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Hydrothermal Clays of Kamchatka Geothermal Fields: Composition, Structure and a Role for Understanding the Evolution of Hydrothermal Systems

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ABSTRACT

Argillaceous rocks and hydrothermal clays capture attention of scientists worldwide due to the fact that they possess special physical-chemical properties and widely occur in ancient and modern volcanic areas. We demonstrated at the previous stage of research (Rychagov et al., 2010: WGC-2010) that hydrothermal clays formed distinctive geological bodies in the hypergenesis zone of the large geothermal systems of South Kamchatka and were very important for study and development of geothermal deposits. They are an upper water-confining stratum and a heat shield within the system structure. It is hypothesized that the stratum of hydrothermal clays creates conditions for the formation of a complex geochemical barrier of noble, non-ferrous, ferrous and rare metals. In elaboration of this concept and for understanding the real role of hydrothermal clays in the evolution of the hydrothermal systems and in the structure of geothermal reservoirs, key sections of clay strata being formed in various physical-chemical conditions are studied in detail: near vapour-gas jets, on hot and cooling areas, on newly-formed thermal fields, beyond the thermal anomalies. Variances in composition and structure of hydrothermal clays being formed at vapour- and water-dominated geothermal deposits are shown. We suppose that the composition, structure and properties of the stratum of clays in the hypergenesis zone reflect the evolution of hydrothermal systems at a certain stage of its development and may serve as criteria for practical assessment of the temperature and fluid regimes of various-type geothermal deposits.

1. INTRODUCTION

Hydrothermal clays and argillically altered rocks are widespread in the areas of modern volcanism. It is known that hydrothermal clays situated near or on the surface may serve as an upper aquifer horizon and thermal shield in the structure of hydrothermal deposit (Hydrothermal…, 1993), while argillic zones that developed along faults to a depth of 500 m and more meters provide the formation of system of blocks having contrasting petrophysical properties and different thermodynamic parameters of fissure–pore solutions circulating in them (Rychagov et al., 1994). The study of the behavior of chemical elements, primarily, metals, at the modern geothermal fields, in particular, conditions of their accumulation, mechanisms of influx and redistribution, and their sources remain an urgent problem in the geochemistry of hydrothermal mineralforming processes. While studying the hydrothermal clays and their constituent minerals, D.S. Korzhinskii, S.I. Naboko, V.L. Rusinov, V.A. Eroshchev-Shak, J. Hemley, A. Reyes, and others leading researchers determined conditions of formation of argillically altered rocks in the areas of modern and ancient volcanism, examined in detail the mineral composition of zones of sulfur and carbonic acid leaching in the general context of evolution of hydrothermal metamorphism of volcanogenic rocks, proposed formation mechanisms of clay and some ore minerals (in particular, pyrite), and considered features of argillic alteration as indicator of retrograde trend in hydrothermal–metasomatic alteration (Eroshev-Shak, 1992; Korobov, 1994; Naboko, 1980; Hemley and Jones, 1964; Reyes, 1990). At the same time, one of the most important aspects of the formation of argillically altered rocks remained unstudied. Detailed layer-by-layer sampling of subsurface horizon of hydrothermal clays showed that it represents a complex geochemical barrier evolving during the entire time of formation of clay sequence (Rychagov et al., 2009). It is known that finely dispersed clay rocks are typical natural nanomaterials (Gusev, 2005), and that colloidal species of sulfides, sulfur, silica, and other compounds significantly contribute in sorption of chemical elements in the supergene zone (Ailer, 1979; Chukhrov, 1955). In the light of these facts, hydrothermal clays may be considered as longlived (during the Holocene or longer) highly dynamic colloidal–dispersal mineralogical–geochemical system that operates at macro, micro and nano-levels in the supergene zone of geothermal deposits.

2. STUDY OBJECTS: BRIEF GEOLOGICAL CHARACTERISTICS

The studies were carried out at the thermal fields of one of the largest geothermal and ore regions of Kamchatka: the Pauzhetka–Kambal'noe–Koshelevskoe area. This area is located in the inner zone of the Kurile–Kamchatka island arc, being confined to the juncture of three main volcanic belts of Kamchatka (Long-Term Center…, 1980) **(Figure 1)**. It occupies the central position in the previously distinguished subring tectono-magmatic structure, which represents a gentle accumulative–tectonic arch 35 × 50 km in size complicated by Quaternary volcanotectonic depression 20 × 25 km in a plan view. The rocks of the area were formed in two stages: lower structural stage is represented by Neogene (Miocene– Pliocene) tuffs and tuffites and upper stage consists of Pleistocene–Holocene volcanics. The studied objects are confined to the upper structural unit. These are the Pauzhetka and Koshelevskoe hydrothermal–magmatic systems, exploited Pauzhetka deposits, and explored Nizhne-Koshelevskoe geothermal fields, tectonomagmatic uplift of the Kambal'nyi Randge, and local thermal anomalies related to these structures.

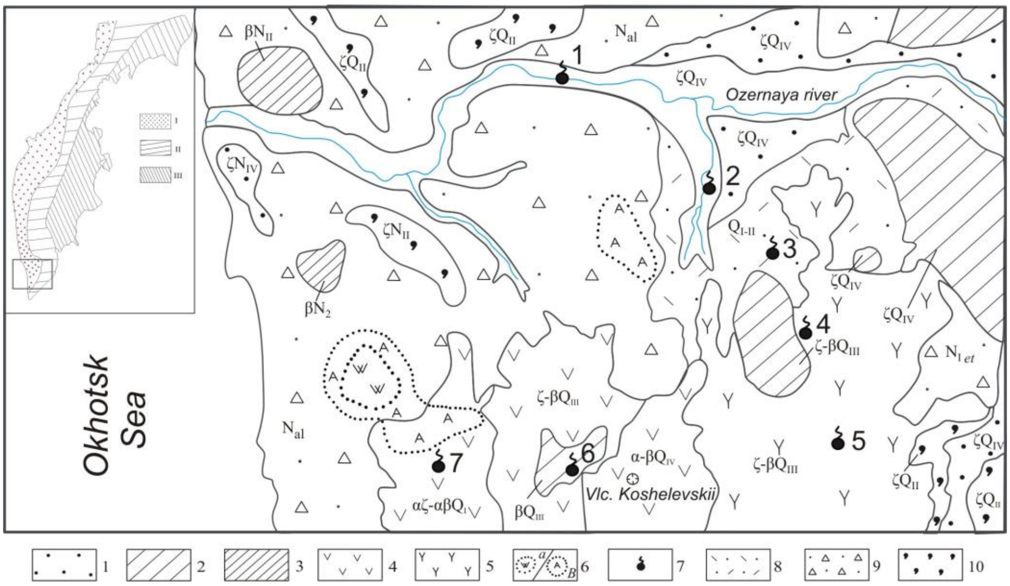

Figure 1: The geological schematic map of the Pauzhetka–Kambal'noe–Koshelevskoe geothermal area. Compiled using materials of scientific studies and state geological surveys on a scale 1 : 200 000. Inset shows the main volcanic fields of Kamchatka: (I) Western Kamchatka, (II) Central Kamchatka, (III) Eastern Kamchatka. Main scheme: (*1*) basement volcanics (lava–pyroclastic sediments), (*2*) volcanogenic–sedimentary sediments (tuffites) of the Pauzhetka Formation; (*3*) ignimbrites; (*4*) dacitic andesites–basaltic andesites of the Koshelevskii volcanic massif; (*5*) volcanics (lava, pyroclastic flows, extrusions) of the Kambal'nyi Range; (*6*) pyroclastic sediments (pumice); (*7*, *8*) subvolcanic and extrusive bodies of the Neogene (*7*) and Quaternary (*8*) age; (*9*) fields of hydrothermally altered rocks, (a) secondary quartzites, (b) argillically altered rocks; (*10*) main modern thermal anomaly of the area: (1) Pervye Goryachie Klyuchi (Pionerlager), (2) Vtorye Goryachie Klyuchi (Pauzhetka deposit), (3) Severnaya Kambal'naya, (4) Tsentral'naya Kambal'naya, (5) Yuzhnaya Kambal'naya, (6) Verkhne-Koshelevskaya, (7) Nizhne-Koshelevskaya.

The Pauzhetka geothermal field is known in our country and abroad owing to the building of the USSR's first geoelectric power station of established capacity of 11 MWe. The field has been exploited since 1966–1967. It has a blocky–bedded structure typical of the hydrothermal systems in the areas of modern volcanism: two aquifers that are located, on average, at depths of 100– 350 and 500–750 m and confined to the subhorizontal sequences of psephitic and agglomerate tuffs of the Pauzhetka Formation and tuffaceous breccias of the Alnei Group. The Anavgai sandstones of the lower aquifer subsequently grade into the Golyginskie ignimbrites of the middle complex and fineclastic tuffites of the Verkhnyaya Pauzhehtka subformation ascribed to the upper complex. The rocks are cut by subvertical blocks owing to the emplacement of minor gabbrodiorite intrusions and active tectonic movements in the preHolocene time and modern period (Hydrothermal…, 1993). Hydrothermal clays were mainly studied at the Verkhne-Pauzhetka thermal field **(Figure 2*a*)**. The field surface is discharged by acid hydrocarbonate–sulfate waters with salinity up to 500– 600 mg/L. The temperature of solutions and hydrothermal clays is no more than 98°C. This geological structure is characterized by local tectonomagmatic uplift of the rocks in the Late Quaternary, ejection of chloride– sodium steamwater mixtures ascending from the lower aquifer; formation of subsurface (0–150 m) liquid–vapor transition zone with quartz–adular metasomatites, and ore geochemical barrier at the zone bound aries (Zhatnuev et al., 1991). All these facts predetermined the interest to studying the subsurface horizon of hydrothermal clays, which overly the thermal field by continuous cover more than 150 × 200 m^2 in area, and, probably, intensely participate in the mineral-forming processes proceeding here.

Figure 2: Verkhne-Pauzhetka thermal field (*a*) and Nizhne-Koshelevskay thermal anomaly (*b*)

The Nizhne-Koshelevskoe geothermal field is among the world's largest vapor-dominated systems such as Larderello (Italy), Matsukawa (Japan), Geysers (US), and Kamojang (Indonesia). Its predicted resources were estimated at 210 kg/s dry vapor (Pisareva, 1987). A large zone of overheated vapor reaching a depth of 1.5 km was distinguished there on the basis of prospecting drilling. The surface heat discharge is confined to the basin, 250 × 500 m^2 in size, consisting of a series of explosive and erosion funnels **(Figure 2*b*)**. The energetic power of the thermal anomaly is 25 Gcal/s (Vakin et al., 1976). It represents the discharge area for acid and weakly acid sulfate and hydrocarbonate–sulfate ammonium waters saturated in carbon dioxide gas, hydrogen sulfide, methane, and heavy hydrocarbons (Lebedev and Dekusar, 1980). The vapor temperature reaches 127°C in fumaroles and mainly 98–105°C in the hydrothermal clays. Active hightemperature gas–hydrothermal processes provide formation of practically uninterrupted subsurface horizon of clays of average thickness 1.5–1.8 m above thermal anomaly. Preliminary studies of hydrothermal clays made it possible to assume a link between endogenous geothermal and subsurface mineralogical–geochemical and hydrochemical processes (Rychagov et al., 2008, 2009).

3. METHODS

Field study of hydrothermal clays involved the excavation of prospect holes and core drilling up to the sequence base, detailed description of recovered sections, layer-by-layer sampling, on average, each 15– 20 cm with measurement of temperature and some other physical characteristics of beds, precipitation of clay minerals, and obtaining gray slime. These procedures were accompanied by hydrogeochemical sampling of all water types discharging near excavations with in situ measurement of pH, Eh, salinity, and temperature. Laboratory studies included description of mineral composition of clays and heavy fractions and accessory minerals extracted from them using MPSU1 binoculars; quantitative mineralogical analysis using conventional X-ray method; the compositional and microstructural study of clays using LEO 1450 VP scanning electron microscope equipped with EDS INCA 300; the XRF measurement of chemical composition of clays using S4 PIONEER spectrometer; atomic absorption analysis for Au determination; atomic fluorescent method for analysis of Hg content, and the total chemical analysis of thermal waters. While discussing, we used previously obtained data on Sr isotope composition of thermal waters, rocks, and clays. The laboratory works were conducted at the Institute of Volcanology and Seismology of the FEB RAS, the Institute of Geochemistry of the Siberian Branch of the RAS, FGUP Central Institute of Geological Exploration for Base and Precious Metals, and at the Department of Engineering and Ecological Geology of the Geological Faculty, Moscow State University.

4. GENERAL CHARACTERISTICS OF HYDROTHERMAL CLAYS

The composition and structure of hydrothermal clays lying on the surface of the thermal fields of the Pauzhetka deposit and Kambal'nyi volcanic range were studied by us earlier (Hydrothermal…, 1993). A zone of sulfuric acid leaching (from 0 to 0.2–0.3 m deep) is represented by varicolored clays consisting mainly of dioctahedral smectites, kaolinites, and limonites. There are also a scattered dissemination of pyrite (up to 2–5 vol %), as well as quartz, native sulfur, jarosite, heulandite, and plagioclases. These clays are underlain (to depths from 5–15 to 20– 35 cm) by a bed of "blue clays", the bluish-black to black color of which is caused by pyrite. The pyrite content in this bed varies from 15–20 to 35% and may reach locally 90%. This bed is distinguished also by the presence of relatively high content of silica minerals (opal, chalcedony, quartz), as well as goethite and hydrogoethite, jarosite, hematite, and individual grains of some other minerals. "Blue clays" are formed on the subaquatic thermodynamic barrier (Pampura and Khlebnikova, 1987) and differ in the relatively high contents of Au, Ag, Hg, alkali and trace elements (Koroleva et al., 1993). The thickness of this layer is no more than 15–20 cm. The "blue clays" rest on most part of montmorillonite-dominated clays of thermal fields. Among other steady minerals are pyrite (usually evenly disseminated), hematite, goethite, and hydrogoethite, feldspars, silica minerals (quartz, chalcedony), illite–smectite and chlorite–smectite, as well as magnetite and Ti-magnetite (Rychagov et al., 2009).

The chemical composition of the sediments subsequently changes with depth **(Table 1)**. The top horizon represented in our case by "blue clays" is characterized by the lowered SiO_2 contents, the highest contents of Al_2O_3 and sulfur (L.O.I. in Table 1). The deficit in the sum of chemical components in the table is typical of this layer and reflects the accumulation of elevated contents of highly-volatile chemical compounds in the upper part of the clay section. Simultaneously, the lower beds become higher in SiO_2 and lower in sulfur, which reflects increasing role of aluminosilicates in clay sequence. The base of the sequence differs in the high content of K_2O and total alkalis. This is probably related to the formation of K-feldspars and hydromicas in the lower units of the clay sequence. Noted zoning is typical of the thermal fields of the Pauzhetka deposit, and partly, of the Kambal'nyi range. The systematic study of the sections of hydrothermal clays of the Nizhne-Koshelevskoe thermal anomaly (25 prospect holes and boreholes from the day surface to the base of clay sequence) showed that they significantly differ from above described sequences in the absence of above-described zoning. Practically each of the sections has individual structure. The surface bed up to 10– 15 cm thick is a zone of mechanical and chemical weathering with oxidation of sulfides, magnetite, and hematite, and precipitation of sulfates and native sulfur at the aquatic temperature barrier. The underlying sequence corresponds mainly to the zone of carbonic acid leaching (montmorillonite + chlorite–smectite + illite–smectite + hematite + magnetite + pyrite), but with high contents of pyrite, marcasite, and silica minerals. Silica minerals (chalcedony, tridymite, cristobalite, and opal) in association with pyrite enrich individual zones, lenses, and fragments of beds at different depths. The horizon of "blue clays" is either absent (at the cooled areas) or varies in thickness from 0.1 to more than 1.0 m (immediately nearly fumaroles, at the steamy grounds and walls of boiling cans), while its vertical distribution depends on the position and thickness of the zone permeable for steam–gas jet. The chemical composition of the clays of the Nizhne-Koshelevskaya thermal anomaly also shows high variability **(Table 2)**. The clays at the boundary of cooling area (HK-5/06) differ in almost equal contents of most components in all layers of the section and the high contents of silica, which is related to the predominance of montmorillonite and other aluminosilicates. The clays in the section of hightemperature fumaroles (NK-11/06) in contrast show the wide variability for all components. Thus, the sequences of hydrothermal clays of the Nizhne-Koshelevskaya anomaly are characterized by the high heterogeneity of the mineral and chemical composition, the elevated contents of pyrite in association with silica minerals, and the sharp vertical and lateral variability in sequence structure. The study of distribution of noble and base metals, mercury, alkali and rare-earth elements showed that the horizon of "blue clays" have the highest contents of these elements (Ag up to 500 mg/t, Sb up to 60 g/t, As up to 300 g/t, and others) among the Pauzhetka clays (Koroleva et al., 1993). However, the average level of contents of ore elements in these clays is not high. At the same time, the entire sequence of hydrothermal clays of the Nizhne-Koshelevskaya thermal anomaly, as well as the Southern Kambal'noe thermal field, differ in the elevated contents of Au, Ag, Hg, B, and other elements and show no any element accumulation at definite geochemical barrier (Rychagov et al., 2008).

Table 1. Chemical composition of hydrothermal clays of the Verkhne-Pauzhetka thermal field in the vertical section of the sequence

Components	Sample numbers						
	VxPP-1/06-1	VxPP-1/06-2	VxPP-1/06-3	VxPP-1/06-4	VxPP-1/06-5	VxPP-1/06-6	VxPP-1/06-7
	Sampling interval, m						
	0.1-0.3	0.3-0.5	0.5-0.7	0.7-0.9	0.9-1.1	1.1-1.3	1.3-1.5
	Content of components, wt %						
SiO_2	45.35	49.73	50.57	51.38	53.12	53.7	54.62
Al_2O_3	24.33	19.62	19.55	18.94	18.56	18.35	18.47
Fe_2O_3	5.84	6.2	7.53	7	6.26	5.64	5.68
FeO	1.44	1.65	0.79	0.86	0.93	1	1.01
CaO	0.372	1.4	2.26	2.49	2.35	2.63	2.55
MgO	1.82	4.92	2.76	2.73	2.61	2.52	2.24
Na_2O	0.32	0.273	0.185	0.175	0.22	0.226	0.24
TiO_2	1.02	0.874	0.918	0.923	0.786	0.82	0.797
K_2O	0.461	1.07	0.463	0.602	1.43	1.36	1.63
MnO	0.109	0.226	0.111	0.117	0.114	0.119	0.11
P_2O_5	0.093	0.13	0.106	0.144	0.115	0.134	0.128
L.O.I.	16.29	13.5	14.56	14.42	13.3	13.17	12.220
Total	97.445	99.593	99.803	99.781	99.795	99.669	99.695

Note: Chemical analysis was performed on «S4 PIONEER» by XRF spectrometry at the Analytical Center of the Institute of Volcanology and Seismology FEB RAS, analysts E.V. Kartasheva and N.I. Chebrova.

5. MINERAL COMPOSITION AND MICROSTRUCTURE OF THE CLAYS

According to data of quantitative mineralogical analysis, the sections of the clays of the Nizhne-Koshelevskaya thermal anomaly are dominated by smectite group. The upper layer contains mixed-layer kaolinite–smectite type clays. Fine pyrite is evenly disseminated over entire sequence **(Table 3)**. All studied intervals in the section of prospect hole NK-3/08 contain cristobalite. The clays of the Verkhne-Pauzhetka thermal field have more complex mineral composition. They are dominated by smectite group and mixed-layer smectite–kaolinite group minerals, which are developed throughout the entire section. The horizon of "blue clays" (15–30 cm) is distinctly distinguished in the section by the presence of quartz, K-feldspar, albite, and higher pyrite content. The hydrothermal clays from the Nizhne-Koshelevskaya thermal anomaly have mainly finely dispersed pseudoglobular microstructures made up of the rounded microaggregates of nanoparticles of ferruginous smectite. In addition, the rocks from the upper portion of the section are characterized by the presence of domain-like microstructures consisting of the domain-like microaggregates of lamellar mixed-layer nanoparticles (kaolinite–smectite with the predominance of smectite layers), which are in contact with each other by basal surfaces **(Figures 3a, 3b)**. The microstructures of hydrothermal clays from the area of the Pauzhetka geothermal deposit are inherited and ascribed to the globular–lamellar type **(Figure 3c)**. The hydrothermal reworking of the fragments of volcanic glass results in the formation of globules 8–10 μm in size **(Figure 3d)**, which are composed of lamellar smectite nanoparticles with high iron content (pseudomorphs after volcanic glass). The microstructures of all studied hydrothermal clays are characterized by the presence of numerous microcrystals of cubic pyrite with face sizes 1–4 μm **(Figure 3e, 3f)**. "Blue clays" are peculiar in that their structural framework is made up of pyrite crystals 0.1–1.0 μm in size and clay minerals **(Figure 3f)**.

The study of individual microcrystals and particles using energy dispersive spectrometer revealed the wide diversity of cations in their chemical composition: Fe, Al, Mg, Ti, Mn, Ca, K, Na, P, F, and others. The identification of many minerals was complicated due to their small size and formation of collomorphic structures, which are typical of the initial stages of devitrification of silicate as well as carbonate, sulfide, and other gels under hydrothermal conditions. The most diverse cationic composition was identified in the hydrothermal clays of the Nizhne-Koshelevskaya thermal anomaly. The heavy fraction of the clays is dominated by pyrite. The

Table 2. Chemical composition of hydrothermal clays of the Nizhne-Koshelevskaya thermal anomaly in the vertical sections of the sequence

Components	Sample numbers									
	NK-5/06-1	NK-5/06-2	NK-5/06-3	NK-5/06-4	NK-11/06-1	NK-11/06-2	NK-11/06-3	NK-11/06-4	NK-11/06-5	NK-11/06-6
	Sampling interval, m									
	0.1-0.3	0.3-0.5	0.5-0.7	0.7-0.9	0.2-0.4	0.4-0.6	0.6-0.8	0.8-1.0	1.0-1.2	1.2-1.35
	Content of components, wt %									
SiO_2	55.63	55.81	54.36	54.71	47.93	50.4	50.95	50.72	49.8	49.65
Al_2O_3	17.94	17.42	18.35	17.5	22.97	21.29	17.41	17.5	15.61	16.17
Fe_2O_3	6	6.29	6.69	7.19	5.62	5.69	7.17	7.85	9.12	10.25
FeO	0.86	0.64	0.79	0.5	1	0.93	1.36	129	1.72	1.72
CaO	0.94	1	1.04	1.08	0.252	0.586	1.95	1.94	2.24	3.09
MgO	2.89	3.25	2.99	3.15	1.29	1.54	2.58	2.22	2.73	3.35
Na_2O	0.143	0.123	0.148	0.134	0.27	0.236	0.224	0.348	0.182	0.554
TiO_2	1.45	1.21	1.44	1.31	1.35	1.22	0.896	1.14	0.906	1.05
K_2O	0.184	0.163	0.22	0.143	0.272	0.484	0.88	1.38	0.968	0.695
MnO	0.087	0.094	0.122	0.114	0.042	0.059	0.118	0.103	0.122	0.161
P_2O_5	0.028	0.031	0.052	0.038	0.162	0.112	0.441	0.42	0.568	0.624
L.O.I.	13.35	13.67	13.43	13.88	17.23	16.06	14.73	13.71	14.13	11.6
Total	99.502	99.701	99.632	99.749	98.388	98.607	98.709	98.621	98.096	98.914

Note: Chemical analysis was performed by XRF spectrometry on «S4 PIONEER» at the Analytical Center of the Institute of Volcanology and Seismology FEB RAS, analysts E.V. Kartasheva and N.I. Chebrova. NK-5/06 is trench excavated at the boundary of the Verkhnii site. NK-11/06 is the prospect hole that recovered the section of high-temperature fumarole.

individual sections of the Nizhne-Koshelevskaya thermal anomaly are distinguished by the high contents of aggregates of silica minerals and by the predominance of hematite in the upper layers with a gradual decrease of quartz grains and increase of pyrite content in the lower layers. Occasional sections are characterized by diversity of the mineral composition in slimes and increase inmagnetite (titanomagnetite) to the base of section. The presence of the great amount of pyroxene grains (up to 65 vol %) in the upper horizons of the sequence is noted for the hydrothermal clays forming in the local erosion funnels under conditions of the modern active denudation of surrounding bedrocks (andesites). The other areas of the thermal anomaly contain individual grains or no pyroxene. Gray slime obtained from the hydrothermal clays of the Verkhne-Pauzhetka thermal field differs from the above described ones and consists mainly of quartz, magnetite, Ti-magnetite, pyrite, marcasite, and hematite. Pyrite prevails in the horizon of “blue clays”; in other beds its content gradually increases to the base of the sequence, where it associates with quartz. Magnetite is present in all beds. Hematite in high amounts (up to 12–15 vol %) is mainly restricted to the middle part of the hydrothermal clay sequence. It is known that pyrite is one of the main ore-bearing minerals at the epithermal gold–base metal deposits (Hydrothermal…, 1993). Pyrite forming in the sequence of hydrothermal clays at the hydrothermal fields mainly occurs as complex aggregates. The crystals of cubic shape were found in the individual clay sections in association with silica minerals (tridymite, cristobalite, and chalcedony) in the vapor-conducting fissure zones. The lower contents, high heterogeneity, and spotted distribution of gold and mercury across pyrite grains (according to microprobe data) against the background high contents of Au (up to 0.1–1.0 g/t) and Hg (up to 10^{-3} %) in the bulk samples (monofractions) of the mineral based on results of atomic absorption, quantitative spectral, and atomic-fluorescent analyses indicate that all these elements occur in the form of microparticles (gold grains and drops of native mercury) in the defect structures of crystals: fissures, chips, pores, and zones of microdeformations. Analysis of data on chemical composition of monofractions and individual pyrite grains makes it possible to focus attention on the possible role of surface of crystals and pyrite aggregates in the accumulation of trace elements. The studies of V.L. Tauson with coauthors showed that surfaces of the grains of hydrothermally synthesized pyrite and pyrrhotite contain “non autonomous mineral phases” accumulating Au, Ag, As, Cd with enrichment coefficient up to 10^4 as compared to the crystal volume (Akimov et al., 2006). The characteristic feature of these phases is their tendency to the excess dissolution of trace elements, which increases the phase stability in hydrothermal environment. Owing to the change in the thermodynamic conditions and solution composition, these phases (representing the finest mineral films) become instable and serve as specific source of ore elements (Tauson et al., 2006).

Table 3. Mineral composition of hydrothermal clays of the Nizhne-Koshelevskaya thermal anomaly (trenches NK-1/07 and NK-3/08) and the Verkhne-Pauzhetka thermal field (trench VxPP-1/07)

Sample no.	Sampling depth (cm)	Mineral composition of clays, in vol. %						
		Smectite-group minerals	Mixed-layer (kaolinite-smectite)	Pyrite	Quartz	Micro-cline	Albite	Cristo-balite
NK-1/07-1	0-10	85.8	13.0	1.2	-	-	-	-
NK-1/07-2	10-30	99.2	-	0.8	-	-	-	-
NK-1/07-3	30-50	98.8	-	1.2	-	-	-	-
NK-1/07-4	50-70	99.7	-	0.3	-	-	-	-
NK-1/07-5	70-80	99.3	-	0.7	-	-	-	-
NK-1/07-6	80-100	99.6	-	0.4	-	-	-	-
NK-3/08-1	35-55	90.0	-	0.3	-	-	-	9.7
NK-3/08-2	55-80	93.5	-	1.1	-	-	-	5.4
NK-3/08-4	100-120	94.1	-	1.7	-	-	-	4.2
NK-3/08-5	120-140	90.3	-	2.1	-	-	-	7.6
NK-3/08-6	140-160	89.5	-	2.3	-	-	-	8.2
NK-3/08-9	200-225	94.1	-	1.4	-	-	-	4.5
VxPP-1/07-1	0-10	64.7	33.2	2.1	-	-	-	-
VxPP-1/07-2	10-15	74.1	25.1	0.8	-	-	-	-
VxPP-1/07-3	15-30	29.8	33.7	4.0	21.3	1.8	9.3	-
VxPP-1/07-4	30-35	82.9	15.9	1.2	-	-	-	-
VxPP-1/07-5	35-55	99.6	-	0.4	-	-	-	-
VxPP-1/07-6	55-60	85.7	13.6	0.8	-	-	-	-

Note: Results were obtained by X-ray method at the Department of Engineering and Ecological Geology of the Geological Faculty, Moskow State University. Analist V.V. Krupskaya.

6. CONCLUSIONS

Layer-by-layer study of sections of hydrothermal clays that form practically uninterrupted areally persistent sequence (on average, 1.5–1.8 m thick and $\geq 10^5$ m^2 in area) on the surface of thermal fields of the Pauzhetka and Nizhne-Koshelevskoe geothermal deposits led us to some conclusions. At the thermal fields of the Pauzhetka deposit, the top layer of the kaolinite–limonite clays (zones of sulfuric-acid leaching) up to 30 cm thick is underlain by the horizon of “blue clays” 20 cm thick, on average. Down section, they are replaced by smectite clays with hematite, pyrite, jarosite, barite, and some other minerals. This horizon has no a definite zoning and thickness no more than 150 cm. The hydrothermal clays of the Nizhne-Koshelevskoe deposit possess a complex structure and diverse sections. The predominant minerals are smectite-group minerals (mixed-layer illite–smectite and chlorite–smectites), pyrite, and silica minerals. The amount of the latters increases to the base of sequence and at local areas permeable for steam–gas jets, with precipitation of silicate gel and its devitrification into tridymite, cristobalite, and chalcedony. Surface horizon is represented by a zone of intense mechanical and chemical weathering of clays of widely variable thickness (from 5–10 to 30–40 cm) on the area of thermal anomaly. These clays are made up of kaolinite, limonite, native sulfur and its compounds, sulfates (barite, gypsum, jarosite), and highly siliceous zeolites; as well as pyrite and often rock fragments. Pyrite forms aggregates at different areas of thermal anomaly and at different horizons. The thickness of pyritized beds (“blue clays”) varies from 10–20 to 100–150 cm. Individual sections contain two and more beds of “blue clays” or represent a single horizon of pyrite-saturated hydrothermal clays. Such sections are usually confined to the steamy grounds, fumaroles, boiling cans, whose temperature and physicochemical regimes are determined by ascending vapor–gas jets (fumarole temperature in the mouths reached 120–125°C, predominant gases are CO_2, H_2S, SO_2, and hydrocarbons).

A horizon of “blue clays” serves as geochemical barrier, containing, on average, 6–10 mg/t Au, up to 500 mg/t Ag, 60 g/t Sb, and 300 g/t As in the individual samples. This geochemical and thermodynamic barrier was termed as the subsurface sulfide barrier (Pampura and Khlebnikova, 1987). Pore solutions in the horizon of “blue clays” are acid and ultraacid high-sailinity (up to 70 g/L)

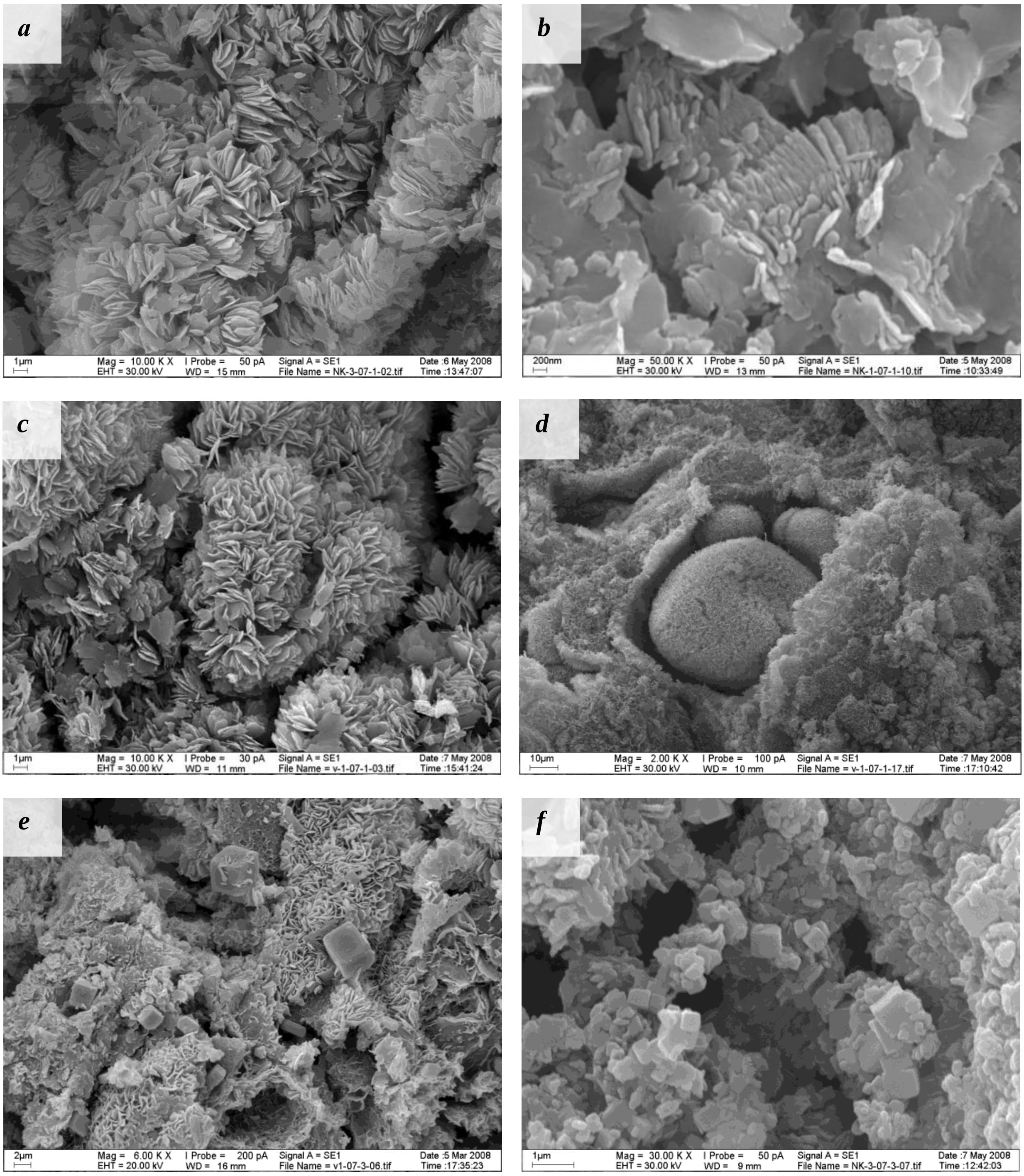

Figure 3. Micro- and nanostructures of hydrothermal clays: (*a, b, f*) clays of the Nizhne-Koshelevskaya thermal anomaly, (*c-e*) clays of the Verkhne-Pauzhetka thermal field. See text for explanation of figure fragments. Data were obtained on a LEO 1450VP scanning electron microscope equipped with EDS INCA 300 by V.N. Sokolov and M.S. Chernov at the Department Engineering and Ecological Geology, Geological Faculty, Moscow State University.

sulfate–chloride waters with high contents of Mn (1–2 mg/L), Fe (10– 580 mg/L), Zn (4–340 mg/L), Cu (0.4–33 mg/L), and Au (0.39–14 μg/L). This horizon marks a change of redox potential and temperature regime of solutions. It was shown previously that the precipitation of gold from steamy hydrothermal vents near surface is determined by decreasing H_2S content in waters owing to the boiling of solutions; the low pH value (up to 5) causes a destabilization of bisulfide complexes and, consequently, the formation of arsenic and stibium sulfides (Eurens and Khays, 1977). At the initial stage of crystallization, sulfides occur in colloidal form, which is capable of efficiently accumulating Au, As, Sb, Hg, and other elements. Sorption capacity of “blue clays” at the Nizhne-Koshelevskoe geothermal deposit is intensified at the expense of precipitation of silicic acid in the form of silicate gel (with subsequent crystallization into tridymite, cristobalite, chalcedony, and quartz). It is known that silicagel is a good sorbent of noble metals, base metals, as well as alkali and rare-earth elements (Chukhrov, 1955; Rychagov et al., 2009).

It was previously established that the studied geological objects are at different stages of the evolution: the Koshelevskaya hydrothermal–magmatic system operates at prograde stage (hightemperature, active role of magmatic fluids), while the Pauzhetka system marks the retrograde stage (cooling, without direct link with deep feeding) (Rychagov, 2003). This fact presumably determines the differences in the chemical and mineral compositions and macrostructure of the subsurface horizon of the hydrothermal clays of the Pauzhetka and Nizhne-Koshelevskoe geothermal deposits. The former may be ascribed to the mature clays (with relatively stable composition and stable structure), while the latters are immature clays with wide variability in chemical composition, as well as macro- and microstructure. In the mature clays, ore elements have been accumulated at the subaquatic (sulfide) geochemical barrier during the entire time of the sequence formation. The age of the subsurface horizon of argillically altered rocks is presumably determined as Holocene, according to the existing estimates of the lifetime of the modern hydrothermal systems (Naboko, 1980). Dynamically evolved (young) hydrothermal clays are enriched in ore elements in all beds, with increasing metal content to the sequence base. This indicates that subsurface horizon of hydrothermal clays can be considered as complex geochemical barrier with high sorption capacity. According to prospecting and isotope–geochemical data, metals were derived from underlying host rocks and gas–hydrothermal fluid ascending from apical parts of subvolcanic intrusions or from the deeper seated horizons of geothermal deposit (Lebedev and Dekusar, 1980; Pozdeev and Nazhalova, 2008). Hydrothermal clays differ in complex microstructure. The clays from the Nizhne-Koshelevskaya thermal anomaly are characterized by the presence of the finer dispersed pseudoglobular and domain-like microstructures consisting of nanoparticles of ferruginous smectite and mixed-layer kaolinite–smectite mineral. A great diversity of cations in the chemical composition of clays can be explained by the presence of areas composed of specific mineral mixtures of crystalline, amorphous, and transitional mineral phases. The microstructures of clays from the Pauzhetka geothermal deposit bear an inherited character. They are ascribed to the globular–lamellar type and consist of lamellar nanoparticles of ferruginous smectite. Pyrite forming in the hydrothermal clays serves as one of major mineral carriers of ore elements. Detailed study of mineral structure, including structure of its grain surface and crystals, provides insight into mechanisms of sorption of metals, alkaline, and rare-earth elements under the modern geothermal conditions.

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