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Hydrothermal Clays on the Surface of Thermal Anomalies as a Control Factor for Temperature and Geochemical Parameters of Geothermal Deposits (South Kamchatka)

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ABSTRACT

Studies were done at the Pauzhetskoye and the Nizhne-Koshelevsky geothermal deposits (South Kamchatka). Hydrothermal clays at the Verkhne-Pauzhetskoye thermal field and the Nizhne-Koshelevskoye thermal anomaly previously surveyed with a set of geological-geophysical and hydrogeothermal rules were sampled layer by layer by means of clearings, driving prospecting holes and manual core drilling. It is established that hydrothermal clays form a continuous stratum from 1.1 to 1.7 meters thick and from 0.015 to >> 0.125 km^2 in area. Chemical characteristics and mineral composition of clays and clay-derived gray sand are given. Grades of Au, Hg, Pb, Cu and other elements are defined for each layer of clay. Variances in element distribution both along the strike and in vertical cross-section of hydrothermal clay strata are shown. The variances are due to temperature, physical-chemical and hydrogeochemical conditions of clay formation in certain sections of thermal fields. One of the basic mineral-concentrators of ore elements in hydrothermal clays apart from sulfates of Ca, Fe, Mg, Ba and Al, and (probably) alumosilicates is pyrite. The paper briefly deals with characteristics of its morphological properties, formation conditions and composition. Differences in sorption properties of pyrite in relation to physical-chemical and temperature conditions of the geothermal environment are demonstrated. Thus, the stratum of hydrothermal clays occurring at the surface of thermal anomalies is established to be of significance as a rather thick independent geological body and is not only a water-confining and heat-insulating layer but also serves as a dynamically active temperature and geochemical barrier within the structure of a geothermal deposit.

1. INTRODUCTION

Formation of hydrothermal clays is associated with certain geological structures – hydrothermal-magmatic systems (Rychagov, 2005) and occurs both on the surface and in the interior of systems. Drilling of geothermal wells allowed us to distinguish zones of argillization of rocks down to depths ≥ 500 m, formed due to infiltration of acid mixed hydrothermal fluids flowing through discontinuous tectonic faulting and boundaries of blocks (Korobov et al., 1993). On the whole, the role of argillized rocks as indicators of temperature regimes and changes in physical-chemical parameters within a geothermal environment is demonstrated. However, due consideration was not given earlier to one of the most important aspects of clays: hydrothermal clays carry information on the dynamics of geochemical regimes within ore-forming hydrothermal-magmatic systems. We demonstrate that hydrothermal clays forming a continuous and on average 1.5-1.7 m thick layer on the surface of geothermal fields are not only the upper impermeable stratum and heat barrier for hydrothermal systems but also a dynamically active geochemical barrier for a number of metals and rare elements (Rychagov et al., 2007, 2008). This article summarizes the next stage of study of the near-surface horizon of hydrothermal clays to understand their significance for controlling parameters of geothermal deposits and for transport and ore element concentration processes in the hypergenesis zone.

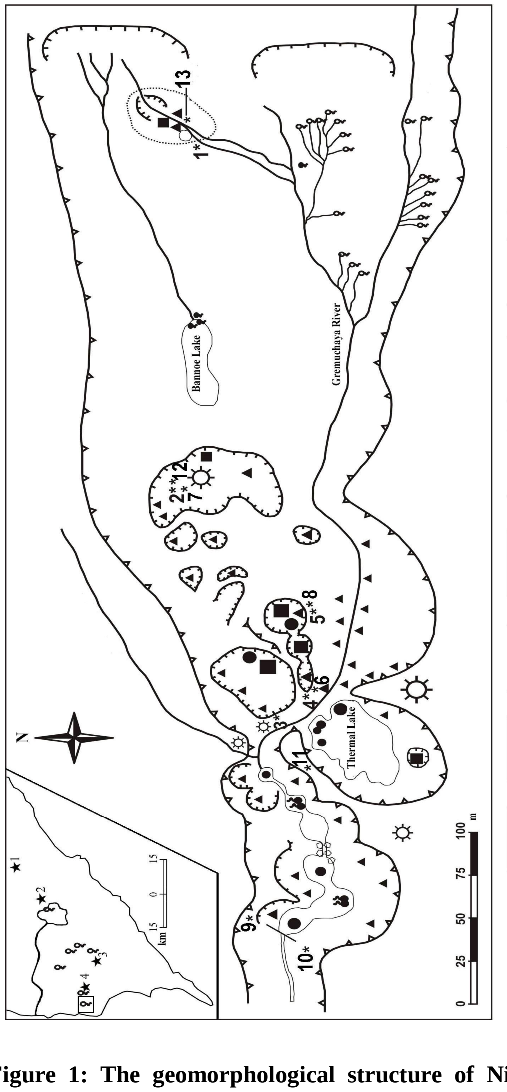


Figure 1: The geomorphological structure of Nizhne-Koshelevsky thermal anomaly. 1 – geomorphological boundary of thermal anomaly; 2 – internal geomorphological boundarys; 3 – local thermal structures; 4 – stone disorders; 5 – separate heights; 6 – boundarys of local thermal field (Verhnee); 7 – vapor-gas sources: a – gas jets, b – mud boilers, c – boiling lakes; 8 – water sources: a – large pulsing ("geisers"), b – thermal springs, c – cold springs

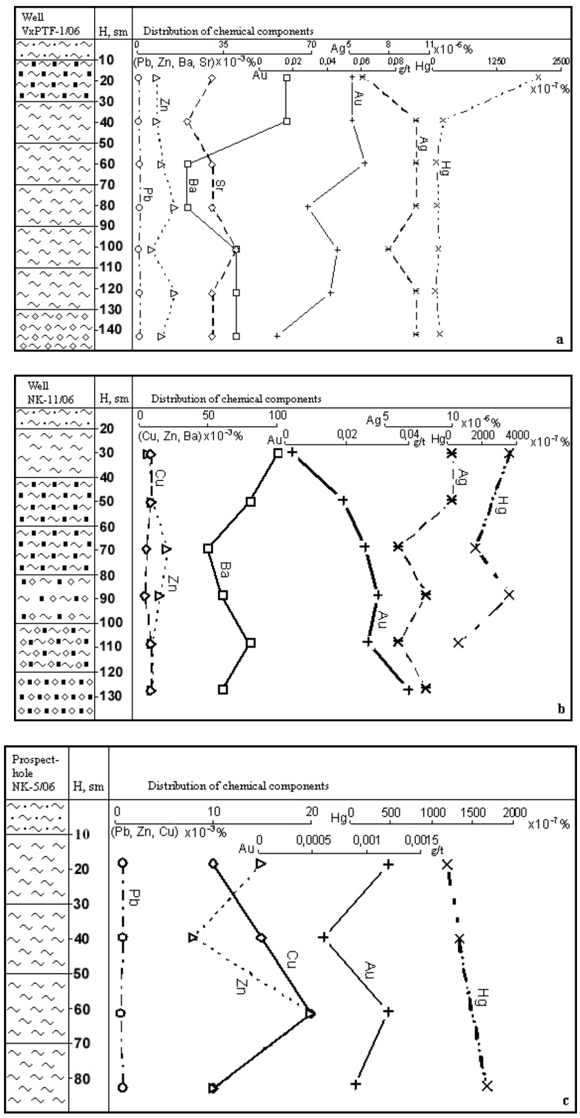
2. GENERAL DESCRIPTION OF HYDROTHERMAL CLAYS

Surveys were done directly at Verkhne(Upper)-Pauzhetsky and South-Kambalny Central thermal fields and at Nizhne(Lower)-Koshelevsky thermal anomaly **(Figure 1)**.

The geological setting of the surveyed district, its geothermal deposits and its thermal anomalies (thermal fields) was described in many papers (Belousov, 1978; Geologo-geofizicheskiy…, 1987) and presented in another report published in proceedings of WGC-2010 (Rychagov, Nuzhdayev, 2010). The general characteristics of the near-surface horizon of hydrothermal clays in Pauzhetsky-Kambalny-Koshelevsky geothermal district were described earlier, including details s of their occurrence, thickness of strata, chemical and mineralogical compositions, zonal sequence. Taken as a whole, the horizon consists of two zones: a sulfuric acid leaching zone at from 0 to 0.2 – 0.3 meters depth and carbon-dioxide leaching zone below 0.2 - 0.3 meters depth. Clays in the carbon-dioxide leaching zone are multicolored and are composed of the following minerals: dioctahedral smectite + kaolinite + pyrite + quartz (or other silica minerals) + native sulfur + jarosite + heulandite + invidual minerals that got in clays during destruction of the enclosing rocks (lavas and andesite tuffs). The zone of carbon-dioxide leaching constitutes the largest portion of the clay strata and is mainly composed of montmorillonite causing greenish-gray coloring of the strata. Other constituent minerals include pyrite, hematite, goethite (hydrogoethite), feldspar, magnetite, titanomagnetite, quartz, chlorite-smectites, and illite-smectites. As a rule, a layer of "blue clay" named so because of its high content of fine-grained disseminated pyrite is emplaced between such zones (Structure…, 1993). The "blue clay" was formed at the subaquatic thermodynamic barrier and is distinguished by relatively high concentrations of Au, Ag, Hg, and alkaline metals (Pampura, Khlebnikova, 1987). Its thickness usually does not exceed 15 - 20 centimeters in the strata of hydrothermal clays of the mature type (namely, Pauzhetsky; Structure…, 1993). When exploring sections of the near-surface horizon of hydrothermal clays through prospecting pits and core drilling wells at the thermal fields of Pauzhetsky deposit, Kambalny ridge and Koshelevsky volcanic massif we identified substantial variances in clay composition among these sites. The Nizhne(Lower)-Koshelevsky thermal anomaly is distinguished by the presence of contrasted physical-chemical conditions for the formation of clays and hydrothermae (fumaroles with temperatures up to 120 ^{0}C, mud pots and water pools, pulsating springs, steaming soils, cold areas, etc.). The thermal fields of Pauzhetsky deposit are made up of relatively homogenous and not large steaming sites with small mud-water springs and mud pots and with temperature of soils ranging from 20-25 to 98 ^{0}C on the surface. It is assumed that the thermal fields of Pauzhetsky deposit are older and their hydrothermal clays are more mature (Rychagov et al., 2007, 2008). Clays from the thermal fields of the Kambalny ridge, at large, can be referred to as the intermediary type both by age and by composition.

3. DETAILED DESCRIPTION OF SECTIONS OF HYDROTHERMAL CLAYS

The section of hydrothermal clays at the Verkhne(Upper)-Pauzhetsky thermal field is characterized by classic zonal structure. The upper layer (0 - 15 cm) is made up of a kaolinite + limonite + smectites + sulfur + barite + Fe-Al-Mg-Ca-sulfates association and corresponds to a sulfuric acid leaching zone. "Blue clay" is formed within an interval of 15 - 30 cm from the surface, whereas deeper there are montmorillonite clays (montmorillonite + chlorite-smectites + illite-smectites + hematite + magnetite + silica minerals). Sections of clays at the Nizhne-Koshelevsky thermal anomaly principally differ from those of the Pauzhetsky deposit. Here zonal structure of strata cannot be distinguished **(Figure 2*a*-*f*)**. Each section has an individual structure. The surface horizon of clays with a thickness of ≥ 10 cm is the zone of mechanical and chemical weathering with active oxidation of pyrite, magnetite and hematite and precipitation of native sulfur and metal sulfates at the aquatic temperature barrier. The thickest subjacent layer of clays corresponds to carbon-dioxide leaching zone (montmorillonite + chlorite-smectites + illite-smectites + hematite + magnetite + pyrite mineral association), however its has an unusually high content of iron sulfides (pyrite and marcasite?) and silica minerals. The stratum is not homogeneous. Layers, saturated with silica minerals (chalcedony, tridymite, crystobalite and opal) in association with pyrite, are identified both near the surface and near the bottom layer. Usually, concentrations of Au, Ag, Hg and rare earth elements in these layers of hydrothermal clays of the Nizhne-Koshelevsky thermal anomaly exceed the average values for hydrothermally-altered rocks in the region by one to three orders of magnitude.



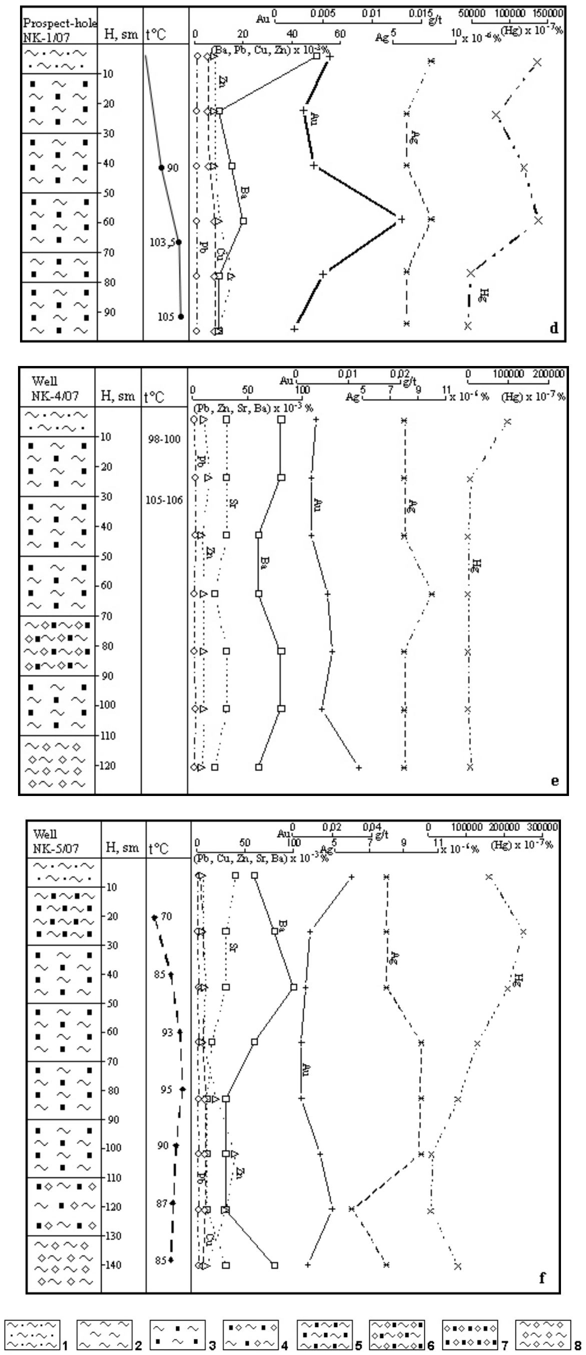


Figure 2: The geological cross sections of hydrothermal clays of Pauzhetsky geothermal deposit (a) and Nizhne-Koshelevsky thermal anomaly (b – f). 1 – hydrothermal clays of a sulfuric acid leaching zone and a zone of physical aeration of rocks; 2 – montmorillonite clays; 3 – the same, with in regular intervals absent-minded of pyrite; 4 – the same, with the high contents of tridymite and other minerals of SiO2; 5 – hydrothermal clays with high contents of pyrite; 6 – the same, with high contents of silica minerals; 7 – the intervals combined by rock fragments, silica minerals and pyrite (and without hydrothermal clays); 8 – hydrothermal clays with a high contents of a fragments of spreading rocks

Thus, the sections of hydrothermal clays at the Nizhne-Koshelevsky thermal anomaly are characterized by non-homogeneity of mineral and chemical compositions, by high concentration of pyrite, by the presence of silica minerals in association with iron sulfides. In some sections, the formation of montmorillonite clays with practically no pyrite in the bottom layer is observed (Figure 2*c*). In other sites of the thermal anomaly, clays of the carbon dioxide leaching zone with relatively uniformly disseminated pyrite are widely-spread (Figure 2d) or the same clays but with separate layers saturated with pyrite and aggregates of silica minerals are present (Figure 2*e*). Based on an analysis of the mineralogical, chemical and geochemical data across the section of well NK-5/07 (Figure 2*f*), the decrease of pyrite quantity towards the bottom layer and its total absence in the base of the section may be caused by inversion of temperature field and cooling of the lower part of the clay horizon. The section of the South-Kambalny Central field is characterized by a high content of pyrite in montmorillonite clays within an interval of 30-135 cm, the upper layer is a transition zone between sulfuric acid and carbon dioxide leaching, and the lower one differs sharply by composition and is 90% composed of montmorillonite. Such a structure of clays similar to some sections of the Nizhne-Koshelevsky thermal anomaly is explained by the fact that the prospecting pit opened an active steam-gas zone. Temperature (from 98 to 107 ^{0}C) and physical-chemical regimes of the zone (the presence of silica and iron colloids in steam-water mixture as well as a high activity of hydrogen sulfide) result in the formation of a thick silicified and pyritized clay stratum. The zone has distinct upper and lower boundaries caused by temperature barriers.

Chemical composition of hydrothermal clays is characterized by an increase of SiO_2 from the upper layer to the lower one **(Table 1)**. Distribution of the remaining components is homogenous in the vertical sections and in the plane of the Nizhne-Koshelevsky thermal anomaly. Content of oxide components ranges within wide limits (weight%): SiO_2 = 39.53 – 58.1, Al_2O_3 = 14.78 – 26.36, FeO + Fe_2O_3 = 2.58 – 10.27, K_2O = 0.2 – 2.13, and sulfur compounds (loss) = 8.67 – 24.58. Hydrothermal clays of the chilled Promezhutochny (“Intermediate”) field (Vakin et al., 1976) have a chemical composition that on averages corresponds to montmorillonite clays (sample NK-Prom-1/06 in Table 1). Samples of argillaceous rocks taken as reference ones from outside the thermal anomaly (sample NK-20/06-2 in Table 1) differ from present-day hydrothermal clays by having a high content of SiO_2, a low sum of FeO + Fe_2O_3 and sulfur compounds. Therefore, the hydrothermal clays of the thermal anomaly are subjected to active present-day process of redistribution of basic ore-forming components between layers and, apparently, within the layers. Such redistribution reflects the very dynamic nature of the composition of crystalline minerals and amorphous phases. Quantitative mineralogical analysis of hydrothermal clay samples demonstrates that the sections of clay stratum in the Nizhne-Koshelevsky thermal anomaly are dominated by montmorillonite (montmorillonite-smectite), the upper layer contains kaolinite, and the fine fraction of pyrite is disseminated throughout the whole section **(Table 2)**. The clays of the Verkhne(Upper)-Pauzhetsky thermal field have a more complicated composition: kaolinite (kaolinite-smectite) is present in all the layers (except for VxPTF-1/07-5) and a “blue clay” horizon is distinguished (VxPTF-1/07-3) by the presence of quartz, potash feldspar, and albite and a higher content of pyrite. The studied samples have pseudomorphic form: thin lamellar clayey particles compose microaggregates mainly repeating the form of spalls and crystals of parent rocks **(Figure 3*a*-*f*)**. Such a structure is typical for most of the clays of the Verkhne(Upper)-Pauzhetsky thermal field (Figure 3*a*-*c*).

Table 1. Chemical compound of hydrothermal clays of Nizhne-Koshelevskoe geothermal deposit

Components	Samples number												
	NK-1/06-1	NK-1/06-2	NK-1/06-3	NK-1/06-4	NK-8/06-1	NK-8/06-2	NK-8/06-3	NK-8/06-4	NK-9/06-1	NK-9/06-2	NK-10/06 -2	NK-Prom -1/06	NK-20/06 -2
	Depth, m												
	0.7-0.9	0.5-0.7	0.3-0.5	0.1-0.3	0.1-0.3	0.3-0.5	0.5-0.7	0.7-0.9	0.0	0.0	0.0	0.1-0.3	0.1-0.3
	Contents, weight %												
SiO_2	53.12	51.52	45.97	39.53	49.61	50.71	52.77	52.75	53.68	54.07	54.96	51.71	61.03
Al_2O_3	21.3	26.36	25.77	25.94	21.7	20.42	19.86	17.54	20.04	17.88	18.78	20.56	20.47
Fe_2O_3	2.86	1.87	2.24	1.75	5.07	4.8	5.53	6.3	5.05	5.19	5.87	7.03	1.49
FeO	0.64	0.71	1.08	1.00	0.64	0.93	0.65	0.64	1.08	1.22	0.79	2.22	0.57
CaO	0.054	0.024	0.01	0.016	0.016	0.06	0.141	0.906	1.08	1.17	0.01	3.35	0.711
MgO	0.307	0.209	0.294	0.219	2.04	2.35	2.61	3.03	1.3	1.54	2.63	2.19	1.13
Na_2O	0.328	0.403	0.427	0.61	0.229	0.209	0.183	0.122	0.548	0.54	0.153	1.54	0.458
TiO_2	0.882	0.853	0.932	1.56	1.01	1.00	0.969	0.96	1.03	1.04	0.995	1.31	1.08
K_2O	0.638	0.607	0.617	1.36	0.29	0.241	0.221	0.408	0.512	0.63	0.252	1.08	0.927
MnO	0.017	0.015	0.014	0.011	0.035	0.038	0.046	0.062	0.071	0.061	0.103	0.099	0.018
P_2O_5	0.136	0.153	0.132	0.217	0.75	0.356	0.2	0.442	0.0201	0.155	0.117	0.073	0.245
loss	17.75	16.09	20.39	24.58	17.0	17.4	15.840	15.76	13.57	14.57	13.85	8.67	11.110
Total	98.032	98.814	97.866	96.793	98.39	98.514	99.02	98.92	98.3411	98.066	98.5	99.832	99.239

The note. Definition of a full chemical hydrothermal clays compound is executed in Analytical Center of Institute of Volcanology and Seismology FED RAS by "PIONEER S4". Analysts E.V. Kartasheva and N.I. Chebrova.

Table 2. Results of hydrothermal clays mineralogical analysis of Nizhne(Lower)-Koshelevsky thermal anomaly (prospect-hole NK-1/07) and Verxne(Upper)-Pauzhetsky thermal field (prospect-hole VxPTF-1/07)

Samples number	Depth, cm	Mineral compound of hydrothermal clays, weight %					
		Montmorillonite-smectite	Kaolinite-smectite	Pyrite	Quartz	Microcline	Albite
NK-1/07-1	0-10	85.8	13.0	1.2	0	0	0
NK-1/07-2	10-30	99.2	0	0.8	0	0	0
NK-1/07-3	30-50	98.8	0	1.2	0	0	0
NK-1/07-4	50-70	99.7	0	0.3	0	0	0
HK-1/07-5	70-80	99.3	0	0.7	0	0	0
NK-1/07-6	80-100	99.6	0	0.4	0	0	0
VxPTF-1/07-1	0-10	64.7	33.2	2.1	0	0	0
VxPTF-1/07-2	10-15	74.1	25.1	0.8	0	0	0
VxPTF-1/07-3	15-30	29.8	33.7	4.0	21.3	1.8	9.3
VxPTF-1/07-4	30-35	82.9	15.9	1.2	0	0	0
VxPTF-1/07-5	35-55	99.6	0	0.4	0	0	0
VxPTF-1/07-6	55-60	85.7	13.6	0.8	0	0	0

The note. The dates were received by X-ray method on Engineering and Ecology department of Moscow State University. Analysts V.N. Sokolov and M.S. Chernov.

The microstructure of clays is transitory between pseudoglobular and spongy. In some areas, spheroid aggregates with a diameter of 1 to 30 μm are observed (Figure 3*a*, 3*d*), in some areas – lamellar aggregates forming sponge-like fine-mesh screen (Figure 3*b*). Pyrite crystals of the cubic system with planes sized ≤ 1-4 μm (Figure 3*e*) grow on the surface of microaggregates and on the walls of pores filled with argillaceous minerals. Figure 3*f* illustrates a fragment of the microstructure of the "blue clay" horizon: a large amount of very fine pyrite crystals sized ≤ 0.5-1.0 μm in association with argillaceous minerals forms a clay structure framework. Study of clay fragments and their separate constituent particles and crystals using energy-dispersive spectrometer demonstrated a significant diversity in cation composition by finding Fe, Al, Mg, Ti, Mn, Ca, K, Na, P, and F (Rychagov et al., 2008). Identification of many minerals is complicated because they form colloform structures characteristic of the initial stages of crystallinity in silica gels. Probably, the formation of isomorphic mineral structures explains the diversity of cation composition found in numerous clay layers. They are typical of the younger hydrothermal clays of the Nizhne-Koshelevsky thermal anomaly.

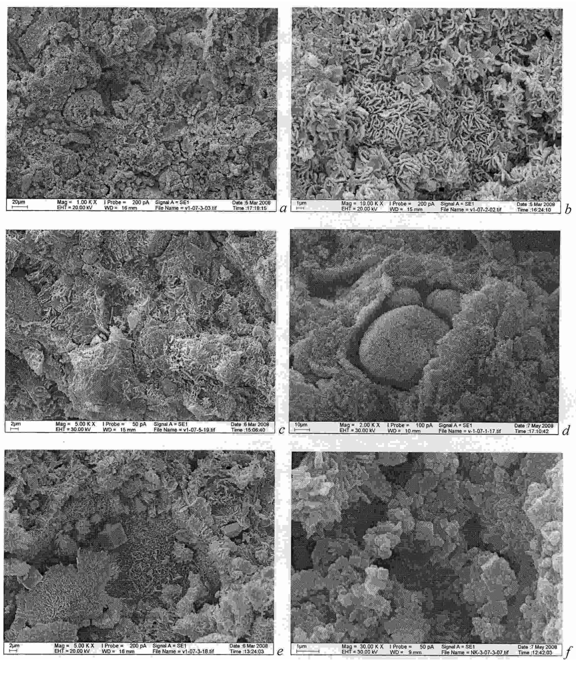


Figure 3: The microstructure of hydrothermal clays according to studying on the raster electronic microscope (REM). The data are received in Moscow State University by Drs. V.N. Sokolov and M.S. Chernov

CONCLUSION

The detailed study of the clay stratum resting on the surface of the geothermal anomalies of the Pauzhetsky-Kambalny-Koshelevsky district demonstrated that the stratum is a geological body of a great importance for structure of hydrothermal-magmatic systems. Hydrothermal clays on the surface geothermal anomalies form practically continuous cover with an average of thickness of 1.5 – 1.7 m and an occurrence area of ≥ n x 10^4 m^2. Clays and pyrite forming within these layers along with other hydrothermal neoformations are distinguished by a high level of concentrations of Au, Ag, Hg, Ba, and B and of alkaline and rare earth elements **(Figure 4)**. Chemical and mineral compositions of clays differ significantly at different sites. The Verkhne(Upper)-Pauzhetsky thermal field is marked by a distinct zone sequence of clays: the upper layer 20-30 cm thick is the zone of sulfuric acid leaching (kaolinite + kaolinite-smectite + limonite + native sulfur + Ca, Ba and other sulfates); the lower layer is the zone of carbon dioxide leaching (montmorillonite + montmorillonite-smectite + chlorite-smectite + illite-smectite + pyrite + hematite + magnetite etc.); and a 15 – 30 cm thick horizon of "blue clay" is emplaced between these two zones. The latter plays a role of subaquatic geochemical (sulfide) barrier (Pampura, Khlebnikova, 1987).

The hydrothermal clays of the Nizhne-Koshelevsky thermal anomaly are characterized by non-homogenous structure from section to section, by availability of thick strata of pyritized and by silicified montmorillonite clays with dominated hematite in some layers. Pyritized and silicified parts of sections are confined to high-temperature fumaroles and "dry" (overheated) steam discharge zones. These sections are distinguished by relatively high concentrations of Au, Ag, Hg, and some other elements in argillaceous minerals and pyrite monofractions. In general, the high geochemical background for the hydrothermal clays of the Nizhne-Koshelevsky thermal anomaly is connected to a flux of a gas-hydrothermal fluid from a deep-seated source, which is supported by geological, geophysical and isotope data (Dolgozhivushiy…, 1980; Lebedev, Dekusar, 1980; Pisareva, 1987). A similar geochemical regime is formed in the South-Kambalny Central thermal field for which there is a well-grounded assumption that the hydrothermal convective cell is connected with a boundary magmatic chamber of Kambalny volcano (Structure…, 1993).

In summary, hydrothermal clays that are formed under the influence of high temperatures, input of metal-bearing solutions, carbon dioxide and hydrocarbons from a depth of >> 2 – 3 km, mixing of these fluids with surface waters and the presence of intensively chilled rocks due to contrasting physical-chemical parameters of the environment characteristically have non-homogenous structure of stratum and form a thermodynamic sulfide barrier with a thickness of 1.0 meter. The barrier, unlike the one at Pauzhetsky thermal fields, is formed at different depths and in some sections (small blocks) of clays around fumaroles, pulsating springs, and in "dry" (overheated) steam blowing zones. Based on this observation, the hydrothermal clays of Pauzhetsky geothermal deposit can be classified as neoformations of the mature type which have been formed throughout the duration of Holocene – the age of the present-day Pauzhetsky hydrothermal system was estimated by S.I. Naboko to be ~ 10 thousand years (Naboko, 1980). The hydrothermal clays of the Nizhne (Lower)-Koshelevsky geothermal deposit and the South-Kambalny thermal fields, apparently, are younger geological formations as are their enclosing geological structures (Structure…, 1993). Hydrothermal clays forming an independent geological body in the hypogene zone of high-temperature geothermal deposits reflect a geochemical regime at the front of an ascending metal-bearing fluid **(Figure 5)**.

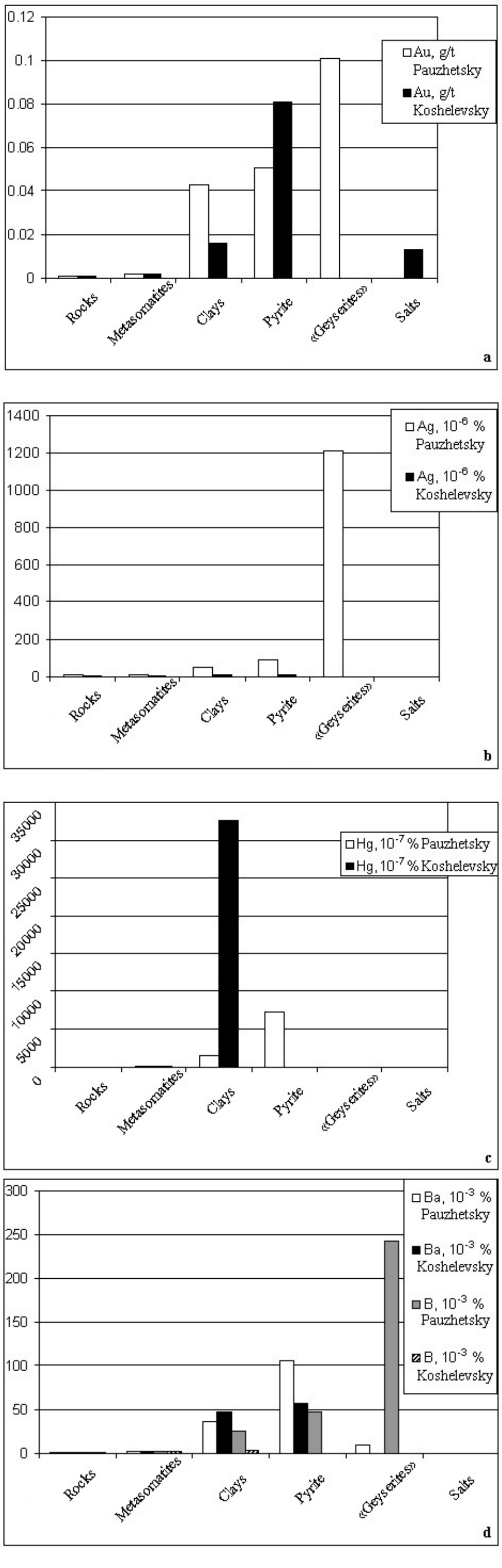


Figure 4: Concentration of Au (a), Ag (b), Hg (c), Ba and B (d) in various types of sediments and rocks of Pauzhetsky and Koshelevsky geothermal deposits

Temperature and physical-chemical conditions and the particular geochemical regime in zones of an ascending metal-bearing fluid of the Nizhne-Koshelevsky thermal anomaly and South-Kambalny thermal field, apparently, determine the following features of hydrothermal clay structure: diversity of mineral composition in the stratum, availability of a wide range of cations (Fe, Mg, Mn, Al, Ti, Ca, K, Na and others) within the structure of mixed-layer minerals, and a great role of colloid compounds in the formation of clays and geochemical barriers. Pyrite, sulfates, and apparently, a number of alumosilicates are minerals that concentrate ore elements in hydrothermal clays. Alumosilicates have porous structure and capacity for a large incorporation of cations as indicated above. In certain sections pyrite is the main sorbent of Au and Hg, whereas in other sections hematite, silica minerals and mixed-layer formations participate in sorption. In general, we need to note that an in-depth study of stratum of hydrothermal clays and the near surface highly mobile system “steam-hydrothermae – argillized rocks” is of great importance for the interpretation of the fluid regime peculiarities of ore-forming hydrothermal-magmatic systems and of the geothermal deposits of island arcs.

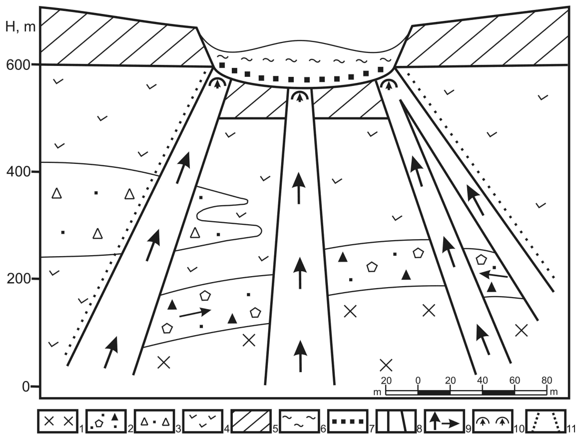


Figure 5: Conceptual model of hydrothermal clays and ore geochemical barrier formation above zone of ascending stream of gas-liquid fluid (on example of Nizhne-Koshelevsky geothermal deposit). 1 – diorite body; 2 – breccia mantle of diorite body; 3 – volcano-sedimentary rocks; 4 – andesite lavas; 5 – upper caprock; 6 – hydrothermal clays; 7 – geochemical barriers; 8 – faults; 9 – streams of fluid; 10 – boiling of fluids in the basis of hydrothermal clays horizon; 11 – boundary of vapor-dominated deep zone

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