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Alkaline Mineralization in a Zone of Hydrothermal Unloading as the Indicator of Deep Metalliferous Fluid (Geothermal Systems of Southern Kamchatka)

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ABSTRACT

Formation of alkaline mineralization in a zone of rocks argillization is not typical case and represents the big scientific and practical interest at studying influence of deep fluids on geothermal systems and deposits. The authors group by means of wells drilling on East-Pauzhetka thermal field have allocated wide number of hydrothermal-metasomatic minerals under the hydrothermal clays: smectites, Fe-Mg chlorites, Ca-Mg carbonates, Ca-Na-K zeolites, potassium feldspar, opal and other silica minerals, phosphates, Fe-Zn-Cu sulfides, titano- and zirconosilicates and other complex mineral mixes. Mineral associations include ore phases, such as rare elements. The data obtained indicate an alkaline environment of mineral formation in the rocks at the base of hydrothermal clays of East-Pauzhetka thermal field. Such situation in the typical zone of acid leaching (argillization of rocks) can be created due to the acid-alkaline evolution of water-salt solutions by mix a deep alkaline highly mineralized (metalliferous) fluid with meteoric and acid waters.

1. INTRODUCTION

The behaviour of rare-earth and other metals during metamorphism and in a hydrothermal environment has been in focus of many scientists (Karpov et al., 2018; Pekov, 2005; Chudaev et al., 2016; Wood, 2003; et al.). Argillized rocks and hydrothermal clays widespread in volcanic areas and having special physiochemical (including sorption), geochemical and other properties evoke a great interest in connection with study of the mechanisms of transport and concentration of metals (Eroshev-Shak, 1992; Korobov, 1994; Osipov, Sokolov, 2003; Razumova, 1977; Hemley, Jones, 1964; Reyes, 1990). Discharge of alkaline solutions in the zone of rock argillization occurs quite rarely in the modern hydrothermal systems of volcanic island arcs (Rychagov et al., 2017) and it is probably a sequence of the influence of a reduced metalliferous fluid on the upper horizons of the earth's crust. The East-Pauzhetka thermal field serves as a model site used for study by a group of authors (Rychagov et al., 2017, 2018), whose additional results are presented in this work.

2. DESCRIPTION OF EAST-PAUZHETKA THERMAL FIELD

The East-Pauzhetka thermal field belongs to the flank of the Pauzhetka hydrothermal system and is situated on the western slope of the Kambalny volcanic ridge that is characterized as a resurgent tectonic magmatic high in the Pauzhetka volcanic-tectonic depression (The Long-Lived…, 1980). The thermal field is confined to a circular upstanding block of the Quaternary age and stretched along radial tectonic faults (Structure ..., 1993). The overall dimensions of the field are ≥ 250 × 500 m, and the hottest area contoured by the 20°C isotherm at a depth of 0.6-0.8 m is 100 × 200 m. Thermal manifestations are represented by steaming soils, steam-gas jets, mud-water boiling pots and warm ponds. The maximum temperatures of the waters that are discharged on the surface are 98°C, the temperatures of soils are 105-107°C, the temperatures of steam-gas jets are 108-109°C. The thermal waters are acid sulphate and low-acid hydrocarbonate-sulphate with a broad cation composition and a general mineralization that is not higher than 0.8 g/l. Steam condensate has a similar chemical composition. The soils are hydrothermal clays that form a continuous cover and stretch far beyond the boundaries of the present-day hot area (Rychagov et al., 2017).

3. LITHOLOGY OF HYDROTHERMAL CLAY MASS AND ITS BASE

The clay mass has a layered structure. The upper horizon is a typical sulphuric acid leaching zone. The clays are composed of kaolinite, hydroxides and Fe and Ti oxides, Fe-Ca-Mg-... sulphates, opal, and chalcedony. There are patches of the preserved pseudomorphic structure of block jointing of source rocks – lavas of andesites. The horizon thickness ranges from 50-80 cm in the hot area and reaches up to > 300-350 cm near boundaries. Below is a horizon with an average thickness of 150 cm composed of montmorillonite soft clays. It is characterized by a large number of lenses, films and thin streaks of opal and α-quartz dispersed in the main mass of pyrite. As described earlier (Rychagov et al., 2017), the horizon of soft clays acts as a water-confining stratum and a thermal insulator, and it plays a crucial role in the formation of mineral ore associations within the structure of the East-Pauzhetka thermal field. Two zones were penetrated under this horizon in Rudniy (“Ore”) area (from bottom to top): silicon-carbonate-sulphide and phosphate-alumosilicate-sulphide ones. Towards the western boundary of the field, the zones converge into a single zone with a more complex composition. A horizon of “dry” sulphidized clays is also extended along the strike of the thermal field. The deposits are smectite clays. The upper layers of the horizon are marked by transition from kaolinite to smectite with abundance of scattered coarsely crystalline pyrite (up to 2–3 mm) and semidecomposed andesite debris. Presence of fragments (up to 15–25 %

by volume) saturated with a siliceous substance is distinctive: they form interlayers, lenses, and “spots” in the main matrix. Most likely, the fragments were formed metasomatically through substitution of andesite debris by silica minerals, as well as smectites, etc. The deposits of the horizon near field boundaries are typical “blue clays” (saturated with sulphides), with the thickness of the horizon increasing.

The base of the clay mass is represented by metasomatic breccias and fissured andesites. This paper mainly focuses on description of hydrothermal and metasomatic alterations in these rocks. The breccias include rounded debris fragments of metasomatites over andesites; the cement is composed of hydrothermal minerals (opal-chalcedony-carbonates-zeolites-alumosilicate-sulphides-phosphates, etc.). In addition to the general alteration of the main mass, there are 3-5 to 20 cm thick zones (veins, streaks) composed of associations of secondary minerals. Fissured andesites are also intensively argillized and are broken up by quartz-carbonate-zeolite zones as well as by zones with more complex compositions. The extent of alteration, number and thickness of zones increase with depth, which is consistent with the geophysical data: rocks in this region of the section have an elevated electrical conductivity (Feofilaktov et al., 2017).

Core holes were drilled in the hot area of Vostochniy (“Eastern”) and in the relatively cold western boundary (Rudniy area) of the thermal field.

4. MINERALIZATION OF ROCKS IN CLAY MASS OF THE VOSTOCHNIY AREA

The rocks are almost completely altered and represented by a zeolite-carbonate-chlorite-silica-alumosilicate aggregate both in the main mass (in cement and fragments of breccia “debris”) and in interstices (**Figure 1**). Primary minerals include: plagioclases (An_{30-70}), titanium-containing augite, amphibole (hornblende), magnetite and titanomagnetite (TiO_2 - 1.9-17 wt. %), manganese-bearing ilmenite (MnO – 2.6-20.9 wt. %), chrome-bearing spinel (MgO – 3-6; Al_2O_3 – 8-18; Cr_2O_3 – 1-23.4 wt. %), single hypidiomorphic grains of quartz up to 1 mm in size with tiny inclusions of potassium feldspar (PFS). Ilmenite forms intergrowths with titanomagnetite, zircon and apatite. Titanium-calcium-siliceous mixtures, sphene and rutile are formed in place of primary titanium-bearing minerals, whereas zeolite is deposited in place of leached fragments. Spinelids are partially substituted by pyrite and often overgrown with pyrite rims. Probably, the extensive occurrence of Mg-Fe chlorite, PFS, quartz, calcite and zeolites can be attributed to the earliest hydrothermal-metasomatic transformations of rocks. Following minerals and mineral phases prevail among the later hydrothermal formations: calcium and sodium calcium zeolite, calcium and magnesium-carbonate, Fe-Mg chlorite, smectite, chlorite-smectite, alumosilicate formation of complex composition, siliceous alumosilicate and zeolite-chalcedony concretions as irregularly-shaped fragments. For the first time in study of the base rocks of the thermal field clays, the formation of relatively large (up to 0.1–0.2 mm) chalcopyrite precipitates and a high As content (up to 5 wt. %) in pyrite were identified. Ca hydrosilicate (possibly, okenite) – a rather rare hydrothermal mineral – was found for the first time too. It fills pores and fissures in association with quartz, calcite and zeolites. Apparently, the formation of Ca hydrosilicate reflects the most recent stage of hydrothermal alterations in the rocks of this area's section.

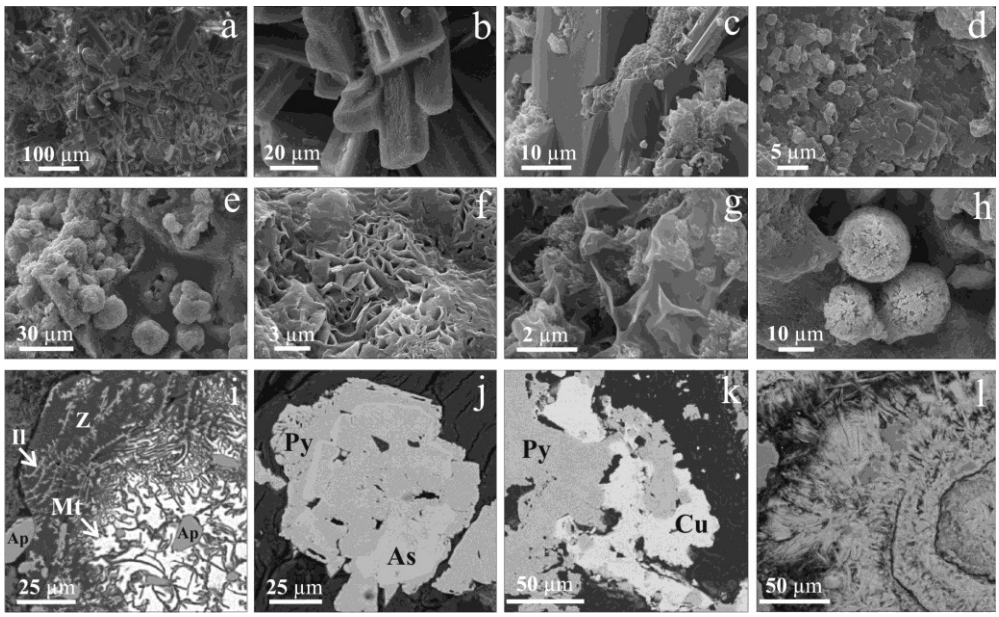


Figure 1. Micromorphology, alteration and formation of minerals at the base of the East-Pauzhetka thermal field clays – according to research data derived using LEO 1450VP SEM equipped with INCA EDS (a – h); and VEGA 3 SEM, equipped with X-MAX 80 EDS (i – l): a – Ca and Ca-Mg zeolites filling veinlets; b – zeolites in the “envelope” of smectite and smectite bridges cementing crystals of zeolites; c – dissolution of zeolite crystals and formation of complex alumosilicate composition aggregates; d – carbonate base of veinlet with the formation of separate grains of Ca-K-Na zeolite; e – silicon-magnesia concretions in the alumosilicate mass; f – siliceous-ferruginous cellular structures; g – the same with the formation of alumosilicate lumpy fragments at the contact of the cells; h – siliceous (opal?) balls in pores among siliceous-zeolite mass; i – altered ilmenite in accretions with F-apatite (Ap), titanomagnetite (Mt) – in the centre of the grain, dendrites of ilmenite (Il) and zeolite (Z) along the edges; j — heterogeneous As distribution in zonal pyrite; k – accretion of chalcopyrite (Cu) with pyrite (Py); l – zonal structures of calcium hydrosilicate.

5. MINERALIZATION OF ROCKS IN CLAY MASS OF THE RUDNIY AREA

The area is located in the region of transition from the hottest part to the cooling one of the East-Pauzhetka thermal field. Here, zones with phosphate-alumosilicate-sulphide and siliceous-carbonate-sulphide mineralization were detected under the horizon of soft clays (Rychagov et al., 2017). The section of the mass of hydrothermal clays is, in general, typical for this thermal field. The source rocks are represented by intensively altered and fissured andesitic lavas. Presence of hydrothermal zones (constituting more than 50 % of the thickness of the lower part of the section) completely filled with secondary minerals is distinctive. The composition of the altered rocks and hydrothermal zones is mainly the same as that of the Vostochniy area and is represented by zeolites, calcite and magnesium-bearing calcite, chlorites, opal, F-Cl-apatite. The primary ore phases have hardly remained: sphene, chlorite, pyrite and others have evolved upon them. Pyrite often contains As (up to 3-5 wt. %): arsenic is included in the composition of the bands localized along the growth zones of pyrite crystals or forms spot areas within its structure. At the same time, the secondary mineralization of this section differs significantly. The composition of zeolites is more diversified: potassium-calcium and calcium-potassium-sodium zeolites are formed against the background of prevailing Ca-zeolites. Smectites are sparsely present among alumosilicate, and Fe-Mg chlorites prevail sometimes with a more complex composition that apparently reflects transition to chlorite-illites and hydromica. Also, this section's hydrothermal zones feature the presence of siliceous-ferruginous "concretions" as veins, lenses, crushed fragments, strip-like rims around andesite debris. The quantity of this material sharply increases towards the base of the penetrated section and makes up to 50 % of the volume of the zones of hydrothermal alterations. The siliceous-ferruginous “concretions” are formed during the first stage of hydrothermal metasomatic transformations of the base rocks of the Rudniy area clay mass. During following stages, they are crushed, fractures are filled by zeolites, carbonates, quartz, sulphides and other minerals, fragments “dissolve”, ferrous iron transforms into ferric iron, and other processes occur.

6. CONCLUSION

On the basis of complex geological-geochemical and mineralogical studies, the following model of ore zone formation in the stratum of geothermal clays is suggested (**Figure 2**). In the hypergenesis zones of modern Pauzhetka hydrothermal system, bed rocks (andesite lavas) are altered into clays under the impact of acid sulphate and hydrocarbonate-sulphate waters. Long evolution of the field (probably, throughout the Holocene) resulted in the formation of a layer of ductile clays with the properties of the upper water-confining layer and heat-insulating layer. This served as an additional factor for formation of decompacted, penetrable for hydrothermae, zones in the basis of the clay stratum (as a rule, the basis of the stratum is confined to the foot or top of lava flows having a higher primary fracturing and brecciatedness of rocks). Introduction of a high temperature alkaline chloride-hydrocarbonate solution into the decompacted area caused its intense boiling, cooling and supersaturation with respect to silica minerals, carbonates, sulphides and formed the corresponding mineral association. Then, this solution mixed with near-surface sulphate waters, became supersaturated to other phases (phosphates, first of all) and phosphate-alumosilicate-sulphide association was formed. As a result, the ore vein with a distinct zone sequence formed. Apparently, the change of structure and complication of the ore vein composition along the strike from the thermal field's Central (hot) area to its boundaries and formation of the single zone can be attributed to a lateral spread of hydrothermae and further influence of an ascending alkaline hydrothermal fluid on the stratum of hydrothermal clays.

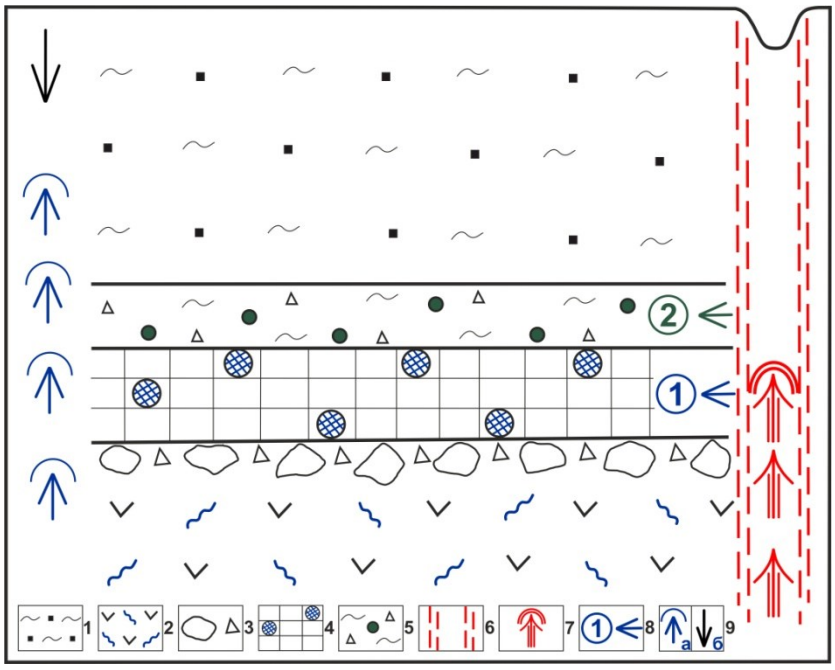


Figure 2. Model formation of hydrothermal clays and ore mineral associations: 1 – horizon of plastic clays, 2 – argillized rocks, 3 – andesite breccias, 4 – silicon-carbonate-sulphide zone with globules of same composition, 5 – horizon of “dry” clays with globules of phosphate-alumosilicate-sulphide composition, 6 – tectonic zone, 7 – metalliferous fluid, 8 – stages of mineral formation, 9 – sulphate waters: a – condensate of acid vapor, b – meteoric water.

The description of the mineral composition of the altered rocks and hydrothermal zones in the base of the clay mass of the East-Pauzhetka thermal field indicates a thorough transformation of the source rocks, an increase in temperature and alkalinity of the environment towards the base of the penetrated section. Mineralogical and geochemical zoning is distinguished as follows (from top to bottom): kaolinite-smectites → smectites → smectite-chlorites → zeolites-carbonates-chlorites → zeolites-illite-hydromica. The formation of the lower zones is related to the addition of alkaline and alkaline-earth elements (first of all, K and Ca) and some ore elements (As and, probably, rare-earth ones). Apparently, the formation of the zone sequence reflects the impact of an alkaline or a highly alkaline fluid on the argillization zone of the East-Pauzhetka thermal field.

The most probable source of phosphorous, alkaline elements, barium, arsenic, REE element and other rare elements are magmatic magma chambers of the Kambalny volcanic ridge.

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