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Nanoparticles and Nanostructures of Hydrothermal Clay Soils, South of Kamchatka Peninsula

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ABSTRACT

Nanomaterials are widely found in nature. Clay soils contain nanoparticles of clay and non-clay minerals, iron oxides, organic substance with sizes less than 100 nm, and they are typical representatives of natural nanomaterials. Samples of hydrothermal clays were derived from the East Pauzhetsky and Lower Koshelevsky thermal fields of South Kamchatka. The composition and structure of the samples were studied using x-ray diffraction analysis and a scanning electron microscope with a energy dispersive spectrometer. We found that hydrothermal clays contained areas composed of mineral nanostructures. The granulometric composition of the samples contained from 5-8 to 28-30% of nanoparticles. The mineral composition of nanofraction consisted mainly of kaolinite, illite, smectites and mixed-layer minerals of kaolinite-smectite, opal, iron oxides. Increase in fine particles in the clay leads to a sharp increase in the number of contacts between mineral particles, and as a result high level of porosity and increase in the specific surface area. The sorption capacity and hydrophilicity of newly formed clay soils improve and their plasticity increases. Moreover, the higher the degree of hydrothermal change of rocks and the higher the content of nanoparticles of clay minerals, the lower their permeability. All this determines the hydrothermal clays of thermal fields as the upper impermeable horizon and heat shield in the structure of geothermal deposits. The obtained data can explain the high physicochemical activity of such clays, as well as the concentration of the main ore, alkaline and rare-earth elements in them.

1. INTRODUCTION

Hydrothermal clays are one of the least studied types of clay soils. Nevertheless, they form sufficiently thick and extended masses in areas of Quaternary volcanism. In the Russian Federation, these include the regions of Kamchatka and the Kuril Islands. In addition, it is in our opinion of notable interest that these hydrothermal-metasomatic neoplasms carry a wealth of information about the nature of the interaction of hydrothermal systems with deep metal-bearing fluids (Rychagov et al., 2012).

The main factors determining the properties of rocks and soils are their composition and structure. For fine formations, such as clay soils, this is a micro- and nanostructure. Research conducted by the authors has shown that it is the characteristics of the composition, as well as the micro- and nano-design of hydrothermal clay soils, which determines their unique properties, the main of which is their high physicochemical activity. Hydrothermal clay soils are defined as the first horizon of the most intense argilization of rocks from the day surface, formed as a result of hydrothermal processing of volcanic rocks, developed within thermal fields - areas of natural near-surface discharge of hydrothermal solutions or vapor-gas mixture.

This study is the result of a synthesis of years of research on the composition, structure and properties of hydrothermal clays, selected from holes in 15 key areas of the thermal fields of the Pauzhetsk hydrothermal system and the Nizhne-Koshelevsky thermal anomaly (South Kamchatka).

2. MACRO STRUCTURE OF HYDROTHERMAL CLAYS

The mass of hydrothermal clays forms a continuous layer in thermal fields with an average thickness of 1.5-2.5 m, sometimes up to 5 m. A panoramic photo of the pit wall of hydrothermal clays in the Nizhne-Koshelevskoe thermal field is shown in Figure 1a. Hydrothermal clay masses are formed in the area of discharge of mineralized and often gas-saturated thermal solutions, which are formed under the influence of deep fluids. Two horizons are almost always distinguished from the top to bottom in hydrothermal clay masses: sulfuric acid and carbon dioxide leaching, characterized by different structure and mineral composition (Rychagov et al., 2012).

Clay soils in the zone of sulfuric acid leaching have an ocher-red color and breccia-like texture. The mineral composition is dominated by kaolinite. Soils are characterized by a block structure, between the blocks there is iron oxides, or thin crusts of silica minerals. In this horizon there are many pseudomorphs on the debris of the original rocks.

The clay in the carbon dioxide leaching zone has a greenish and bluish gray color. This zone has the largest thickness in the hydrothermal clay mass. The mineral composition is dominated by clay minerals of the smectite group and mixed-layer mineral kaolinite-smectite. It also contains pseudomorphs on the debris of the original rocks. A characteristic feature of the zone of carbon dioxide leaching is the presence of steaming areas, they are confined to the crust of pyrite microcrystals, marcasite and silica minerals. Such structures have increased fragility.

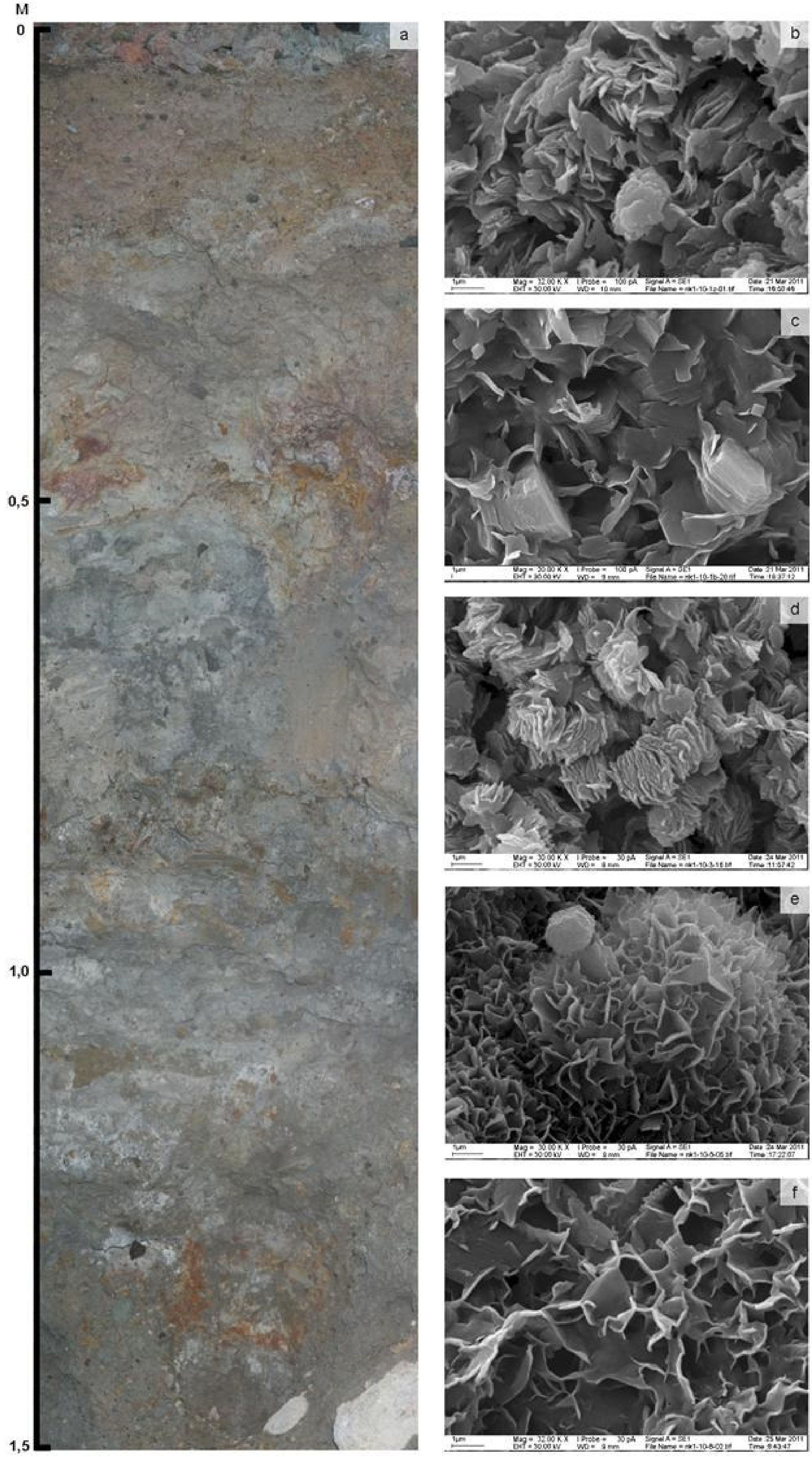


Figure 1. Panoramic photo of the pit wall of hydrothermal clays in the Nizhne-Koshelevskoe thermal field (a) and SEM images of nanostructures of hydrothermal clays (data derived using LEO 1450VP SEM equipped with INCA EDS) (b-f): b – domain-like nanostructure, c – honeycomb-domain nanostructure, d – domain-like nanostructure, e – globular-lamellar nanostructure, f – spongy nanostructure.

Between the upper and lower zones, the horizon of "blue clays" is often distinguished (intensively pyritized with other sulphides) with a capacity of 20-30 cm. It is formed on geochemical (thermodynamic) barriers and has a special structure: the predominance of smectite group minerals (mainly montmorillonite) in association with small (0.5-1.0 microns) pyrite crystals, the content of which reaches 10%.

The granulometric composition of hydrothermal clays is dominated by the clay and silt fractions (Figure 2), with the content of the clay fraction reaching 75-90%. However, in the natural composition, the clay fraction of such clays is completely aggregated, which is associated with increased acidity of the medium. With an increase in the depth of the ground, the content of the sandy and silt fractions increases.

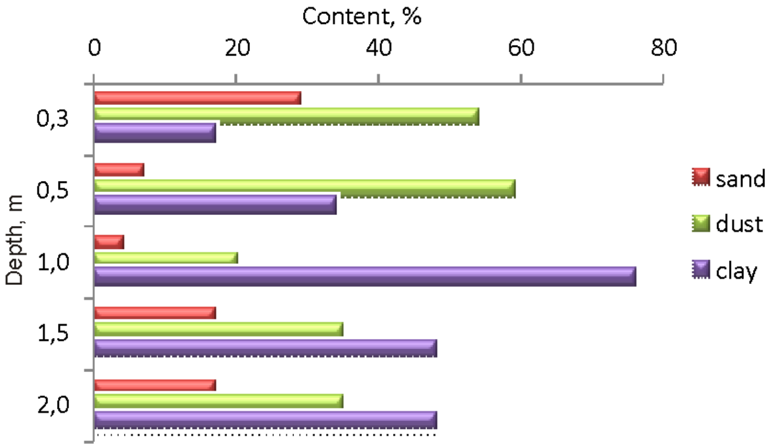
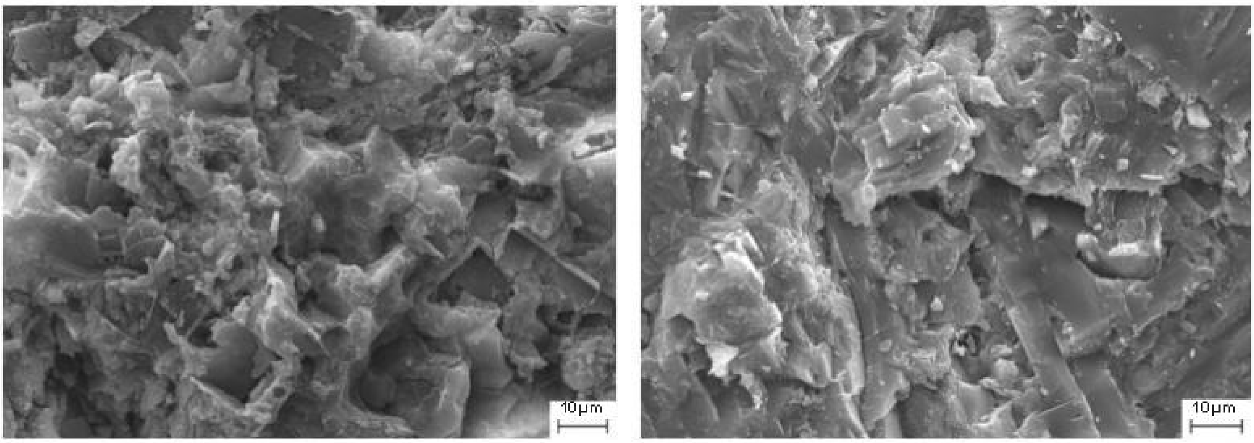


Figure 2. The granulometric composition of hydrothermal clays.

3. MICRO AND NANO STRUCTURE OF HYDROTHERMAL CLAYS

Micromorphological studies of the horizons of hydrothermal clay masses showed that the upper zone dominated by a domain-like nanostructure, folded with lamellar clay particles of kaolin pseudohexagonal shape, collected in a domain-like packs (Figure 1b,d). In some areas of the upper zone, where the content of mixed-layer kaolin-smectite-type formations become larger, where the honeycomb-domain nanostructure is typical (Figure 1c). Such nanostructure is composed of sheet-like clay nanoparticles of mixed-layer minerals forming a honeycomb network embedded with bundles (domains) of microaggregates of hexagonal kaolinite particles (Osipov and Sokolov, 2013).

The lower zone of hydrothermal clays is characterized by a globular-lamellar and spongy nanostructure. Globular-lamellar nanostructure is composed of microaggregates of clayey nanoparticles of ferruginous smectite, which are in contact with each other as a base-end at an acute angle (Figure 1e). Microaggregates have a rounded shape resembling globules, 2-10 microns in size. The spongy nanostructure is composed of sheet-shaped clay particles up to 2–3 μm in size, of montmorillonite composition (Figure 1f). The particles are in contact by a type of base-end and form a continuous honeycomb network. The matrix microstructure prevails to the base of the hydrothermal clay masses (Figure 3a): the matrices consist of randomly arranged clay particles and their microaggregates of smectite composition, in which sand and dust grains of primary rocks are immersed. At the base of the hydrothermal clays, the microstructure of the samples becomes indistinguishable from the microstructure of the original rock, for example, andesite (Figure 3b).



a **b**

Figure 3. SEM image of a fragment of hydrothermal clay from the base of the mass of clays (a) and andesite (b).

The “blue clays” horizon is characterized by a heterogeneous micro- and nanostructure, the surfaces of individual clay particles and microaggregates in them are growth zones of numerous small pyrite crystals.

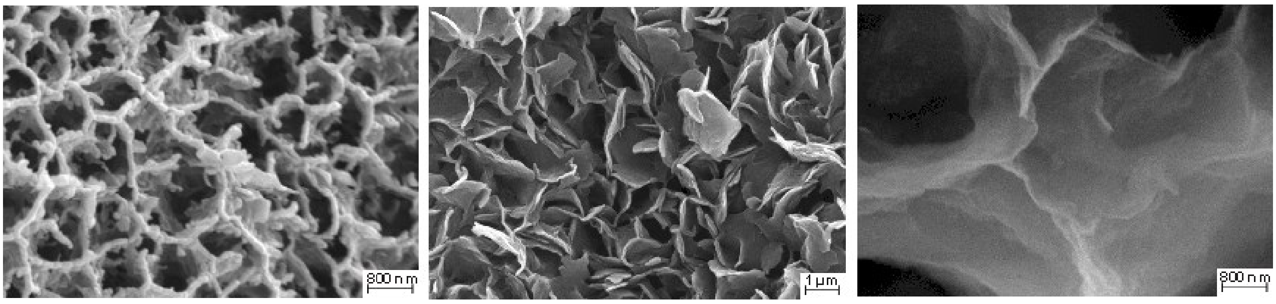
It should be noted that most samples of hydrothermal clay soils are characterized by a heterogeneous structure. Thus, in samples from the lower part of the section, a pseudo-spongy microstructure is present in some areas, while in others, a domain-like or honeycomb one is present. Such nature of the change in the type of microstructures is explained by the heterogeneity of the composition and structure of the original rocks, as well as the wide development of mixed-layer minerals in clays.

Quantitative analysis of the microstructure by SEM images (Osipov, Sokolov, 2013) using the STIMAN software (Sokolov at al., 2004), showed that large (10-100 microns) and small intermicroaggregate (1-10 microns) micropores predominate in the pore spaces of hydrothermal clays. Their contribution to the total porosity is significant and reaches 70%. The inter-ultramicroaggregate (0.1–1 μm) and interparticle (<0.1 μm) micropores constitute 15–25% and 1–3% of the total porosity, respectively.

4. NANOPARTICLES OF HYDROTHERMAL CLAYS

Special studies of the dispersed composition showed that all hydrothermal clays contain mineral nanoparticles (fractions <100 nm), the content of which in the upper part of the sections reaches 28-30% and decreases to its base to 5-8%. The study of the mineral composition of the fraction of nanoscale particles revealed the presence not only of smectite itself and kaolinite, as discrete clay minerals, but also of mixed-layer minerals such as kaolinite-smectite. Samples from the upper part of the section contained mostly particles with diameters ranging from 10 to30 nm, whereas samples from the lower part had diameters ranging from 70 to 90 nm.

Studies using SEM sediment ultrafine fraction (<100nm) showed that the nanoparticles form a honeycomb nanostructure (Figure 4). It is characterized by the presence of isometric open cells, whose walls are composed of microaggregates interacting in a base–base and end–base type with the formation of long-range and near-coagulation contacts (Osipov and Sokolov, 2013). The pore space is composed mainly of large intermicroaggregate pores of a cellular type, which have a rounded and less commonly isometric form. Prevailing microaggregates are leaf shaped. The surface of the microaggregates of the sample from the top of the section (Figure 4a) is covered with the smallest globular formations and film. According to the chemical and mineral compositions, these are the peculiar "shirts" of iron hydroxides and salts present in the composition of the fraction.



a b c

Figure 4. SEM images of nanofraction of hydrothermal clays: a – kaolinite, goethite and amorphous phase; b – kaolinite; c – smectite.

Our analysis of nanofraction demonstrated that the upper part of the clay mass has the maximum concentration of nanoparticles. At the same time, kaolinite is the predominant clay mineral in the upper zone of hydrothermal clays. Smectites and mixed-layer kaolin-smectite minerals become predominant with increasing depth. The content of smectite packages increases with depth in the mixed-layer kaolinite-smectite mineral. This can be explained by the initial stage of crystallization of kaolinite (low degree of crystallinity of kaolinite) and low content of SiO_2 minerals in the upper part. Moreover, despite the increase of smectite and mixed-layer minerals with depth, there is an increase of SiO_2 minerals as well, which can act as cement between particles and lead to the formation of phase contacts inside microaggregates.

Nanoparticles often form aggregates not only with relatively easily destroyed long-range coagulation contacts, but also with poorly hydrating — transient and phase contacts. Also, the content of Ca-montmorillonite increases with depth, the particles of which form rather large microaggregates. Ultimately, this leads to a decrease in the content of nanofraction to the base of the clay mass. As a result, clay is formed with a mixed type of contacts (phase and coagulation).

5. CONCLUSIONS

In the upper horizons of the hydrothermal clays of the thermal fields of southern Kamchatka, composed mainly of highly dispersed and highly defective kaolinite, a high content of ultrafine fraction was found, reaching 30%. At the same time, a highly porous domain-like nanostructure is formed in them, which causes a large specific surface area. This is determined by their high physicochemical activity, which is not characteristic of the group of kaolinite minerals.

The mineral composition of the lower horizons of hydrothermal clays is dominated by smectite group minerals, often represented by Ca-montmorillonite. Such particles of montmorillonite, which are organized in "cramped conditions", form dense anisometric microaggregates with strong interparticle bonds, and spongy microstructures. This leads to a low content of nanofraction. Despite the lower dispersion, relative to the kaolinite horizons, the high values of the physicochemical properties of the lower horizons with a high content of the smectite component are explained by the features of the crystal lattice of smectites with active interlayer centers.

Increase in fine particles in the clay leads to a sharp increase in the number of contacts between mineral particles, and as a result a high level of porosity and increase in the specific surface area. The sorption capacity and hydrophilicity of newly formed clay soils improves, their plasticity increases. Moreover, the higher the degree of hydrothermal change of rocks and the higher the content of nanoparticles of clay minerals, the lower their permeability.

Thus, our studies have shown that hydrothermal solutions when mixed with atmospheric water saturated with oxygen, intensively change rocks with the formation of hydrothermal clays with a high content of clay mineral nanoparticles. As a result of hydrothermal transformations, highly porous ultrafine mineral micro- and nanosystems are formed in the rocks, with a predominance of mixed type of structural bonds in them, which leads to an increase in physical and chemical activity, a decrease in permeability and in the strength of such rocks. All this determines the hydrothermal clays of thermal fields as the upper impermeable horizon and heat shield in the structure of geothermal deposits.

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