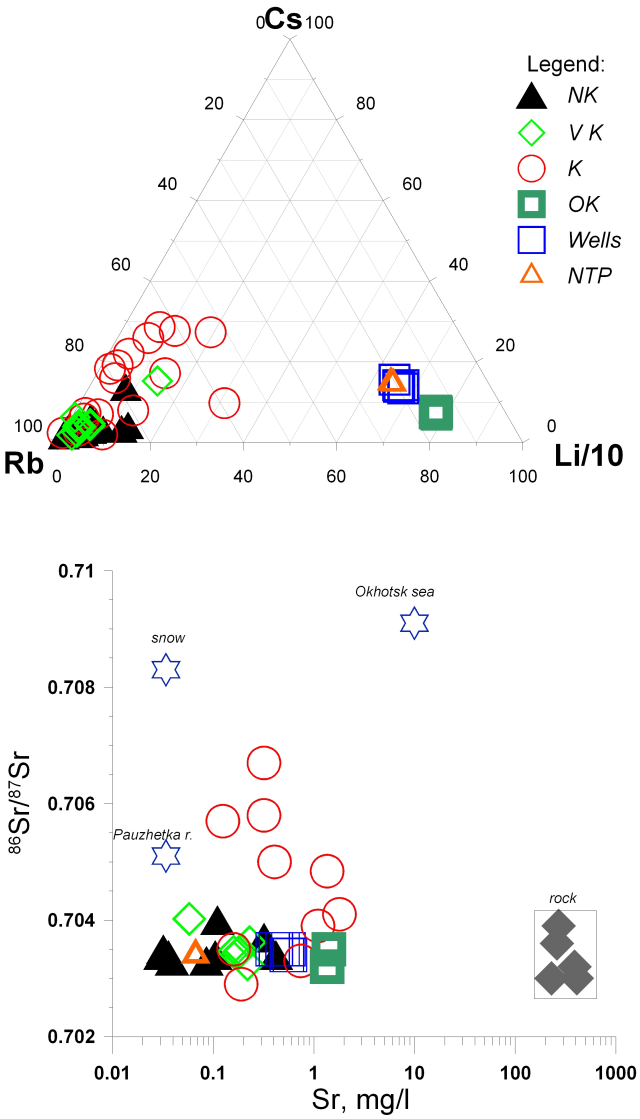


Figure 3: Ratio of micro components in thermal waters in the are: a – ratio Li/Rb/Cs; b – ratio of strontium isotopes and strontium concentrations.