

Cation Migration in Hydrothermal Clays: The Problem of Mineralization Criteria in Gas–Hydrothermal Fluids of Hydrothermal Fields in Southern Kamchatka

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Received June 20, 2011

Abstract—Based on a comprehensive study of the hydrothermal clay layer that occurs in geothermal fields, the conditions of formation of cation composition in argillitized rocks are discussed. Under the influence of gas–water fluids and pore solutions, micro- and nano-mineral mixtures are formed in hydrothermal clays; these mixtures include crystalline, amorphous, and transitional mineral phases. A considerable role in their composition belongs to cations of several metals (Fe, Al, Ti, Na, Mg, Ca, K, Mn, and Ba), as well as Si, C, N, S, and volatiles (F[−] and Cl[−]). The sources of cations and other elements are unaltered host rocks, newly formed hydrothermal–metasomatic rocks, hydrothermal clays, salt deposits, siliceous, carbonate, and other sediments, as well as deep fluids. In the structures of geothermal anomalies and deposits the “hydrothermal metasomatic rock—gas–water fluid—newly formed mineral chemical compounds” united system is formed. Each of the elements of this system takes part in the transportation, accumulation, and redistribution of metals. This approach to studies of the geochemistry of present-day geothermal systems may serve as a foundation for developing criteria for the presence of mineralization in metasomatites, gas–hydrothermal fluids, and new mineral associations.

DOI: 10.1134/S0742046312040069

INTRODUCTION

The problems of mineralization in present-day hydrothermal solutions, steam hydrothermal occurrences, and volcanic and geothermal gases have been given much space in works by many scientists [Aver'ev, 1966; Arsanova, 1974; Baskov and Surikov, 1975; Gol'eva, 1974; Zelenov, 1974; Ivanov, 1960; Karpov, 1988; Kononov, 1983; Lebedev, 1980; Menyailov and Nikitina, 1974; Nikitina, 1978; Ozerova, 1965; Piip, 1937; Polyak et al., 1979]. Evaluation of the mineralization in different volcanogenic rock associations and the facies of metasomatites and hydrothermally altered rocks has been the basis of many research works [Vasilevskii, 1973; Korzhinsky, 1982; Smirnov et al., 1974]. S.I. Naboko was the first to formulate and substantiate the thesis of the necessity of simultaneously studying mineralization in present-day hydro-

thermal solutions and in precipitating sediments and metasomatites that form under their influence. This will help us to solve one of the most difficult problems in mineral and ore development in the areas of the present-day and Quaternary volcanism [Naboko, 1980].

Although this problem has been discussed by many specialists, it is far from solved. Thus, evaluation of mineralization in natural waters and hydrothermal metasomatic rocks based on the principle “a high level of mineralization means metalliferous, little mineralization means not metalliferous” is dominant; the threshold criteria for cation concentrations of even the formal type are not defined. But in the areas of present-day volcanism hydrothermal solutions with extremely low general mineralization (from dozens to a few hundred mg/L), and consequently, low concen-

trations of trace elements, prevail. The same is true for metasomatites and salt deposits. To determine the mineralization in solutions and corresponding sediments S.I. Naboko classified types of water using the well-known hydrochemical and geochemical classifications by V.V. Ivanov, V.I. Kononov, G.I. Arsanova, and others, and noted the specialization of waters for certain trace elements [Naboko, 1980]. However, in each case, for a concrete hydrothermal system or a geothermal field, the problem of which solutions, gases, metasomatites, and neogenetic associations should be considered as metalliferous and which should be considered "barren" is still urgent. Discussion of this problem constitutes the basis for solving the problem of the interrelationships between present-day and ancient mineralizing hydrothermal systems.

In order to obtain criteria for the evaluation of the "gas–solution–neogenetic mineral–metasomatites" system we turned our attention to the migration of cations and anions in a highly dynamic system, viz., the hydrothermal clays of geothermal fields. Our consideration is based on and develops the ideas of S.I. Naboko and other workers using a great amount of recently obtained data, as well as new experimental and analytical possibilities.

THE GEOLOGICAL STRUCTURES OF THE STUDIED OBJECTS

Our studies were carried out using the example of the Pauzhetka–Kambalny–Koshelev geothermal (ore) area, which belongs to the South Kamchatka geothermal province and occurs at the junction of the three volcanic belts of Kamchatka. The area is identified as a long-lived (from the Early Oligocene to Holocene) volcanic or volcanogenic mineralization center [*Dolgozhivushchii tsentr ...*, 1980; *Prognoznaya otsenka ...*, 1977]. The direct objects of studies are the Pauzhetka and Nizhne-Koshelev geothermal deposits and the larger geothermal anomalies (fields): Nizhne- and Verkhne-Koshelev, Verkhne- and Vostochno-Pauzhetka; and Severo-, Tsenral'no- and Yuzhno-Kambalny. Detailed geological descriptions of these structures can be found in [Belousov, 1978; *Pauzhetkie ...*, 1965; Rychagov et al., 2008, 2009; *Struktura ...*, 1993]. The Pauzhetka geothermal deposit is classified as a water-dominated one. In spite of the high temperatures of hydrotherms in the lower water-bearing horizon (up to 220°C at depths of 600–900 m), the evolution of gas–hydrothermal fluids and metasomatic processes is regressive in character [Rychagov, 2003; *Struktura ...*, 1993]. The natural thermal fields, Verkhne- and Vostochno-Pauzhetka, are located in the structures of the neotectonic tectono-magmatic uplifts and reflect the geochemical and physico-chemical regimes in boiling hydrotherm zones up to 150–200 m thick, which have been identified in the depths of these geological blocks [Zhatnuev et al., 1996]. The Nizhne-Koshelev geothermal field is

a steam-dominated one; it is the only such field among the drilled fields of this type in Kamchatka [Pisareva, 1987]. The zone of overheated steam, with an estimated power yield of ≥ 90 MW_e, widens to a depth of over 1500 m and is spatially connected with the dome-like protrusion of a hypabissal diorite body. Geothermal boreholes have penetrated the following zones of this protrusion (from bottom to top): diorites (more than 150 m), diorite porphyries (200–300 m) and a breccia mantle from 100 to 200 m thick. The geological, geophysical, hydrodynamic, and isotope–geochemical data set point to the role of this multiphase hypabissal complex as a source of deformation strain and heat at the paleo- and the present-day evolution phases of the geological structure. The evolution of the paleo-hydrothermal system is observed in the zonal distribution of facies of the secondary minerals: in the apical zone of the hypabissal body, secondary quartzites occur; towards the top they are replaced by mid- and low-temperature propylites of quartz–chlorite–hydromica composition. The rising stream of the present-day gas–hydrothermal fluids tends toward this hypabissal body and is probably related to it paragenetically. At the ground surface, due to the interaction of rising fluids with host water-bearing rocks, a geothermal anomaly $\geq 300 \times 500$ m in extent with a heat power of 25000 kcal/s is formed [Vakin et al., 1976]. In general, the Koshelev hydrothermal–magmatic system has high thermodynamic parameters, is connected to a magmatic supply source, and corresponds to the progressive phase of evolution [Rychagov, 2003].

THE PHYSICAL AND CHEMICAL CONDITIONS FOR THE DISCHARGE OF STEAM HYDROTHERMALS IN THERMAL FIELDS

On the surface of the Pauzhetka and Nizhne-Koshelev hydrothermal fields acidic and faintly acidic sulfate waters of mixed cation compositions (Ca–Na–Mg–K) and hydrocarbonate–sulfate ammonium waters are formed [Rychagov et al., 2008]. The mineralization of waters that are formed at the surface rarely exceeds 1 g/L. Alkaline-metal and alkaline-earth specializations of the geothermal area waters are known [Pampura, 1985]. The deep waters are alkaline-metal boron chloride–sodium with mineralization ≥ 3 –5 g/L or alkaline-earth hydrocarbonate-calcic. The latter solutions characterize the zone of water mixing at depths of more than 500–1000 m in the structure of the Nizhne-Koshelev field. All the waters (of deep, mixed, and surface waters) typically contain dissolved and colloidal silicic acid. The colloidal form plays a significant role in precipitation of sediments on the surface of the thermal fields and in the saturation of argillitized metasomatites with siliceous minerals [Rychagov et al. 2006]. Natural waters that discharge on the surface of the Kambalny Ridge and Nizhne-

Koshelev thermal anomaly are formed with the participation of deep fluids, which is supported by a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and high concentrations of Au, alkaline metals, and rare earth metals [Struktura ..., 1993]. The waters of the Puzhetka thermal fields are formed in the course of active interaction of mixed steam-heated sulfate–hydrocarbonate–calcium waters with rocks and hydrothermal clays, which determines their diverse composition and relatively high mineralization (up to 1.0–1.5 g/L). The gases include CO_2 (which usually dominates), H_2S , SO_2 , HCl , HF , H_2 , CO , CH_4 , and N_2 [Lebedev and Dekusar, 1980; Pozdeev and Nazhalova, 2008]. Carbon dioxide, hydrogen sulfide, and sulfur dioxide are the most typical gases in the steam hydrotherms that discharge on the surface of the Puzhetka geothermal field. Among the gases of the Verkhne-Koshelev thermal anomaly, the sum of acidic gases dominates, attesting to the presence of a shallow hot magmatic body in the erosional funnel of Valentin Volcano. The latter is an extrusive–hypabissal complex and is responsible for the present-day steam–gas activity. In the Nizhne-Koshelev thermal anomaly, in addition to CO_2 in dissolved gases, one also notes high concentrations of methane (up to 67 vol %) and heavy hydrocarbons [Vakin et al., 1976; Pozdeev and Nazhalova, 2008]. The isotope composition of helium attests to the deep character of the geothermal heat source and to the rising fluid flow in this part of the Koshelev volcanic massif [Kononov, 1983; Polyak et al., 1979].

A cover of hydrothermal clays is actively formed on the thermal fields. It has been ascertained that this “independent” geological body plays an important role in the structure of hydrothermal fields as the upper aquiclude and heat insulator, as well as a complex and highly dynamic geochemical barrier [Rychagov et al., 2009, 2008]. We previously studied the chemical and mineral compositions, properties, and conditions of formation of hydrothermal clays in all the above-mentioned geothermal fields in detail. In the present paper, we pay attention to the peculiarities of the micro- and nano-structures of these specific rock associations in connection to processes of cation replacement in the minerals of hydrothermal clays.

THE MICRO- AND NANOSTRUCTURES AND CHARACTERISTIC FEATURES OF THE COMPOSITION OF HYDROTHERMAL CLAYS

In general, the hydrothermal clays that occur on the surface of geothermal fields are characterized by chemical, geochemical, and mineralogical zonalities: the upper layer (≥ 30 –40 cm thick on the average) consists of products of sulfuric acid leaching, the lower layer (as a rule more than 100–150 cm thick) is made of products of carbonic acid leaching [Eroshchev-Shak, 1992; Korobov, 1994; Naboko, 1980]. We dem-

onstrate that such a zonality takes place for hydrothermal systems at a regressive stage of development and, partly, at an extreme one. During the progressive stage of hydrothermal field evolution, zonality can be identified only for some individual localities and concrete sections; hydrothermal clays are saturated with pyrite, colloids of sulfides and silicic acid, and siliceous minerals [Rychagov et al., 2010].

According to the data of qualitative mineralogical analysis performed by the standard radiographic method, the sequence of hydrothermal clays in the Nizhne-Koshelev thermal anomaly is dominated by minerals of the smectite group. Mixed-layer formations of the kaolinite–smectite type are observed in the upper horizons.

Studies of the characteristics of the micro- and nanostructures, as well as of the chemical and elemental compositions of clays, were carried out using an LEO 1450VP scanning electron microscope equipped with an INCA 300 energy dispersive spectrometer. Such studies indicated that the clay deposits of the Nizhne-Koshelev thermal anomaly are characterized by domain-like nanostructures that are composed of associations of axial-oriented nano particles of mixed-layer kaolinite–smectite minerals (Fig. 1a). The micro- and nanostructures of the hydrothermal clays of the Puzhetka field are of an inherited character and can be classified as belonging to the globular–lamellar type. Reworking of volcanic glass fragments produced globules with a diameter of ≤ 8 –10 μm . These consist of lamellar nanoparticles of smectite composition with a high iron content (see Fig. 1b). The presence of numerous pyrite crystals of cubic syngony with facets of ≤ 1 –4 μm is also notable. The “blue clays” that formed at geochemical (thermodynamic) barriers have a special structure, viz., pyrite crystals 0.5–1.0 μm in size in association with clayey minerals and silica form the carcasses of these clay structures [Rychagov et al., 2010].

Studies of certain fragments of clays using an energy-dispersive spectrometer indicated the considerable variety of cations, viz., Fe, Al, Mg, Ti, Mn, Ca, K, Na, Ba, Ni, and P, as well as F, Cl and other volatiles, were found. Figures 2a and 2b display some of the results of chemical microprobe analysis at individual spots of the microstructures of hydrothermal clays. Diagnostics of many minerals is hampered or practically impossible because of the extremely small sizes of particles and the formation of colloform and different transition structures that are characteristic of the initial phases of crystallization of silicate, carbonate, sulfide, and other gels. The diversity of cation composition is observed at the sites of clays that are composed of micro- and nanomineral mixtures that consist of crystalline, amorphous, and transitional phases. The chemical compositions and properties of the transitional structures differ considerably from those of the crystalline ones. Mineral mixtures, especially amorphous and transitional phases, are most typical of the

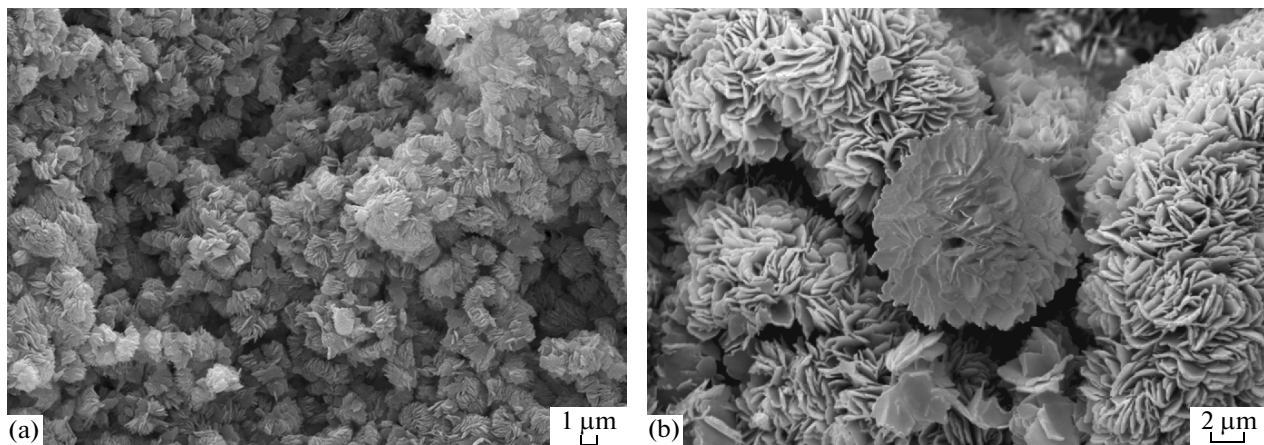


Fig. 1. Typical micro- and nanostructures of hydrothermal clays of the Nizhne-Koshelev thermal anomaly (a) and the Verkhne-Pauzhetka thermal field (b).

Nizhne-Koshelev thermal anomaly, where the compositions and structures of hydrothermal clays are actively formed under the influence of rising high-temperature gaseous–hydrothermal flows. The mineral composition of the hydrothermal clays of the “mature type” that form under the conditions of the Pauzhetka geothermal field is more persistent across sections and consists of crystalline mineral phases (table) against the background of a similarly broad range of cations. The replacement of cations in minerals of the montmorillonite–kaolinite family and the formation of large amounts of crystalline and probably transitional mineral phases within the group of layered silicates occurs [Godovikov, 1975]. New mineral phases are actively formed not only in the basic matrix of clays but also on pyrite crystal facets (Figs. 3a, 3b). However, on the surface of pyrite crystals from hydrothermal clays of the Nizhne-Koshelev thermal anomaly no neogenetic minerals are usually detected at the level of sensitivity and resolving power of analysis techniques available.

MINERAL FORMATION ON THE SURFACES OF PYRITE GRAINS

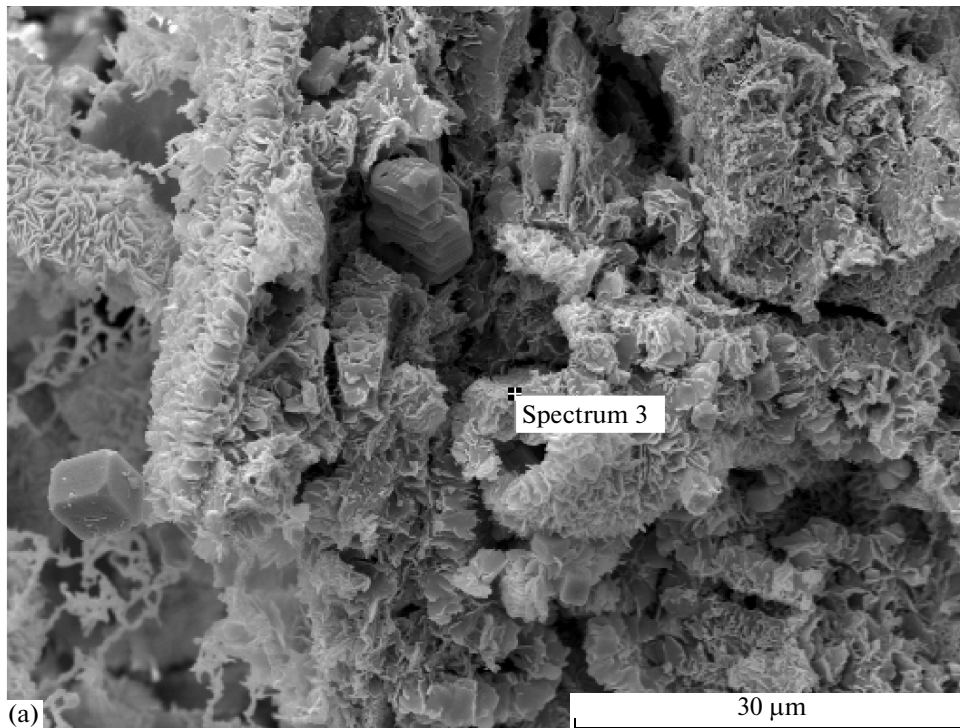
The compositions of pyrite grain surfaces that form in the hydrothermal clays of the Nizhne-Koshelev thermal anomaly were studied using the methods of X-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES); the first results were presented in [Rychagov and Shchegol'kov, 2011]. The spectra were taken using an Las-3000 instrument (Riber Co.) equipped with an OPX-150 hemispherical analyzer of photoelectrons with retarded potential and an OPC-200 Auger-electron spectrometer of the “cylinder mirror” type. The vacuum in the analytical chamber was 5×10^{-9} mm of mercury. Electron stimulation was performed by X-ray emission from an aluminum anode Al $K_{\alpha} = 1486.6$ eV with a voltage at the

tube of 12 kV and an emission current of 20 mA. Photoelectron spectra were calibrated on the basis of the C1s peak with a binding energy (E_b) of 285 eV. Auger spectra were recorded in the differential form $dN(E)/dE$ at an energy of the initial electron beam of 2.5 keV and a modulation voltage of 2.3 V.

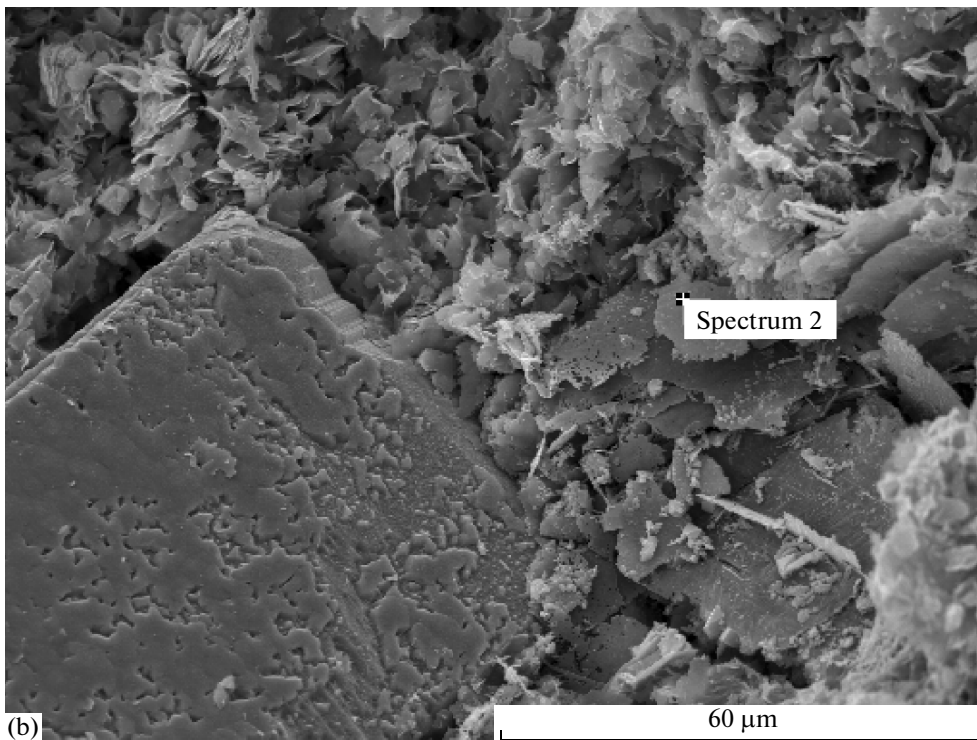
Mono fractions of 0.1–0.63 mm pyrite crystals were selected for analysis. These were mounted on a two-side carbonaceous sticky electroconductive band and placed in an analytical chamber. RFE spectra were obtained for selections (from 500 to 700 pieces) of pyrite mono fractions that were separated from different parts of the sequence sections of the hydrothermal clays. Auger spectra were taken from the surface of individual pyrite crystals, in some cases by using surface etching by argon plasma at an electron beam energy of 2 keV and an emission current of 20 mA.

The XPS and AES methods have a high localization capacity in depth (0.5–5 nm depending on the conditions of spectra recording) and allow analysis of the chemical compositions of thin layers and films on a sample surface. One typical feature of pyrite grains is the presence of high N, Ti, and Si concentrations in surface layers. XPS data show that Ti and N are not chemically bonded, but are different chemical compounds on the surfaces of pyrite grains. Ti occurs as dioxide (TiO_2), N is in reduced form (bonds N–H and C–N), and Si may occur either in silicate form or as amorphous silica.

The auger spectra indicate a sharp decrease of the Si peak intensity (down to background values) and a decrease of the peak at 387 eV in the area of superimposition of Ti and N lines in the process of ionic etching of a pyrite grain surface over 40 minutes. This may happen in the case of a simultaneous (coordinated) decrease in the concentrations of Si and of one of the two above-mentioned elements. Titanium is such an element. Si and Ti are related (lithophile) elements; the oxidized state of Ti is in better agreement with the



Oxides	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	FeO
wt %	1	4	25	59	1	1	1	8



Oxides	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	TiO ₂	FeO
wt %	12	9	5	1	72	1

Fig. 2. Microstructure and chemical composition of hydrothermal clays. (a) Fragment of a microstructure composed of micro-aggregates of clay mineral particles of the kaolinite–montmorillonite type; (b) mineral particle of complex composition dominated by titanium.

The quantitative mineral compositions of the hydrothermal clays of the Verkhne-Pauzhetka thermal field and the Nizhne-Koshelev thermal anomaly

Sample	Depth of sampling, cm	General characteristic of material	Montmorillonite	Mixed-layer (kaolinite–smectite)	Pyrite	Cristobalite	Heulandite	Amorphous oxides
VxPP-1/07-1	0–10	Limonitized clays	64.7	33.2	2.1	–	–	–
VxPP-1/07-2	10–15	Transition to “blue clays”	74.1	25.1	0.8	–	–	–
VxPP-1/07-3	15–30	“Blue clays”	62.3	33.7	4.0	–	–	–
VxPP-1/07-4	30–35	Transition to montmorillonite clays	82.9	15.9	1.2	–	–	–
VxPP-1/07-5	35–55	Montmorillonite clays	99.6	–	0.4	–	–	–
VxPP-1/07-6	55–60	Montmorillonite clays	85.5	13.6	0.9	–	–	–
NK-3/08-1	5–30	Limonitized and kaolinized clays	–	76.9	–	–	–	23.1
NK-3/08-2	30–50	“Blue clays”	69.3	–	0.2	5.7	1.5	23.3
NK-3/08-5	95–115	same	81.9	–	2.0	–	–	16.1
NK-3/08-7	135–155	same	70.6	–	9.3	–	–	20.1
NK-3/08-8	155–175	same	84.5	–	2.4	–	–	13.2
NK-3/08-9	175–195	same, with hematite	94.0	–	1.5	–	–	4.4
NK-3/08-13	260–280	Montmorillonite clays	83.2	–	1.6	–	–	15.2

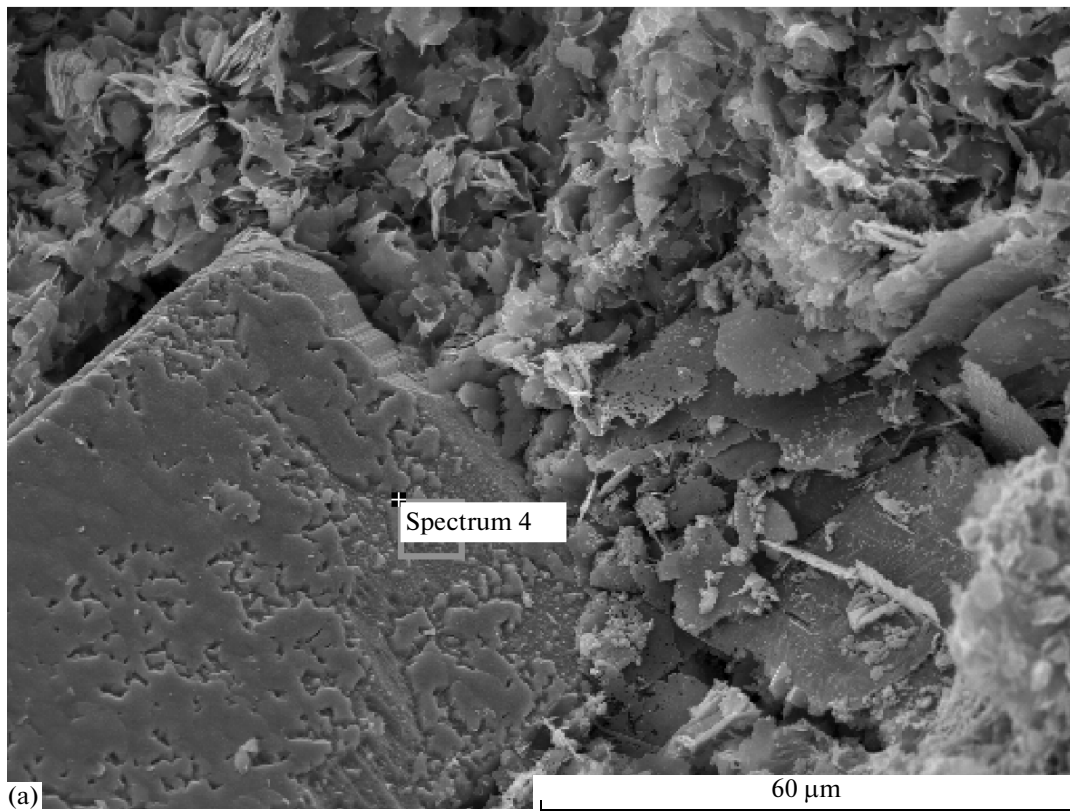
VxPP-1/07 is a pit that was dug in the central part of the Verkhne-Pauzhetka thermal field. NK-3/08 is a pit that was dug in the Verkhni locality of the Nizhne-Koshelev thermal anomaly. The data were collected by V.V. Krupskaya of the Faculty of Geology at Moscow State University.

oxide–silicate layer than reduced nitrogen. Formation of poorly soluble hydrates $n\text{TiO}_2 \cdot m\text{H}_2\text{O}$ is more characteristic of titanium. Due to this, simultaneous precipitation of titanium and silicon is likely. Here, nitrogen in a reduced form (for example, bound in ammonia, as is typical of steam hydrotherms in the Nizhne-Koshelev geothermal field) doesn't form chemical compounds with SiO_2 . Based on the etching time and the average rate of sputtering of silicates and silica (1.5 \AA/s), the oxide–silicate layer is no thicker than a few hundred nanometers [Rychagov and Shchegol'kov, 2011]. Obviously, Ti and Si enter in one mineral phase of a film type that is segregated on the surfaces of pyrite grains.

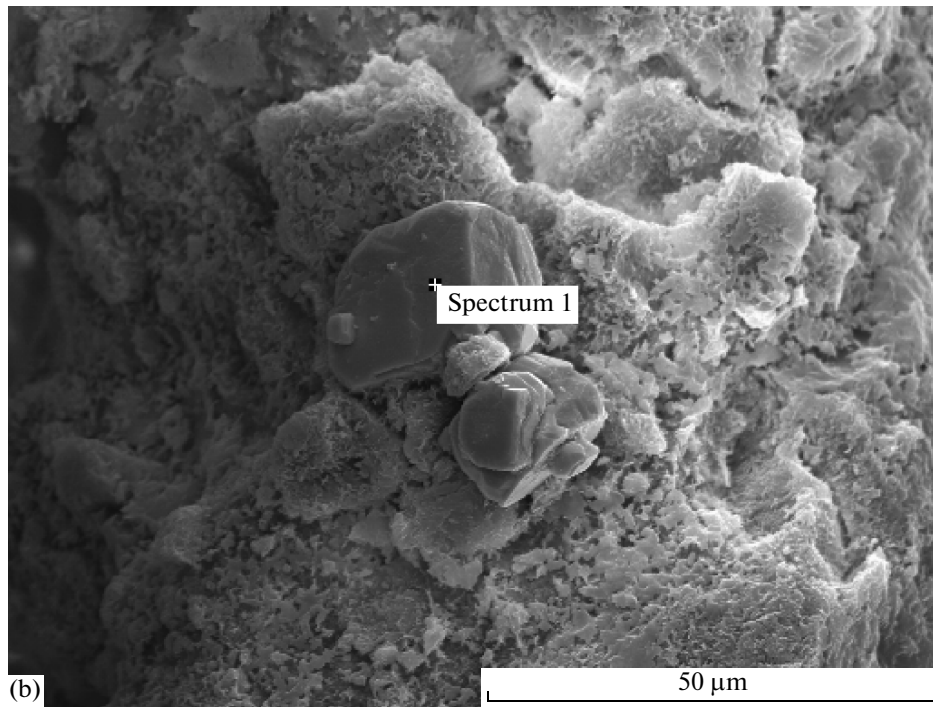
The S2p photoelectron spectra of all the analyzed samples of pyrite monofractions show two peaks in the intervals E_b of 167–168 eV and 160.5–161.5 eV, the first of which corresponds to the intermediate state of sulfur between sulfate and sulfide (Fig. 4). The second peak has a larger half width, possibly indicating the presence of two sulfur forms: monosulfide and probably disulfide. Earlier, V.L. Tauson and his colleagues

discovered sulfur in disulfide, monosulfide, and, rarely, polysulfide forms on the natural surface of synthesized and natural pyrite, and also showed the presence of a pyrrhotite-like non-autonomous phase [Tauson et al., 2008, 2009a]. The latter is typical of hotter and deeper (mesothermal) ore deposits [Tauson et al., 2009a]. Apparently, for the pyrite that has segregated from hydrothermal clays of the Nizhne-Koshelev thermal anomaly due the influence of deep fluid, we may also suppose the presence of a pyrrhotite-like phase in the thinnest mineral film on the pyrite grain surfaces, which also agrees with the presence of reduced nitrogen in film composition.

The Fe2p spectra involves two peaks in the intervals Eb 707.5–709 eV and 711–712.5 eV which, when considered along with the above data on the chemical composition of sulfur, is interpreted as a result of the presence of Fe thiosulfate on the pyrite grain surface. This is an uncommon situation. As a rule, the oxidized surface of pyrites is dominated by oxysulfate (Eb S2p = 168–170 eV) chemical compounds of iron, while the quantity of sulfide ions (Eb S2p = 160–162 eV) is insignif-



Oxides	Na ₂ O	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	TiO ₂	FeO	NiO
wt %	1	4	3	47	1	3	38	3



Oxides	SO ₃	FeO
wt %	74	26

Fig. 3. Typical microstructures and chemical composition of the surfaces of pyrite grains that were segregated from hydrothermal clays of the Verkhne-Pauzhetka thermal field (a) and the Nizhne-Koshelev thermal anomaly (b).

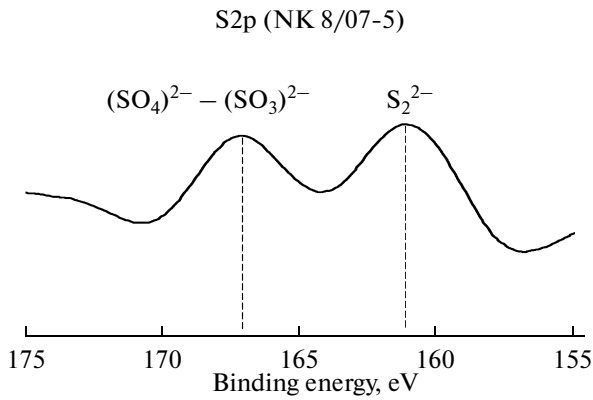


Fig. 4. S2p photo electron spectra demonstrating the chemical state of sulfur on the surfaces of pyrite grains, the Nizhne-Koshelev thermal anomaly (section NK-8/07, bed 5). For other explanations, see the text.

icant. The thiosulfate ion probably results from “soft” oxidation of pyrite by hydrosulfite ion (HSO₃⁻); pyrrhotite (FeS) may oxidize in a similar manner. In harsher environments (oxidation by oxygen dissolved in water) oxidation continues until sulfates are reached [Busev and Simonova, 1975]. The stability of thiosulfate ions may occur via the reduction potential of the environment. For example, the thiosulfate of iron is found on the pyrite grains of the Sukhoi Log deposit, which is characterized by reduction conditions of mineralization [Tauson et al., 2009]. The reduction properties of fluids in the Nizhne-Koshelev thermal anomaly are suggested, as shown above, by non-oxidized form of nitrogen that are identified on the surfaces of pyrite grains under the titanium-bearing oxide–silicate layer.

Studies of pyrite using a CMM-2000-15 atomic-force microscope showed that the mineral films that were identified are of colloidal kidney-shaped, kidney pseudo-globular, etc. micro- and nanotextures (Fig. 5). These textures reflect connection of the present-day mineral sediments with hydrotherms whose compositions contain slightly soluble chemical compounds of several cations in a colloidal state. Therefore, the surface of pyrite grains segregated from hydrothermal clays of the Nizhne-Koshelev thermal anomaly is covered with a mineral film with a thickness from several nm or less to hundreds of nm. This film is of layered structure and has different chemical compositions, with the upper layer being a titanium-bearing oxide–silicate phase and the lower consisting of thiosulfate complexes of iron with reduced nitrogen. The film serves as a kind of buffer in the “mineral–solution–gas” system; its formation probably reflects the influence of reduced fluids on the near-surface horizons of the geothermal field.

THE SOLUBILITY OF SOME SULFIDES AND THE TRANSPORT OF METALS IN AN AQUEOUS ENVIRONMENT

The minerals formed by transitional metals (including Fe, Ti, Au, and Hg) in most cases are poorly soluble chemical compounds. In spite of the fact that the total concentrations of metals in saturated solutions of these compounds are low, the presence of anions that are capable of being ligands may increase them significantly. In that case a metal will go from the poorly soluble compound into the solution as a com-

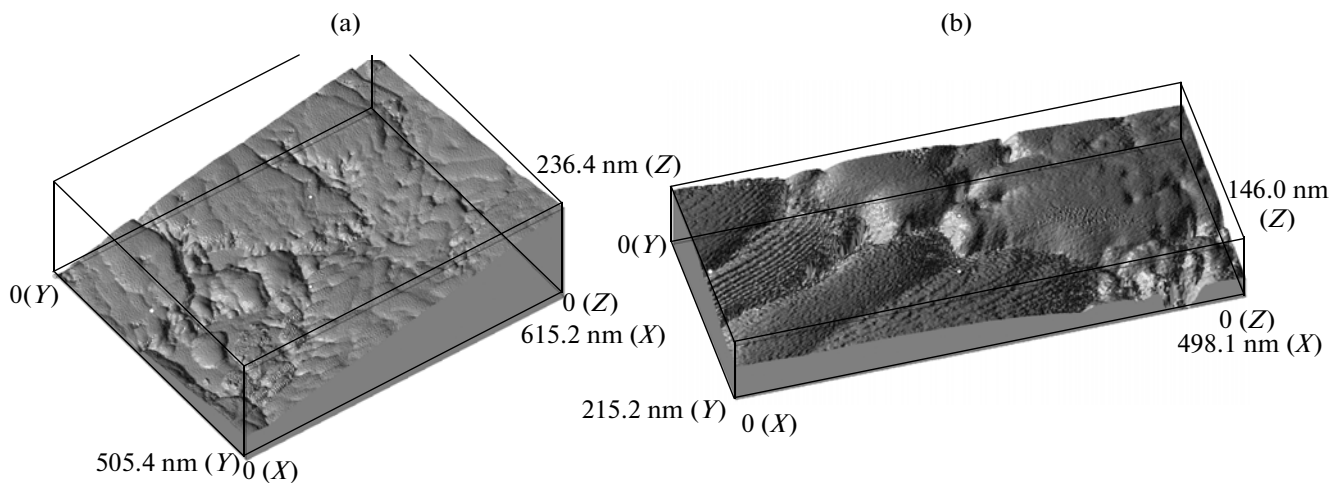
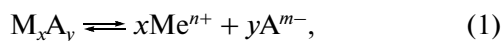


Fig. 5. Colloform kidney-like, globular, layered, and other micro- and nanostructures of neogenetic minerals on the surfaces of pyrite grains that were segregated from hydrothermal clays of the Nizhne-Koshelev thermal anomaly. (a) Dimensions of scanned surface are 615.2 nm (X-axis), 505.4 nm (Y-axis), and 236.4 nm (Z-axis); (b) same, 498.1 nm (X-axis), 215.2 nm (Y-axis), and 146.0 nm (Z-axis).

plex chemical compound. The transport of metal in a solution containing ligands occurs as follows:



Here, A is an anion generator, for example, sulfur, and L^{q-} is a ligand (Cl^- , F^- , OH^- , NH_3 , S_n^{2-} , HS^- , SO_4^{2-} , $S_2O_3^{2-}$, CN^- , and others). Formation of the complex displaces the equilibrium (1) to the right, to the side of dissolution. The form of metal occurrence in a solution depends both on the metal's nature (the stability of complexes with specific ligands) and on the conditions (the temperature, pH, and redox-potential of the medium). The disintegration of a complex chemical compound results in transition of the metal into a bonded form (shift of equilibrium (2) to the left), viz., into sulfides, oxides, hydroxides, silicates, and carbonates.

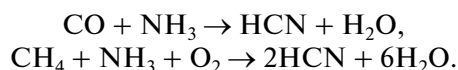
Calculations of changes in the solubility of some sulfides in the presence of thiosulfate- and cyanide ions were performed. These ions form strong complexes with such metals as mercury, silver, and gold. The calculation is based on consideration of all complex forms of the metal that occur in the solution, which is in equilibrium with the precipitate of the poorly soluble compound. The constants of equilibrium for reactions of complex formation and products of solubility are taken from [Lur'e, 1989; *Novyi Spravochnik ...*, 2004a, 2004b].

The calculations demonstrate that even very low concentrations of these ions change metal contents in a solution by several orders of magnitude. A good example is furnished by mercury sulfide, this being one of the least soluble chemical compounds of this element. Nevertheless, Hg forms strong cyanide ($[Hg(CN)_n]^{2-n}$), thiosulfate ($[Hg(S_2O_3)_n]^{2-2n}$) and polysulfide ($[HgS_n]^{2-2n}$) complexes [Analiticheskaya khimiya ..., 1974]. Obviously, if a solution in contact with HgS contains suitable anions, the equilibrium $HgS \rightleftharpoons Hg^{2+} + S^{2-}$ shifts toward dissolution due to mercury being bonded into soluble complexes: $Hg^{2+} + nL^{z-} \rightleftharpoons [HgL_n]^{2-nz}$. In the presence of $S_2O_3^{2-}$ (Fig. 6a) and CN^- (Fig. 6b) the mercury concentration increases and the solubility is observed to be affected by pH. In the absence of thiosulfate and cyanide (0 mol/L, see curve 1) the solubility of cinnabar depends on the pH of the medium only. Cinnabar solubility is higher in a strongly acidic (due to sulfide-ion protonation) and strongly alkaline (due to the formation of soluble mercury hydro complexes) environments and the lowest solubility of mercury sulfides corresponds to a pH from 3 to 8. If a source solution in contact with HgS has a low pH, then an increase of this parameter will lead to oversaturation of the solution relative to HgS and this mineral will precipitate.

In the presence of CN^- and $S_2O_3^{2-}$ HgS ions the solubility generally increases, with the dependence on the pH of the medium being preserved. The lowest solubility occurs in an alkaline medium. In a wide range of pH (from 0 to 7–8) the solubility of HgS is high and mercury migrates in natural waters. Should we assume ligand oxidation leading to disintegration of complexes, the oversaturation relative to HgS will be still higher, because complex generation increases the solubility by several orders of magnitude (from 7 to 10). We note that the total concentration of mercury with due account for complex compound generation is low, but is still much higher than the solubility of HgS in the absence of ligands. Consequently, disintegration of soluble complexes results in the segregation of this chemical compound from the solution and to the generation of the respective mineral (cinnabar or meta-cinnabar).

In the previous section we showed that thiosulfates are present in a geothermal mineral-forming medium. Iron thiosulfate exists in a pH range from 3.5 to 7.0 at the concentration $FeS_2O_3 = 10^{-4} - 10^{-5}$ mol/L, which corresponds to the most abundant solutions in the hypergenesis zone of the Nizhne-Koshelev geothermal field (Fig. 7). Another possible source of thiosulfate ions is the interaction of sulfurous acid with sulfide ions or sulfur.

Based on the totality of hydrogeochemical, gas-geochemical and other data we assume that CN^- may be present in steam hydrotherms. Cyanide ions may form as a result of the following reactions:



Thus, CN^- and $S_2O_3^{2-}$ ions strongly bond mercury. A variation in the parameters of the medium (and resulting disintegration of thiosulfate and cyanide complexes) leads to segregation of HgS from the solution and the formation of cinnabar in hydrothermal clays and bottom sediments. The same happens with polysulfide Hg complexes. When the concentration of H_2S is high, mercury may pass to the solution from the poorly soluble HgS as $[Hg(HS)_xS_y]^{(q)}$. When the hydrogen sulfide concentration decreases, Hg separates back from the solution as a sulfide.

One of the indicator elements of hydrothermal processes is silver. Argentite (acanthite) Ag_2S is the most common silver mineral. Ag is strongly bonded by both cyanide and thiosulfate ions. The solubility of Ag_2S depends more critically on pH compared to HgS, because the formation of hydro complexes $[Ag(OH)_n]^{1-n}$ is less typical of silver and, consequently, the solubility in alkaline media decreases significantly. The dependence of solubility for Ag_2S on pH in the absence of ligands (with the exception of OH^-) indicates that this compound can be transferred from an acidic medium to a neutral or alkaline medium

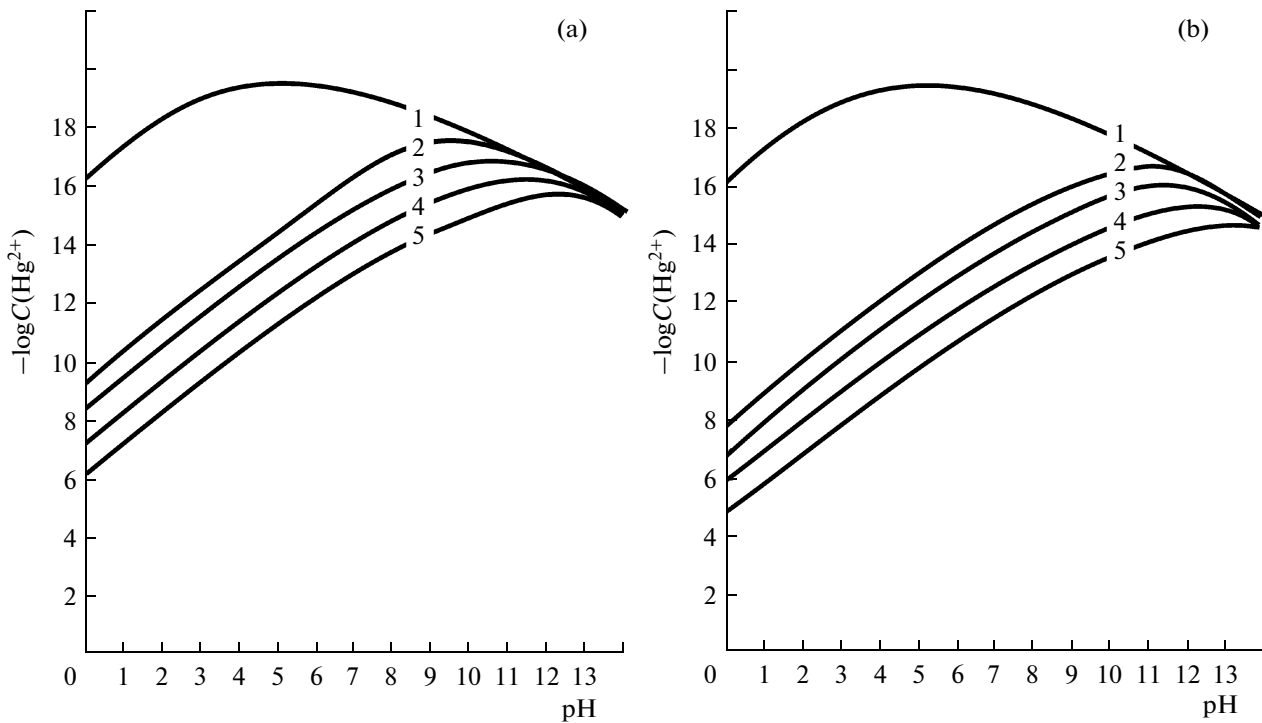


Fig. 6. The total concentration of mercury in solution. (a) for different concentrations of thiosulfate ($\text{S}_2\text{O}_3^{2-}$): (1) 0, (2) 10^{-8} , (3) 10^{-7} , (4) 10^{-6} , (5) 10^{-5} mol/L; (b) for different concentrations of cyanide (CN^-): (1) 0, (2) 10^{-8} , (3) 10^{-7} , (4) 10^{-6} , (5) 10^{-5} mol/L.

(Figs. 8a, 8b). The solubility of Ag_2S changes by five or more orders of magnitude in the process. The presence of small amounts of thiosulfate ions (from $n \times 10^{-8}$ to $n \times 10^{-5}$ mol/L) at the same pH results in an increase in Ag concentrations by several times. The presence of cyanide ions more strongly affects the solubility of Ag_2S , with the amount of Ag that is transferred to the

solution increasing by one to three orders of magnitude. Therefore, disintegration of cyanide and (or) thiosulfate complexes of silver will lead to strong oversaturation of the solution in Ag_2S and this mineral (or other minerals that may happen to satisfy the conditions) will segregate. Thus, silver may be transported in the form of soluble complex chemical compounds;

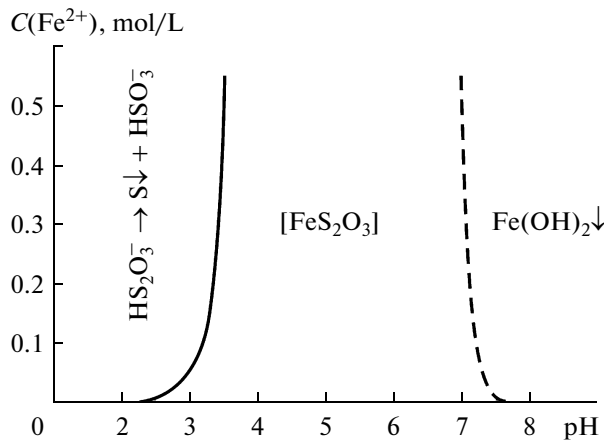


Fig. 7. The field of stability for iron thiosulfate in hydrothermal solutions at different concentrations of iron and from hyperacidic to alkaline media.

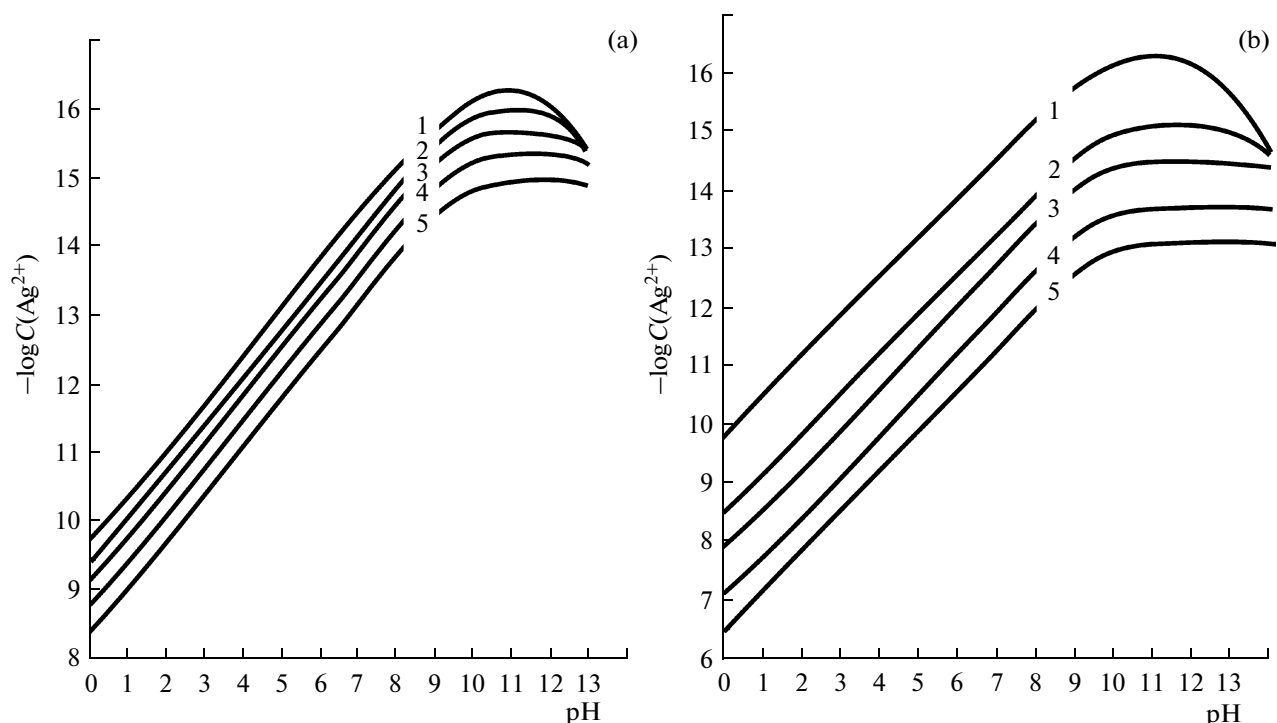


Fig. 8. The total concentration of silver in solution. (a) At different concentrations of thiosulfate ($S_2O_3^{2-}$): (1) 0, (2) 10^{-8} , (3) 10^{-7} , (4) 10^{-6} , (5) 10^{-5} mol/L; (b) at different concentrations of cyanide (CN^-): (1) 0, (2) 10^{-8} , (3) 10^{-7} , (4) 10^{-6} , (5) 10^{-5} mol/L.

this makes the solution metalliferous in spite of low total concentrations of Ag^+ .

CONCLUSIONS

Highly dynamic processes that generate cationic and anionic compositions occur in hydrothermal clays that form in geothermal fields. The initial stages of crystallization of silicate, sulfide, carbonate, and other gels involve generation of mineral mixtures. These are amorphous, crystalline, and transitional phases that are characterized by a long sequence of cations: Fe, Al, Mg, Ti, Mn, Ca, K, Na, Ba, Ni, and others. Halogenide ions (F^- and Cl^-) are also present. Active cationic replacement and formation of new mineral phases take place in micro- and nanostructures of hydrothermal clays. New mineral phases also form on the surfaces of some mineral grains, in particular, pyrite. Pyrite occurs widely in hydrothermal clays and, as was shown earlier, has high sorption properties. But, at the same time, the presence of micro- and nanofilms on its grains may be of special importance. The films are from a few nm to a few hundreds of nm thick and consist of independent mineral phases. Their two-layer (probably multi-layer) structure reflects conditions of interaction between the minerals in the clays and gaseous hydrothermal solutions. The lower layer forms in a substantially reducing geothermal medium

and consists of thiosulfate iron complexes with reduced nitrogen. The upper layer consists of a titanium-bearing oxide–silicate phase and characterizes the change of the medium to an acidic or faintly acidic medium. These mineral micro- and nanofilms on the surfaces of pyrite grains may also contain Cu, K, P, and other cations (unpublished data of Yu.V. Shchegol'kov and S.N. Rychagov); consequently, they possess sorption properties that are different from those of pyrite crystals.

The generation of mineral micro- and nanostructures in hydrothermal clays takes place under the influence of reduced (above through-crust faults) and acidic or hyperacidic (above cooling magmatic bodies) gas–hydrothermal fluids. The presence of ligands among fluids (halogenide, thiosulfate, cyanide, sulfide, and polysulfide ions) leads to the formation of corresponding complex chemical compounds and to chemical transport of metals, viz., dissolution of their complex compounds and saturation of solutions in some physical and chemical conditions and disintegration of compounds and transition of complex compounds of metals into sulfides, oxides, hydroxides, silicates, and carbonates in other conditions.

It thus appears that the criterion by which one can evaluate the presence of metals in gas–hydrothermal fluids in present-day volcanic areas is first of all the existence of a “hydrothermal–metasomatic rocks–

fluid–neogenetic mineral compounds” system. Investigations of the interconnections and interdependence of each element in this system provide the basis for the elaboration of concrete criteria to be used for evaluating the presence of metals in steam–gas and water fluids. In our opinion, one such criterion is the presence of conditions for the chemical transport of metals in gaseous, water, and mineral media. The present authors demonstrated that in the zone of hypergenesis of geothermal fields, first of all in a highly dynamic medium such as hydrothermal clay, one finds the processes that determine the evolution of present-day mineral and ore formation

We are grateful to G.P. Koroleva, A.A. Nuzhdaev, A.G. Ilgen (Taranbekova), E.G. Kalacheva and other colleagues in expedition work for their participation in collecting the factual material; to G.P. Sandimirova, N.E. Smolyanskaya, G.I. Shcherbakova, L.D. Andru-laitis, E.V. Kartasheva, N.I. Chebrova, S.V. Sergeeva and other workers at analytical laboratories of the Institute of Geochemistry, Siberian Branch, RAS, and Institute of Volcanology and Seismology, Far East Branch, RAS for the great number of high-precision analytical studies. The chief conclusions of this work were presented at the Conference of the Institute of Volcanology and Seismology, Far East Branch, RAS, devoted to the Day of the Volcanologist (2011). We are grateful to all the specialists who took part in the discussion of this paper.

This work was financially supported by the Russian Foundation for Basic Research, projects nos. 10-05-00503a and 10-05-00009a, and by the Presidium of the Far East Branch, RAS, projects nos. 09-II-SO-08-004, 09-II-SO-08-006, 09-III-A-08-418.

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