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GEOCHEMISTRY

Hydrothermal Clays as a Highly Dynamical Colloid–Disperse Mineralogical–Geochemical System

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In spite of the high degree of study of argillitized rocks formed in the areas of modern volcanism [4, 7, 9, 12], the special role of the near-surface horizon of hydrothermal clays is established. They are the upper aquiclude, thermal screen, and complex geochemical barrier in the structure of geothermal deposits [8]. It is known that clays are typical natural nanomaterials [2] of high sorptive ability. Colloid forms of sulfides, silica, and other compounds actively participate in the sorption of metals [11]. All this allows us to consider hydrothermal clays as a long-living ($\geq 10^4$ years) mineralogical–geochemical system functioning on the macro-, micro-, and nanolevels in the hypergenesis zone of geothermal deposits.

The Pauzhetsko–Kambal'no–Koshelevskii geothermal region is located at the junction of three volcanic belts of Kamchatka and forms the Southern Kamchatka long-living volcanogenic–ore center [3, 8]. The Pauzhetskoe deposit is known all over the world thanks to the first GeoES in the USSR with a power of 11 MW. Relaxation of poor-acid hydrocarbonate–sulfate waters with mineralization up to 500–600 mg/l and temperature up to 98°C occurs in the Verkhne–Pauzhetskoe thermal field. Boiling of hot springs with the formation of ore geochemical barriers at the boundaries of the zone takes place within the field [9]. All these facts have attracted interest in the study of hydrothermal clays overlying the thermal field by a continuous cover on the area of >150 × 200 m. The Nizhne–Koshelevskoe deposit is in the same row with the largest vapor-dominating systems of the world: there is the zone of overheated vapor spreading to a depth of >1.5 km and located above the subintrusive body of diorite porphyrites [6]. Relaxation of heat on the surface is located in the basin with a size of 250 × 500 m, in which explosive and erosion cones are the most typical structures. The power of the thermal anomaly is 25 Gcal/s [1]. Acid and poor-acid sulfate and hydrocarbonate–sulfate ammonium waters saturated with CO_2, H_2S, CH_4, C_7H_{12}, and other gases relax on the surface [1, 8]. Vapor temperatures in the fumarole mouths reach 127°C; soils are heated up to 98–105°C. As a consequence of high-dynamical processes of leaching in the "gas–water–rock" system, a near-surface argillizite series with a thickness of 1.5–1.8 m is formed.

Composition of hydrothermal clays. Vertical zonation is typical for thermal fields of the Pauzhetskoe deposit. The zone of sulfate leaching (to a depth of up to 0.2–0.3 m) is composed of dioctahedral smectite, kaolinite, and limonite. Pyrite (up to 2–5 vol %), quartz, native sulfur, jarosite, heulandite, and plagioclase occur as well. These clays in the depth range from 5–15 cm to 20–35 cm are underlain by a layer of "blue clays": the concentration of pyrite in it varies from 15–20 to 35%, and locally reaching 90%. The layer is also distinguished by a relatively high content of silica minerals; hoethite and hydrohoethite, jarosite, hematite, and some grains of accessory minerals are registered. "Blue clays" are formed on the subaqueous (sulfide [5]) thermodynamic barrier and are distinguished by relatively high concentrations of Au, Ag, Hg, alkaline, and rare elements [9]. The thickness of the layer usually does not exceed 15–20 cm. "Blue clays" are underlain by the main volume of clays composed of minerals of the smectite group. They always contain pyrite, hematite, goethite, hydrohoethite, feldspars, quartz, chalcedony, illite- and chlorite-smectites; magnetite and titanomagnetite are observed. The chemical composition of deposits successively changes with depth: the concentration of SiO_2 increases, and the concentration of sulfur compounds decreases, which provides evidence for an increased role of alumosilicates in the composition of clay series. The base of the series is characterized by high contents of K_2O and other alkalis. This is most likely controlled by the formation of potassic feldspars and hydromicas in the lower layers.

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Each section of the Nizhne-Koshelevskaya thermal anomaly is unique. The surface layer with a thickness of up to 10–15 cm is the zone of mechanical and physical weathering with oxidation of ore minerals and precipitation of sulfates and native sulfur on the temperature barrier. The underlying series corresponds to the zone of carbonic acid leaching, but with a high concentration of pyrite, marcasite, and silica minerals. The horizon of blue clays is not distinguished in cooled areas, and its thickness varies from 0.1 to 1.0 m directly near fumaroles and in the walls of the boiling caldron. The depth of blue clay occurrence depends on the presence and thickness of the zone permeable for a vapor–gaseous jet. Thus, the sections of hydrothermal clays of the Nizhne-Koshelevskaya thermal anomaly are characterized by heterogeneity of mineral and chemical compositions (mosaic–block character of component distribution) and a high concentration of pyrite and silica minerals.

Microstructures of hydrothermal clays are inherited; finely dispersed pseudo-globular, domainlike, and globular–plate micro- and nanostructures composed of microagregates of nanoparticles of ferruginous smectite, kaolinite, and mixed-layered formations are typical for them (Figs. 1a, 1b). Blue clays are characterized by a high content of pyrite microcrystals of cubic shape with a face size of 0.5–1.0 μm. The study on an energy-dispersive spectrometer demonstrated the diversity of the cation composition of microcrystals and particles: Fe, Al, Mg, Ti, Mn, Ca, K, Na, P, F, and others were registered. The diagnostics of many minerals is complicated, which is explained by their small size and the formation of colloform structures typical for the initial stages of crystallization of silicate, as well as carbonate, sulfide, and other gels under hydrothermal conditions.

It is known that pyrite is one of the minerals concentrating ore elements in the epithermal polymetallic deposits [9]. Pyrite formation in the hydrothermal clay series of the geothermal fields basically occurs as complex aggregates. Pyrite crystals of cubic habit are associated with silica minerals in the vapor-permitting fracture zones. The low concentrations, heterogeneity, and spotted character of Au and Hg distribution in cross sections of pyrite grains (by the data of microprobe analysis) against the background of high concentrations of Au (0.1–1.0 ppm) and Hg (up to 10^{-3}%) in mineral monofractions, according to the results of atomic–absorption analysis, provide evidence for the presence of these elements in the native state in defect crystal structures. The study of pyrite using the atomic–force microscope demonstrated that the grain surfaces had a colloform nodular nanostructure with a segregation size from tens μm to several nm (Fig. 2). Ionic etching of pyrite grain surfaces and successive measuring of the composition at various depths confirms the presence of mineral film (of nonautonomous phase formation, by [10]), with a thickness of tens of angstroms, in which the concentration of Fe and S regularly increases, whereas O and C, decreases with depth; Si is present only in the upper part of the layer; and Ti was registered as well.

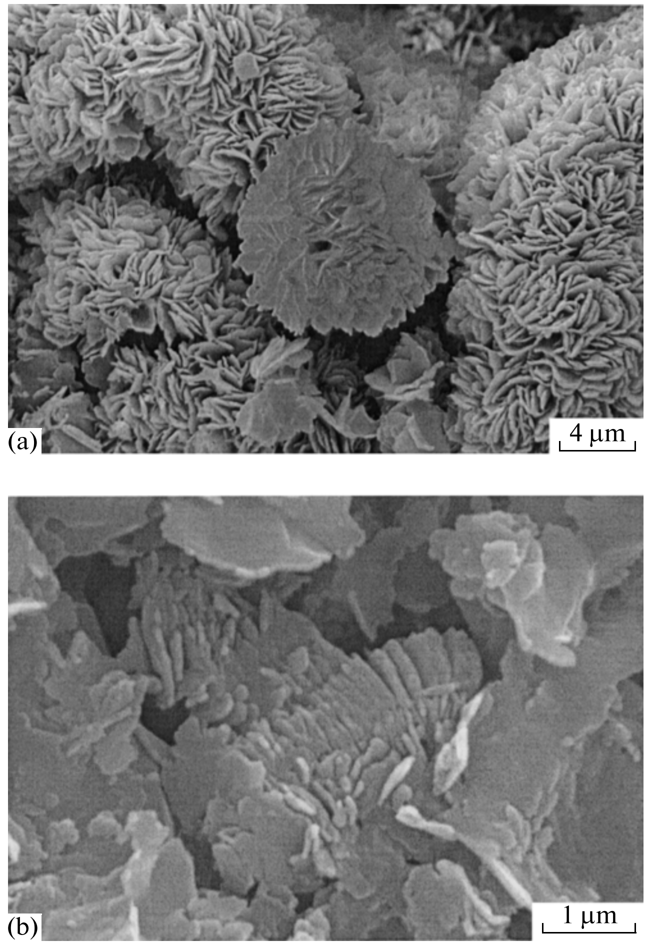

Fig. 1. Micro- and nanostructures of hydrothermal clays: (a) pseudoglobular microtexture of clay from the Verkhne-Pauzhetskoe thermal field composed of microaggregates of ferruginous smectite nanoparticles; (b) domain-like nanotexture of clay from the Nizhne-Koshelevskaya thermal anomaly composed of tabular kaolinite nanoparticles.

Hydrothermal clays forming practically complete series with an area of ≥1 km^2 and an average thickness of 1.5–1.8 m on the surface of geothermal deposits have complex chemical and mineral compositions. The composition of clays reflects the age of hydrothermal systems: immature (Nizhne-Koshelevskaya thermal anomaly) and mature (Pauzhetskoe deposit) are distinguished. The first are formed under the conditions of a high-temperature acid to ultra-acid gaseous–liquid medium with dynamically changing physicochemical parameters and in the presence of a direct link between hydrotherms and magmatic fluids. The second characterize the regressive stage of the hydrothermal system. Hydrothermal clays of this stage are characterized by continuous zonation and the formation of extensive horizon of blue clays. Blue clays

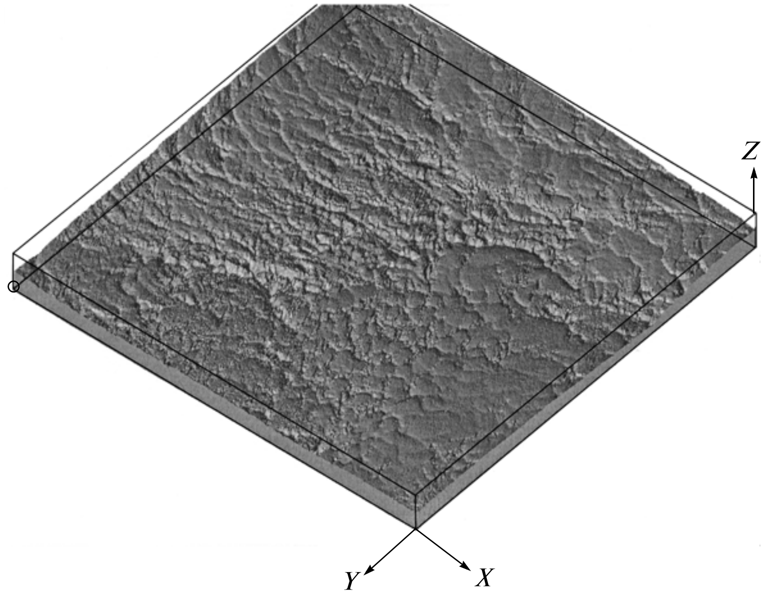

Fig. 2. Micro- and nanostructures of the surface of pyrite grain extracted from hydrothermal clays of the Nizhne-Koshelevskaya thermal anomaly. The length of sides is 3.75 μm by the *X* and *Y* axes; 1.748 μm, by the *Z* axis.

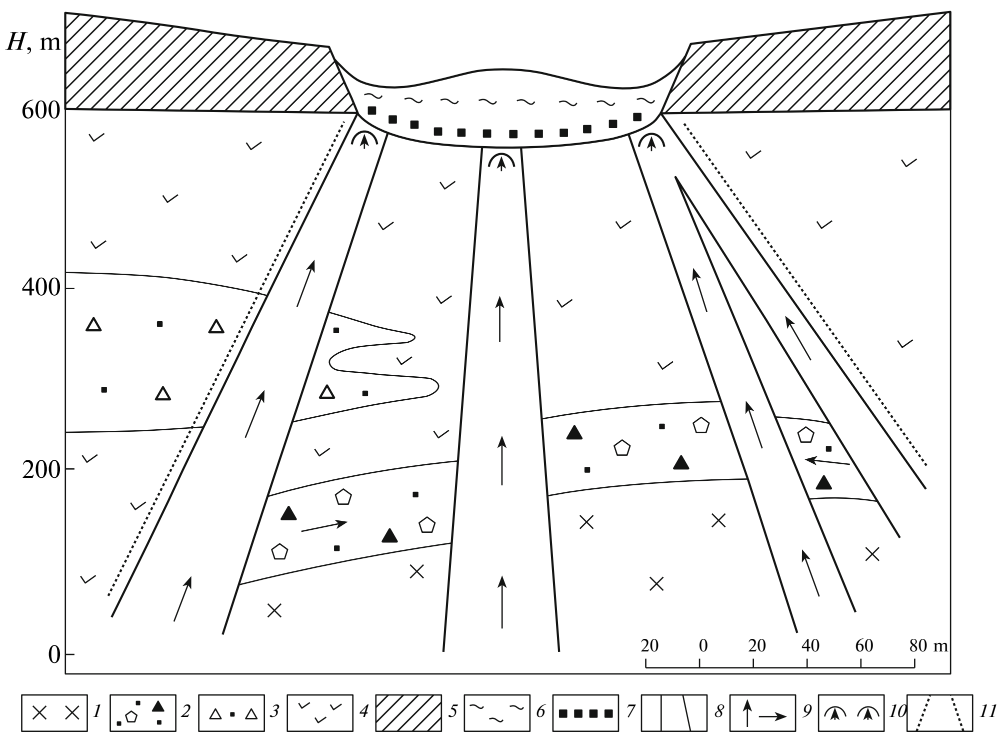

Fig. 3. Geological–geochemical model of the formation of the series of hydrothermal clays in the structure of the Nizhne-Koshelevskoe hydrothermal deposit. (*1*) Subvolcanic diorite body; (*2*) apical contact zone of diorite composed of breccias of various genetic types; (*3*) volcanogenic–sedimentary rocks; (*4*) andesitic lava series; (*5*) lavas of andesite and andesibasalt, which are the upper water barrier in the structure of the geothermal deposit; (*6*) hydrothermal clays; (*7*) thermodynamic and geochemical barriers; (*8*) zones of tectonic tensile dislocations; (*9*) directions of high-temperature gaseous–aqueous flow motion; (*10*) zone of the vapor/gas transition near the surface; (*11*) supposed boundary of the main modern zone of hydrotherm boiling over the hot subvolcanic diorite body, by [6].

are a geochemical barrier for Au, Ag, Hg, Cu, Pb, As, B, and others. Blue clays in argillizite of the immature type form layers with a thickness of up to 1 m at different depths and are located in the areas heated by circulation of vapor–gaseous jets. These argillizites are enriched in Au, Ag, Hg, and others most likely at the expense of high sorptive activity of colloid compounds of sulfides, silicic acid, and sulfur. Thus, the total series is a complex geochemical barrier at the stage of progressive evolution of hydrothermal systems. Redistribution of metals and other elements in the series of argillized rocks and their accumulation on the subaqueous geochemical barrier in blue clays most likely occur during system cooling.

Variability of the mineral composition, the great role of amorphous phases, and the high activity of cations (Fe, Al, Mg, Ti, Mn, K, Ca, Na, P, F, and others) with transition from amorphous to crystalline mineral phases are typical for hydrothermal clays of an immature type. Clay and other minerals are characterized by pseudoglobular, domainlike, globular–tabular, and colloform micro- and nanostructures reflecting the starting stage of the clay formation. Pyrite is one of the minerals concentrating ore elements. The high sorptive capacity of pyrite is most likely controlled by the formation of a specific mineral film on the crystal surface. High Ti concentrations are registered in the film composition that provides evidence for activity of this element under geothermal conditions. The study of hydrothermal clays allowed us to establish the link between deep fluid and near-surface gaseous–hydrogeochemical and mineralogical–geochemical processes (Fig. 3).

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