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Diagenetic Alterations of Copper Sulfides in Modern Ore-Bearing Sediments of the Logatchev-1 Hydrothermal Field (Mid-Atlantic Ridge 14°45′ N)

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Abstract—Sulfide ore samples recovered by corers from and beyond Orebody 1 in the Logatchev-1 hydrothermal field (Mid-Atlantic Ridge, 14°45′ N) are studied by optical, electron microscopic, X-ray microspectral, and X-ray diffraction methods. The major and ore minerals are identified. Sulfides of the Cu–S system, the major ore-forming minerals in sediments, are investigated in detail. Specific features of their composition, structure, secondary alterations, and distribution in sediments of the Logatchev-1 field are considered. It has been established that sulfide concretions in modern sediments primarily consist of nonstoichiometric minerals of the chalcocite–digenite series, i.e., djurleite ($Cu_{1.96}S$) and roxbyite ($Cu_{1.75–1.86}S$). It is assumed that copper sulfides primarily precipitated from hydrothermal solutions as high-temperature hexagonal chalcocite that was replaced after the hydrothermal activity by djurleite, roxbyite, and other nonstoichiometric minerals of the Cu–S system. Based on the comparison of their paragenetic associations with those of copper sulfides in hydrothermal chimneys, the paper discusses constraints of the diagenetic transformation of sulfides in ore-bearing sediments and the halmyrolysis of modern hydrothermal edifices located in contact with seawater. Roxbyite recently discovered in oceanic sediments plays a specific role in these processes.

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The Logatchev-1 hydrothermal field was discovered in 1994–1995 in the MAR 14°45′ N area during the cruise of the R/V *Professor Logatchev* accomplished by the Sevmorgeologiya Industrial-Geological Association (Batuev *et al.*, 1994; Krasnov *et al.*, 1995a, 1995b). The Logatchev-1 field incorporates modern oceanic sulfides associated with serpentinized ultramafic rocks in low-spreading zones. Such hydrothermal fields are characterized by copper specialization of sulfide ores. The mineral composition of sulfide edifices of the Logatchev-1 field, which formed on the seafloor under the influence of hydrothermal fluids, has been studied in numerous works of Yu.A. Bogdanov, N.S. Bortnikov, N.N. Mozgova *et al.*, A.Yu. Lein, and other researchers published in the last decade. Bottom sediments of the Logatchev-1 field recovered by corer from the foothill of a hydrothermal edifice were first described in (Bogdanov *et al.*, 1997). However, sulfide fragments were not considered in this publication. The present communication considers sulfide minerals in ore aggregates recovered by corers from the largest orebody in the Logatchev-1 field during cruises 20 and 22 of the R/V *Professor Logatchev* in 2003–2004. The main attention is given to the study of sulfides of the Cu–S system that are the major ore-forming minerals in sediments.

At present, we know ten natural compounds of the Cu–S system and two synthetic phases (hexagonal chalcocite and cubic digenite) that are unstable at room temperature. Copper sulfides are dominated by nonstoichiometric minerals that make up a compositional succession ranging from chalcocite (Cu_2S) to covellite (CuS): djurleite ($Cu_{1.93–1.96}S$)–roxbyite ($Cu_{1.72–1.86}S$)–digenite ($Cu_{1.75–1.8}S$)–anilite ($Cu_{1.75}S$)–geerite ($Cu_{1.5–1.6}S$)–spionkopite ($Cu_{1.4}S$)–yarrowite ($Cu_{1.1}S$)[1]. The succession can be divided into the chalcocite–digenite or Cu-rich sulfide (Cu_2S–$Cu_{1.75}S$) and the geerite–covellite or Cu-poor sulfide ($Cu_{1.5–1.6}S$–CuS) series (Gablina, 1993). Many nonstoichiometric minerals have a narrow stability range. Therefore, they can serve as indicators of the constraints of mineral formation and subsequent transformations. As was demonstrated in (Gablina, 1993, 1997, 2004), stoichiometric minerals of the Cu–S system and digenite are found in both endogenic and exogenic ores, whereas nonstoichiometric minerals of this series are typical of exogenic ores. Moreover, the Cu-rich sulfides (djurleite and digenite) are characteristic of primary ores in cupriferous sandstones and shales

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[1] See (Gablina *et al.,* 2004) for details concerning nonstoichiometric minerals of the Cu–S system.

and of ores in secondary sulfide enrichment zones. The Cu-poor sulfides of the geerite–covellite series are typical of the oxidation zone.

The abundance of minerals of the Cu–S system is related to the fact that even a slight compositional alteration in this system leads to the structural rearrangement and the consequent formation of a new mineral species. Nonstoichiometry is caused by the presence of a certain amount of bivalent (oxidized) Cu, in addition to the monovalent Cu, in the crystal structure of copper sulfides. Calculations made by Belov (1953) and other researchers have shown that the content of oxidized cations in copper sulfide has a negative correlation with the Cu/S ratio. This conclusion was later supported by XRD investigations (Goble, 1985).

Copper sulfides are abundant in sulfide edifices of the modern Logatchev-1 hydrothermal field. They are mainly represented by nonstoichiometric minerals (djurleite, anilite, geerite, spionkopite, yarrowite, and covellite) that make up fine polymineral associations. Two-phase anilite–djurleite associations are most widespread. Chalcocite is only observed as rare relicts in association with nonstoichiometric minerals (Gablina *et al.*, 2000). Roxbyite has been found as rare mineral on chimney walls (Mozgova *et al.*, 2005). At the same time, together with djurleite, roxbyite is a major Cu ore-forming mineral in ore-bearing sediments of the Logatchev-1 field (Semkova and Stepanova, 2004a, 2004b). Roxbyite is the last nonstoichiometric mineral of the Cu–S system identified in continental ores (Mumme *et al.*, 1988). In natural formations, Clarck (1972) first reported an unnamed mineral with the roxbyite-type structure from the large El Tinait porphyry copper deposit (Chile). This mineral of hexagonal symmetry was associated with djurleite and its formula was identified as $Cu_{1.83}S$. Such a phase was obtained by chemical and electrochemical reactions. The first method was based on the leaching of Cu from synthetic chalcocite using hydrochloric acid at room temperature (Flamini *et al.*, 1973), while the second method was based on the incomplete anode oxidation of chalcocite (Cavalotti and Salvago, 1969; Brage and Lamache, 1979; Koch and McIntyre, 1976). Djurleite was the intermediate products in both reactions. Ragozzini *et al.* (1986) reported a mineral with characteristics of roxbyite associated with djurleite in the Olympic Dam stratiform Cu–U–Au deposit. They presented a preliminary description of this mineral, but its name was not proposed. Mumme *et al.* (1988), who named roxbyite after the location of the deposit, found this mineral in copper concentrates of flotation and products of the reaction of copper concentrates with H_2SO_4. They studied its composition, structure, and physical properties.

We have found roxbyite for the first time in ocean. In terms of composition, this mineral occupies an intermediate position between djurleite and digenite (often, closer to digenite). However, roxbyite is distinguished from digenite and anilite by the crystal lattice structure. For example, the structure of roxbyite is based on the hexagonal close packing of sulfur atoms, while structures of digenite and anilite are based on the cubic close packing. Whiteside and Goble (1986) experimentally demonstrated that a compound with the roxbyite-type composition and structure is formed under specific physicochemical conditions.

The present communication reports first results of the study of specific features of the composition, secondary alteration, and distribution of copper sulfides in sediments of the Logatchev-1 field. Based on the comparison of their paragenetic associations with those of copper sulfides in hydrothermal chimneys, we discuss constraints of the halmyrolysis of modern hydrothermal edifices, which are located in contact with seawater, and the diagenetic transformation of sulfides in metalliferous sediments. A specific role in these processes belongs to the mineral discovered in oceanic sediments (roxbyite).

MATERIALS AND METHODS

We studied samples of sulfide ores and ore-bearing sediments taken from the largest orebody in the Logatchev-1 field (MAR 14°45′ N) during cruises 20 and 22 of the R/V *Professor Logatchev* accomplished by the Polyarnaya Ekspeditsiya Federal Geological Association in 2003–2004. The samples were taken within the copper zone of Orebody 1 (depth 2920–2980 m) from ore-bearing and metalliferous sediments penetrated by corers to a depth of 3 m at different distances from an active smoker.

Optical, electron-microscopic, X-ray microspectral, and X-ray diffraction methods were used for the analyses. Optical microscopic investigations were carried out on polished samples prepared without heating. Electron microscopic investigations were performed using a CamScan MV2300 scanning electron microscope equipped with an INCA Energy 200 energy-dispersive microanalytical system at the Geological Institute, Moscow (N.V. Gor'kova, operator). The chemical composition of minerals was studied with a JEM-100C microscope equipped with Link ISIS energy-dispersive spectrometer at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Moscow (N.V. Trubkin, operator). Microprobe measurements (acceleration 25 kV, beam current 30 nA) were carried out using natural pyrite (standard for S and Fe) and pure metals (standards for other elements).

Identification of minerals was mainly based on the XRD analysis (X-ray diffraction and powder Debye technique) of grains extracted under an optical or binocular microscope. The XRD analysis was carried out using a DRON-2 diffractometer (Co radiation, goniometer rotation 0.5°/min, chart strip feed 600 mm/h, internal standard Ge) in the X-ray laboratory of the Department of Crystallography, Geological Faculty, St. Petersburg State University. Debyegrams were

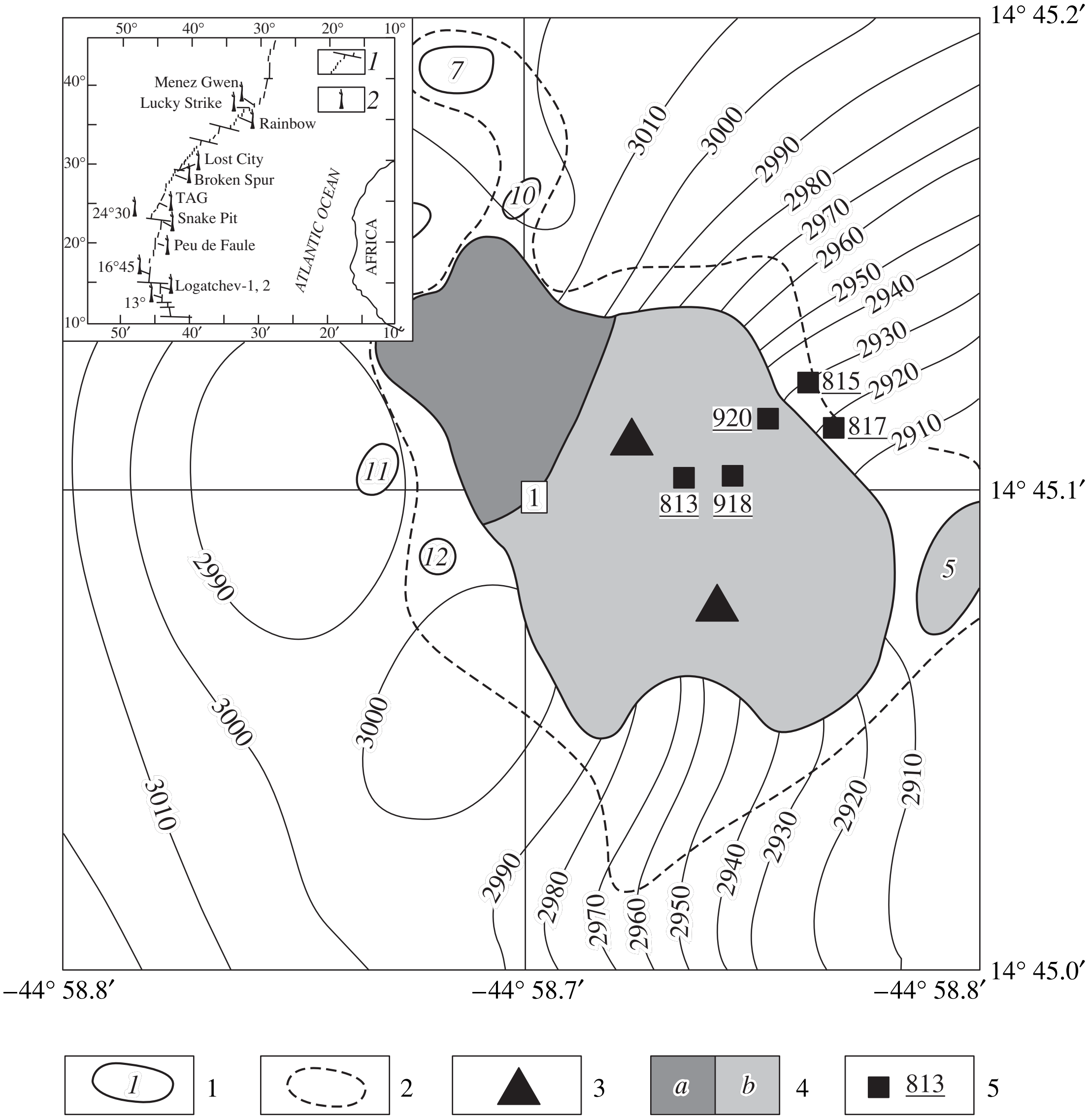

Fig. 1. The Logatchev-1 hydrothermal field. (1) Outlines of orebodies and their numbers; (2) outlines of ore-bearing sediments; (3) active high-temperature sources; (4) ore specialization zones: (*a*) Cu, (*b*) Fe–Zn; (5) sampling stations and their numbers.

obtained using Gandolfi-57.3 and RKD-57.3 cameras (unfiltered Fe radiation, exposure 6 h) in the X-ray laboratory of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (O.Yu. Kuznetsova and L.A. Levitskaya, analysts).

LOCATION AND CHARACTERISTICS OF SAMPLES

The Logatchev-1 hydrothermal field incorporates 15 sulfide mounds up to 20 m high. The samples (Fig. 1) were taken from the largest Orebody 1 (200 × 100 m) that extends along the southeastern direction (Batuev *et al.*, 1994). The major part of the mound is inactive at present. Active black smokers are present in its central and southern parts. In terms of the content of major ore-forming elements and mineral composition, Orebody 1 is characterized by the following lateral zonality: iron–zinc zone developed in the northwestern part gives way to copper zone in the central and southeastern parts (Borodaev *et al.*, 2000). The copper zone is primarily composed of copper sulfides dominated by nonstoichiometric minerals (Gablina *et al.*, 2000). Based on fluid inclusion data on anhydrite from chimney fragments (Bortnikov *et al.*, 2004), salt content in the hydrothermal ore-forming fluid varies from 4.2 to 26 wt % NaCl equiv and its temperature is as much as 270–365°C (hydrostatic pressure is 300 bar at a depth of approximately 3 km). Previous investigations of sediments from a depth of 241 cm near the foothill of a large sulfide mound (Bogdanov *et al.*, 1997; Gurvich, 1998; and others) show that the sediments are composed of particles ranging in size from <0.001 mm to 3 cm. The major part (more than 30%) is composed of fractions ranging from <0.001 mm to 0.1 mm. More than 50% of the sediment consists of carbonate material ($CaCO_3$ 53.2–78.7%) mainly represented by foraminiferal tests and coccoliths. Mollusk fragments are subordinate. The carbonate-free portion of the fine fraction (<0.001 mm) includes poorly crystallized clay minerals (Fe-smectite, mixed-layer phase of the smectite-illite type, kaolinite, iron hydroxides, and chlorite). The coarser material is primarily composed of fragments of serpentinitized peridotites.

The ore-bearing sediments are developed within and beyond the orebody. The cores recovered sediments of the western part of Orebody 1 (within the copper zone) that extend from the central zone (with active sources) to the periphery beyond the orebody (Fig. 1). The sediments represent water-saturated carbonate muds with fragments of altered peridotites and gabbroids of the underlying substrate. Upon drying, the samples are disintegrated and locally coated with a green powdery mass of brochantite. The sediments are characterized by alternation of orange, beige, red-brown, gray-green, brown-black, and black layers (Fig. 2). The black, gray-green, and, in part, brown-black sediments are dominated by compact (oval and lumpy equant) sulfide concretions ranging in size from 5–7 mm to 1.5–2 cm. Their porous slaggy surface is usually coated with a black carbonaceous substance. Coatings of brown ferruginous ocher and copper slag are less common. Some dark interlayers (e.g., in Well 813) represent brecciated sulfide ores that are cemented with carbonates and submerged in the black mud. The thickness of sulfide-bearing black muds increases from the center of orebody (5–10 cm) to its periphery (up to 1 m or more).

RESULTS

Mineragraphic investigations of samples of metalliferous sediments showed that sulfide concretions are mainly composed of copper sulfides with relicts of pyrite, chalcopyrite, sphalerite, and bornite. The concretions have allotriomorphic-granular texture, which sometimes resembles recrystallized colloid and becomes more distinct after etching with 10% HNO_3, and lumpy structure. The copper sulfides, generally, make up fine emulsion-lamellar intergrowths of two or more minerals of the chalcocite–digenite series (chalcocite–djurleite, djurleite–roxbyite, or sometimes djurleite–anilite). Monomineral roxbyite segregations are less common. Sulfide concretions are intensely dissolved and leached. They are crosscut by cracks and leaching pores and cavities that are filled with aragonite, atacamite, calcite, dolomite, and less common iron hydroxides. These processes are most prominent along the periphery of sulfide concretions.

Electron-microscopic investigations of the unaltered surface and internal structure of sulfide concretions from ore-bearing sediments revealed that they have equant or irregular-oval shape with sinuous boundaries corroded by calcite and dolomite (Fig. 3). The organogenic structure is less common (Fig. 3d). The internal zone and surface of sulfide concretions in sediments are friable and porous, because they are composed of loose clusters of hexagonal, sometimes flattened, lamellar bipyramidal (barrel-shaped) crystals with a length of 15–20 μm and diameter varying from 4–8 μm at the apex to 10–15 μm in the central part (Fig. 4).

Rare relicts of compact homogeneous masses represent intergrowths of differently oriented copper sulfide crystals (Fig. 3b). The crystalline structure of concretions becomes distinct during their dissolution that usually begins along the boundaries of grains (Figs. 4a, 4b). The crystals are intensely fractured, particularly, along cleavage planes. Fracturing of crystals is intensified on the surface of sulfide concretions and in solution openings. Numerous leaching cavities (from 0.*n* to 8–10 μm across) appear on lateral faces of crystals (Fig. 4c). Crystals of copper sulfide are overgrown with small (1–2 μm) nodules of atacamite and carbonates(?), tiny globules and their clusters, and fine-fibrous mosslike concretions that can be colonies of partially fossilized microorganisms (Figs. 4c, 4d). Energy-dispersive spectra indicate the presence of abundant carbon and oxygen in altered copper sulfides. Such organic clusters are also developed along cleavage planes and leaching cleavages. Therefore, some crystals are intensely altered and almost completely disintegrated (Fig. 4d). Large cavities on the surface of sulfide concretions are filled with druses of well-developed columnar aragonite crystals (Fig. 5). Carbonates make up pseudomorphs after sulfide concretions in more compact masses.

Results of the **X-ray diffraction investigation** of the mineral composition of sediments at all stations are given in Table 1. It is evident that the sediments are mainly composed of carbonates (calcite, aragonite, and dolomite), goethite, as well as authigenic and clastic silicate minerals. Magnesite and siderite (based on energy-dispersive spectra) have been recorded for the first time. Copper minerals include, in addition to sulfides, atacamite and clinoatacamite.

Copper sulfides were identified by X-ray diffraction methods (diffractometry, Debye powder technique, and single crystal analysis in a Gandolfi camera). Copper sulfides have been found at three stations (813, 918, and 817) located along the meridional profile. In the core of Station 815, sulfides are only represented by sphalerite. The X-ray phase analysis did not detect any sulfides at Station 920. It is evident from Table 1 that sulfide ores of the Logatchev-1 field contain all currently known minerals of the Cu–S system. However, Cu-rich sulfides of the chalcocite–digenite series are most widespread. Minerals of the geerite–covellite series represent secondary or rare minerals. In the majority of samples, roxbyite is associated with djurleite. The association with djurleite and anilite is less common.

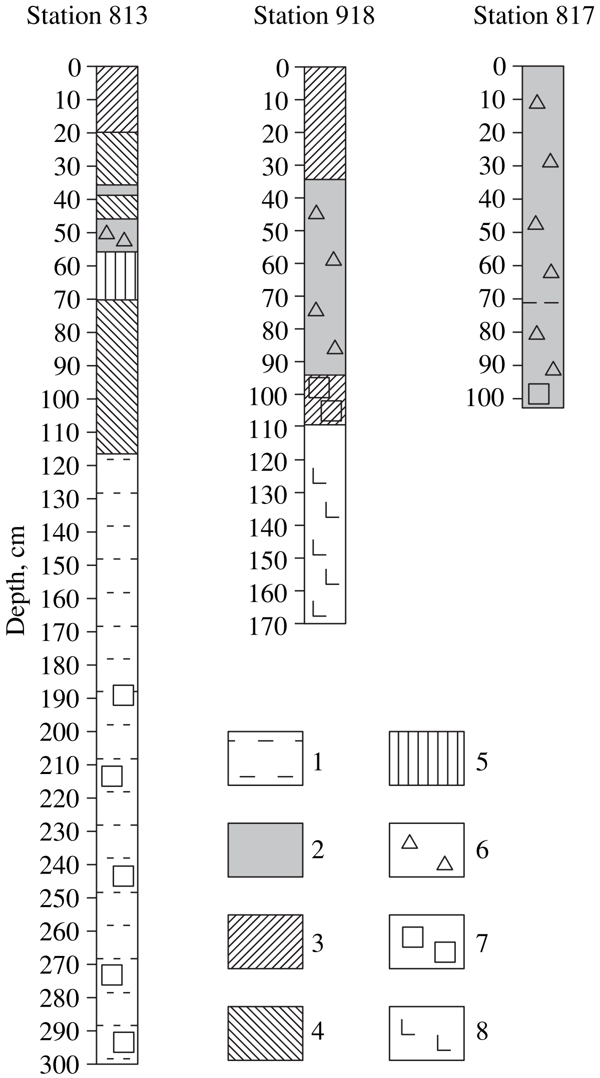

Fig. 2. Lithological columns of holes drilled in the copper zone of Orebody 1 in the Logatchev-1 field. (1) Pelagic sediments (beige carbonate sediment); (2–5) ore-bearing sediments: (2) black, (3) brown-black and red-brown, (4) orange, (5) gray-green; (6) macroscopic ore segregations; (7) fragments of altered rocks; (8) red brecciated serpentinized peridotites and gabbroids.

Djurleite is occasionally associated with anilite and digenite. In some samples, roxbyite and djurleite are associated with a small amount of chalcocite. Monomineral chalcocite is observed in rare samples. Some sulfide clusters in the ore-bearing sediments are composed of nearly monomineral roxbyite grains.

The abundance of roxbyite in metalliferous sediments of the Logatchev-1 field is of specific interest. This mineral, only recently discovered in oceanic ores (Semkova and Stepanova, 2004), is insufficiently described in the Russian literature. However, it has a great significance for the interpretation of constraints of mineral formation. Therefore, we shall discuss this issue in more detail. As was mentioned above, roxbyite was first reported from continental ores and dressing products of the Olympic Dam deposit (Mumme *et al.*, 1988). They investigated roxbyite monocrystals from the concentrate and described its structure as monoclinic type on the basis of the hexagonal closed packing of sulfur atoms with the following unit cell parameters: a = 53.79, b = 30.90, and c = 13.36 Å. Results of the XRD investigation of roxbyite monocrystal and blend taken from sulfide concretions in the Logatchev-1 field (Table 2) show that the values of major reflections in this mineral are similar to those in the ASTM database (Mumme *et al.*, 1988). However, the peak of crystallites analyzed in the Gandolfi camera is characterized by a higher intensity (1.948 and 1.943) relative to the ASTM data (1.938), probably, owing to an admixture of djurleite. Based on refined indexes *hkl*, Semkova could more precisely determine the following unit cell parameters of roxbyite taken from sediments in the Logatchev-1 field: $a = 53.693 \pm 0.054$, $b = 30.895 \pm 0.018$, and $c = 13.332 \pm 0.017$ Å; $\beta = 89.72 \pm 0.016$ (Table 3).

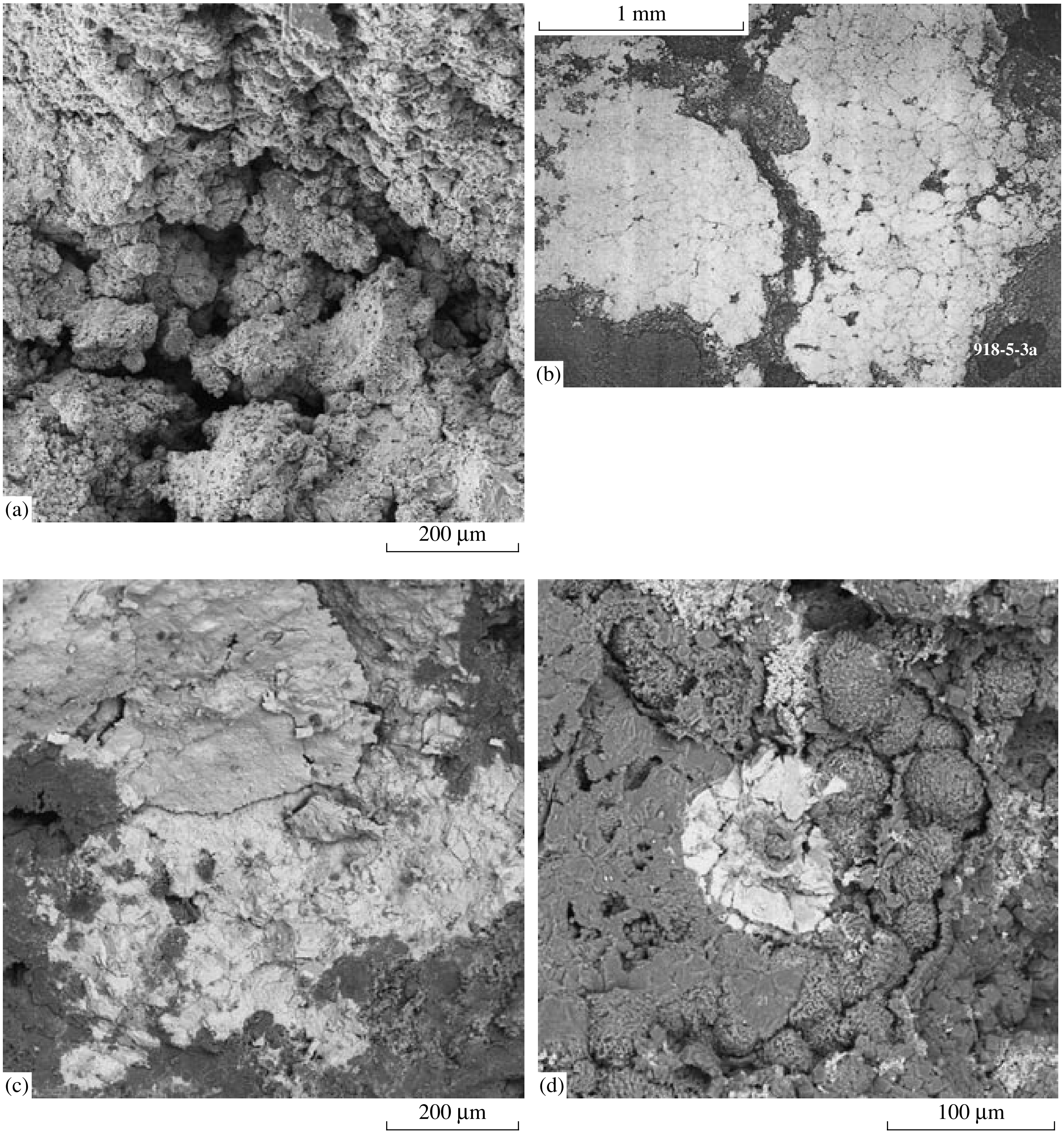

Fig. 3. SEM images of sulfide nodules. (a) Secondary electron image of the sulfide nodule, Sample 918-5 (Station 918, interval 57–62 cm). (b–d) Back-scattered images: (b) fine-grained allotriomorphic texture of copper sulfide concretions (light) replaced by carbonates (dark gray) along margins and grain boundaries, polished section, Sample 918-5, interval 57–62 cm; (c) character of the replacement of sulfide concretions (light) by carbonates (dark), Sample 918-2 (Station 918, interval 35–37 cm); (d) organogenic (foraminiferal?) texture of sulfide concretions (light) replaced by rhombohedral dolomite, Sample 918-2.

Based on results of the X-ray diffraction and microprobe analyses, we compared the distribution of copper sulfides along the strike of metalliferous sediments (Table 4). It is evident that Cu-rich sulfides of the chalcocite–digenite series are ubiquitous, while Cu-poor sulfides of the geerite–covellite series are mainly developed beyond the orebody (Station 817). The vertical distribution of copper sulfides is yet insufficiently studied. In cores from stations 813 and 817, the upsection predominance of sulfides of copper is replaced by the

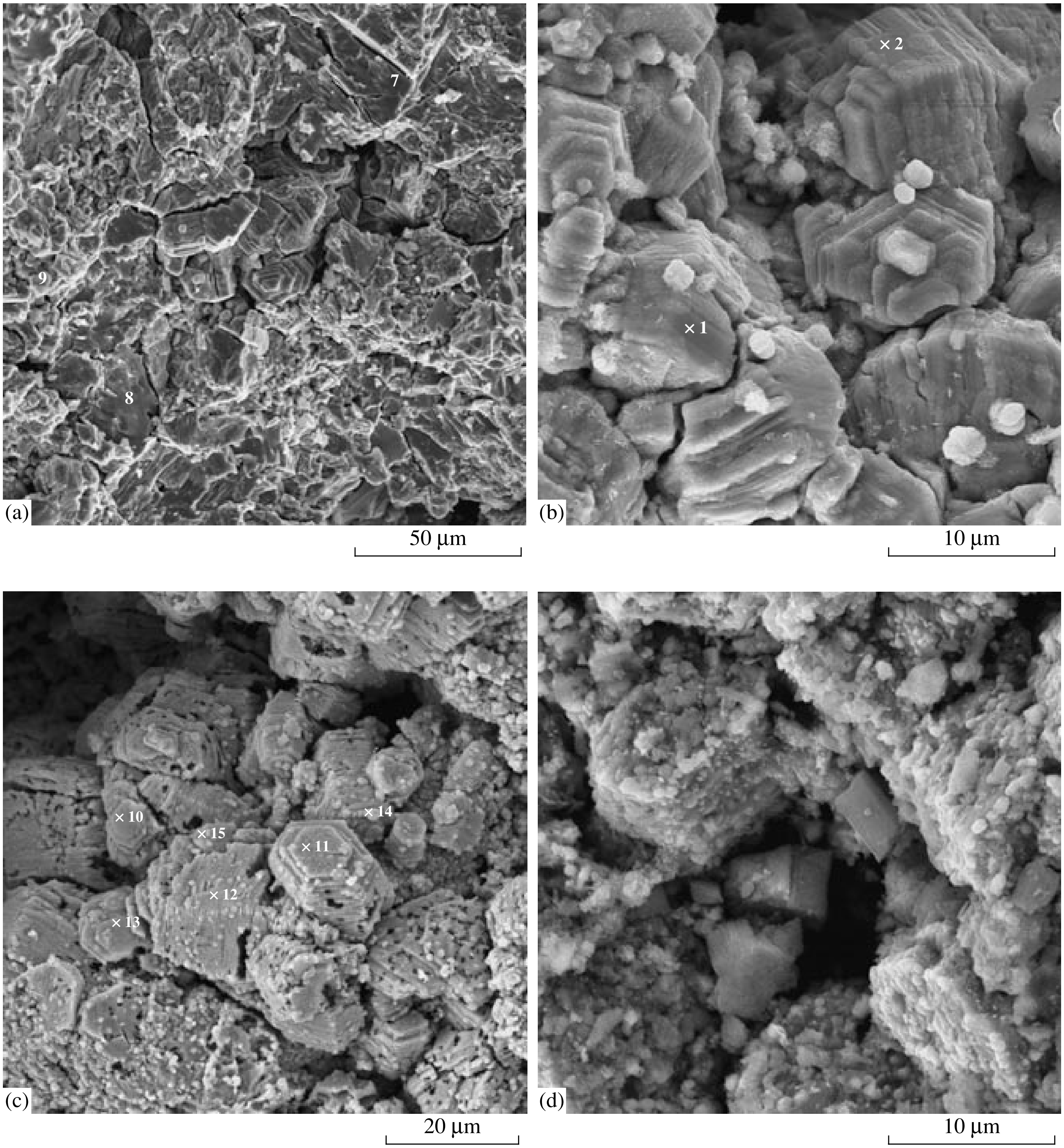

Fig. 4. Alteration of copper sulfides in sediments of the Logatchev-1 field. SEM images, Sample 918-5, fresh chip (Station 918, interval 57–62 cm). (a) Initial stage of destruction: dissolution of massive ores produces hexagonal copper sulfide (center); peaks of crystals and leaching cavities contain rare globules formed by microorganisms. (b) Closeup of (a), the crystal composition matches Cu_2S. (c) More intensely altered sector: the crystals contain numerous pores and solution openings; edges and cavities include microorganism colonies (Cu and S are supplemented with carbon and oxygen). (d) Complete replacement of sulfides by microorganism colonies and carbonates; the cavity includes calcite crystals.

chloride varieties. At Station 813, Cu-bearing minerals are only represented by atacamite in red-colored sediments that overlie cupriferous units and only iron hydroxides are present in the underlying sediments (stations 813 and 918). In Station 817 core, which is entirely composed of black ore-bearing sediments (Fig. 2), the lower section contains abundant sulfides associated with atacamite, clinoatacamite, chalcopyrite, pyrite, and sphalerite. Upward the section, the content of copper sulfides appreciably decreases and they are mainly

Fig. 5. Aragonite crystals in solution openings on the surface of sulfide concretions. SEM image, Sample 918-5.

represented by Cu-poor species of the yarrowite–covellite series. Atacamite, clinoatacamite, pyrite, and sphalerite are also present here. Core from the most thoroughly investigated Station 918 lacks any distinct trends in the distribution of sulfides.

Chemical composition of copper sulfides. Results of the EPMA study of the major copper sulfides (chalcocite, djurleite, and roxbyite), which make up monomineral concretions, are given in Table 5. It is evident that compositions of chalcocite and djurleite match the standard versions. The composition of roxbyite has an average composition of $Cu_{1.80}S$ (variation from $Cu_{1.72}S$ to $Cu_{1.90}S$). According to the published data, the Cu/S ratio in natural and synthetic roxbyite can vary from 1.75 to 1.86 (Cavalotti and Salvago, 1969; Flamini *et al.*, 1973; Koch and McIntyre, 1976; Brage and Lamache, 1979; Mumme *et al.*, 1988). In experiments with the chemical synthesis based on the leaching of Cu from synthetic chalcocite by 1% HCl solution at room temperature, the roxbyite-type phase varied from $Cu_{1.765}S$ to $Cu_{1.790}S$ and the average composition was $Cu_{1.788}S$ (Flamini *et al.*, 1973). In samples with the maximal Cu content ($Cu_{1.79}S$), the XRD data indicate the admixture of djurleite, while samples with the minimal Cu content ($Cu_{1.765}S$) contain anilite. It is probable that the extreme values of the Cu/S ratio in our measurements and the relevant XRD data are also related to admixtures associated with roxbyite (anilite, digenite, and djurleite). Roxbyite from the Tinait and Olympic Dam deposits are characterized by the presence of Fe that serves the role of stabilizer (Mumme *et al.*, 1988). For example, natural roxbyite from the Olympic Dam stratiform Cu–U–Au deposit has an average composition of $Cu_{1.80}Fe_{0.03}S$ or $Me_{1.83}S$ (variation range $Me_{1.80\text{-}1.85}S$). However, the concept of the stabilizing role of Fe contradicts experimental data on the leaching of Cu from synthetic chalcocite and the formation of Fe-free roxbyite. The experimentally obtained phase $Cu_{1.788}S$ retained stability up to a temperature of 50°C when it began to transform partially into digenite. At 90°C, this phase was completely transformed into digenite.

In roxbyite from the Logatchev-1 field, the Fe content varies from 0 to 1.35% (average 0.52%). Thus, the mineral formula corresponds to $Cu_{1.80}Fe_{0.01}S$ that is similar to the composition of roxbyite from the Olympic Dam deposit. Interestingly, Fe is absent in our chalcocite and djurleite samples from the Logatchev-1 field.

Comparison with copper sulfides from sulfide chimneys of hydrothermal edifices on the seafloor in the Logatchev-1 field. As was demonstrated in (Gablina *et al.*, 2000; Mozgova *et al.*, 2005), modern hydrothermal edifices on the seafloor in the Logatchev-1 hydrothermal field contain all known nonstoichiometric minerals of the Cu–S system. However, they are dominated by Cu-rich sulfides of the chalcocite–digenite series mainly composed of fine two-phase (djurleite–anilite) associations. Results of their XRD analysis are presented in Table 6. The Cu/S ratio in the djurleite–anilite association varies from 1.83 to 1.92 (average 1.87, based on 14 analyses). The Fe content in this phase varies from 0 in veinlets to 1–≈3% in the case of the metasomatic replacement of chalcopyrite (isocubanite) by copper sulfides. Chalcocite is present as a rare admixture associated with djurleite and other copper sulfides. The preservation of hexagonal bipyramidal crystals of chalcocite on the chimney walls (Fig. 6) testifies to its precipitation as high-temperature (>103°C) hexagonal modification from hydrothermal solutions. In terms of habit and size, the crystals are analogous to crystals described above that compose sulfide concretions in sediments. However, copper sulfide crystals on chimney walls are more compact and virtually devoid of cracks. They are dissolved to a variable extent and completely replaced by nonstoichiometric copper sulfides at margins. Their composition varies from $Cu_{1.49}S$ to $Cu_{1.86}S$, and Fe is absent. According to the XRD data, these crystallites contain the djurleite–anilite association and the blend of these minerals with Cu-poor sulfides of the geerite–covellite series (spionkopite and yarrowite). Table 2 presents *d* values of the rare mineral roxbyite. The distribution of copper sulfides in hydrothermal edifices on the seafloor within Orebody 1 shows certain trends. For example, relicts of hexagonal chalcocite crystals on the chimney wall are found in the active hydrothermal source area. Farther from active sources within the copper zone, one can see the development of minerals of the anilite–djurleite association that replace iron sulfides (pyrite and others) and Fe–Cu sulfides (chalcopyrite, bornite, and others). Minerals of the geerite–covellite series universally replace all other sulfides. Some Cu-poor copper sulfides, particularly covellite, are more common in copper zone sectors located near the active sources. Succession of the precipitation of copper sulfides can be different: (1) djurleite–anilite–geerite–spionkopite–yarrowite–covellite; (2) chalcocite–djurleite (±anilite)–spionkopite–yarrowite; (3) djurleite (±anilite)–covellite; or (4) chalcocite–djurleite–roxbyite.

In ore-bearing sediments of the Logatchev-1 field, copper sulfides are also mainly represented by members of the Cu-rich chalcocite–digenite series. However, in contrast to hydrothermal edifices on the seafloor, the ore-bearing sediments are dominated by djurleite and roxbyite, while digenite and anilite are subordinate. Based on the typical morphology of crystallites of hexagonal chalcocite, the presence of monomineral segregations of chalcocite, and its development in polymineral associations, modern sulfide concretions in sediments represent paramorphoses of the monoclinic chalcocite and nonstoichiometric minerals (djurleite and roxbyite) after the hexagonal chalcocite. In this case, the replacement could take place in the following sequence: chalcocite–djurleite–roxbyite. Judging from the composition of some polymineral associations, primary ores could contain high-temperature digenite, the exsolution of which after decrease in temperature produced the low-temperature digenite, anilite, or anilite–djurleite association. Further alterations of sulfides successively produced Cu-poor minerals of the geerite–covellite series, atacamite, clinoatacamite, and other oxidized minerals.

DISCUSSION

Comparison of the composition and alteration style of copper sulfides in hydrothermal sulfide concretions on the seafloor and in ore-bearing sediments revealed that they have not only several similar features, but also significant distinctions. The major similarities are as follows: the predominance of Cu-rich nonstoichiometric minerals of the chalcocite–digenite series in copper ores; the presence of relicts of high-temperature hexagonal chalcocite; the replacement of iron sulfides and Cu–Fe sulfides by copper sulfides; and, finally, the replacement of copper sulfides by Cu-poor sulfides of the geerite–covellite series. The distinctions are mainly related to the morphology and composition of copper sulfide concretions.

The presence of relicts of hexagonal chalcocite implies that both types of sulfide concretions initially formed at high temperatures under the influence of hydrothermal fluids, in which increase in the Cu concentration was accompanied by decrease in the sulfide ion content. It is known that the high-temperature hexagonal chalcocite is not quenched and is transformed into the monoclinic modification if the environment temperature becomes <103°C (Roseboom, 1966; Djurle, 1958; and others). Stability of the monoclinic modification, in turn, is constrained by chemical

Table 1. Minerals of the Logatchev-1 field (based on XFA data)

Mineral	Formula	Abundance
Sulfides		
Chalcocite	Cu_2S	□
Djurleite	$Cu_{1.93-1.96}S$	■
Roxbyite	$Cu_{1.75-1.82}S$	■
Digenite	$Cu_{1.75-1.78}S$	□
Anilite	$Cu_{1.75}S$	+
Geerite	$Cu_{1.5-1.6}S$	+
Spionkopite	$Cu_{1.4}S$	+
Yarrowite	$Cu_{1.1}S$	□
Covellite	$Cu_2CuS(S_2)$	□
Bornite	Cu_5FeS_4	+
Chalcopyrite	$CuFeS_2$	□
Pyrite	FeS_2	□
Marcasite	FeS_2	+
Sphalerite (?)	ZnS	□
Chlorides		
Atacamite	$Cu_2Cl(OH)_3$	■
Clinoatacamite	$Cu_2Cl(OH)_3$	□
Paratacamite	$(Cu,Zn)_2Cl(OH)_3$	+
Oxides		
Tenorite	CuO	+
Trevorite (?)	$NiFe_2O_4$	+
Goethite	$HFeO_2$	■
Hematite	Fe_2O_3	+
Pyrochroite	$Mn(OH)_2$	+
Quartz	SiO_2	□
Carbonates		
Calcite[1]	$CaCO_3$	■
Aragonite	$CaCO_3$	■
Magnesite	$(Mg, Fe)CO_3$	+
Dolomite	$CaMg(CO_3)_2$	□
Siderite (?)*	$FeCO_3$	+
Sulfates		
Devilline (?)	$CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$	+
Gypsum	$Ca(SO_4) \cdot 2H_2O$	+
Brochantite	$Cu_4(SO)_4(OH)_6$	+
Barite	$BaSO_4$	+
Silicates		
Anorthite	$(Ca,Na)(Al_2Si_2O_8)$	□
Albite	$NaAlSi_3O_8$	+
Chabazite	$Ca_2Al_4Si_8O_{24} \cdot 12H_2O$	+
Nontronite	$Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$	+
Amphiboles		+
Chrysotile[2]	$Mg_3Si_2O_5(OH)_4$	□
Talc[3]	$Mg_3(Si_4O_{10})(OH)_2$	□
Jonesite (?)	$K_2Ba_4Ti_4Al_2Si_{10}O_{36} \cdot 6H_2O$	+
Mg-chlorite	$(Mg_5Al)(AlSi_3O_{10})(OH)_8$	■
Mixed-layer minerals		□
Smectites		□

Note: Minerals: (■) Major, (□) secondary, (+) accessory. (*) Based on EPMA data; [1]locally, Mg-bearing; [2]probably, Ni-bearing (nepouite, ASTM 25-524); [3]probably, Ni-bearing (willemseite, ASTM 22-711).

Table 2. Interplanar distances of roxbyite

Roxbyite JCPDS 23-958 (Mumme *et al*., 1988)		Roxbyite from the Logatchev-1 field					
		Sample M-2 (chimney wall) Gandolfi		Sample 918-6 (concretion in sediments, Station 918) Gandolfi		Sample 918-20/2 (concretion in sediments, Station 918) Diffractometer	
I	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*I*	*d*, Å
10	6.72						
		2	5.208				
10	4.75						
20	4.24					5	4.22∅
10	3.88						
30	3.60					7	3.583
55	3.35	2	3.348	4	3.34	20	3.345
5	3.16	1	3.165				
45	3.00	2	3.003	3	2.990	25	2.994
75	2.864	2	2.871[1]	4	2.859	35	2.856
65	2.630	5	2.629	7	2.631a	35	2.623
35	2.537					35	2.530
		2	2.518[1]				
25	2.452					15	2.444
90	2.374	8	2.389[1]	9	2.381	50	2.370
10	2.300						
15	2.238					15	2.254
10	2.178					10	2.171
10	2.123	3	2.132	5	2.133		
10	2.023	1	2.035				
10	1.979						
5	1.962						
100	1.938	10	1.948[1]	9	1.943	100	1.933
10	1.896						
90	1.861	9	1.863	10	1.861	55	1.855
10	1.794						
10	1.762						
5	1.705						
40	1.678	4	1.675	6	1.672	20	1.673
5	1.656						
20	1.628	3	1.631	4	1.624	10	1.624b
5	1.584						
10	1.560						
10	1.540						
5	1.526						
20	1.501			3	1.497	7	1.497b
10	1.482						
10	1.463						
10	1.444						
10	1.431						
10	1.399						
	1.342			2	1.340		
	1.268						
	1.246						
	1.186						
	1.134						
				3	1.086[2]		
				1	1.070		
				2	1.032		

Note: [1]Djurleite reflections or coinciding with djurleite; [2]chalcocite reflections.

Table 3. Interplanar distances and unit cell parameters of roxbyite from sediments at Station 817 of the Logatchev-1 hydrothermal field

Roxbyite, ASTM 23-958 (Mumme *et al.*, 1988)			Roxbyite from the Logatchev-1 field, Sample 817-9/2, depth 86–88 cm		
d (Å)	*I*	*h k l*	*d* (Å)	*I*	*h k l*
6.72	10	4 4 0			
6.72	10	0 0 2			
4.75	10	8 0 2			
4.75	10	4 4 2			
4.25	20	12 2 0			
4.24	20	10 0 2	4.24*	20	12 0 1
3.88	10	8 6 1			
3.88	10	0 8 0			
3.600	30	3 7 2	3.603*	35	3 7 2
3.600	30	1 5 3			
3.350	55	16 0 0	3.352*	65	12 4 2
3.160	5	6 0 4			
3.000	45	8 0 4	3.004*	50	16 0 2
2.864	75	18 2 1	2.864*	90	18 2 1
2.864	75	12 8 1			
2.630	65	20 0 1	2.628*	60	10 10 1
2.630	65	10 10 1			
2.537	35	20 4 0	2.535*	40	16 4 3
2.537	35	0 10 3			
2.452	25	1 5 5	2.446*	25	12 8 3
2.452	25	22 0 0			
2.374	90		2.374*	95	20 4 2
2.300	10	10 10 3			
2.300	10	6 6 5			
2.238	15	1 13 2			
2.238	15	8 6 5			
2.178	10	5 1 6			
2.178	10	1 3 6			
2.123	10	6 14 1			
2.023	10				
1.979	10				
1.962	5				
1.938	100	0 16 0	1.934*	100	25 1 3
1.938	100	0 8 6			
1.896	10	1 1 7			
1.896	10	0 2 7			
1.861	90	8 8 6	1.860*	75	12 6 6
1.794	10				
1.762	10				
1.705	5				
1.679	40		1.677b	30	24 12 1
				$a = 53.693 \pm 0.054$	
				$b = 30.895 \pm 0.018$	
				$c = 13.332 \pm 0.017$	
				$\beta = 89.72 \pm 0.16$	

Note: (b) Broad diffuse peaks; *peaks used for the calculation of unit cell parameters.

Table 4. Distribution of copper sulfides in sediments of the Logatchev-1 field based on XRD (diffractometry and Debyegram technique) and EPMA data

Mineral	Chemical formula	Station		
		813	918	817
Chalcocite	$Cu_{2.01–2.03}S$*		■	□
Djurleite	$Cu_{1.94–1.97}S$*	■	□	□
Roxbyite	$Cu_{1.72–1.90}S$*	□	■	■
Digenite	$Cu_{1.75–1.78}S$			■
Anilite	$Cu_{1.75}S$		□	
Geerite	$Cu_{1.5–1.6}S$			□
Spionkopite	$Cu_{1.4}S$			+
Yarrowite	$Cu_{1.1}S$			■
Covellite	CuS	□		+

Note: Minerals: (■) Major, (□) secondary, (+) rare. (*) Compositions of minerals studied in the present work (Table 5).

parameters. For example, the presence of even a small amount of reactive oxygen in aqueous medium promotes the partial loss of Cu in chalcocite and its transformation into djurleite. The subsequent products of dissolution (Cu leaching) can be present as roxbyite, anilite, and minerals of the geerite–covellite series.

In hydrothermal sulfide chimneys of the Logatchev-1 field, copper sulfides sometimes precipitated as hexagonal chalcocite on outer walls (Fig. 6). However, they were mainly developed along fractures and as metasomatic replacement of outer walls of chimneys composed of concentric-zonal aggregates of iron and copper–iron sulfides, such as bornite, chalcopyrite, isocubanite, pyrite, and others (Gablina *et al.*, 2000). Such zonality has been investigated in detail for the Rainbow sulfide edifice (Borodaev *et al.*, 2004). The zonality is a result of geochemical contradiction during the reaction of the hot acid methane- and H_2S-containing hydrothermal brines with the cold low-alkaline oxygenated seawater. The development of the outer (copper sulfide) zone indicates decrease in the sulfide ion concentration and increase in the redox potential from the conduit of hydrothermal solutions to outer walls contacting with the seawater. Fresh copper sulfides in the edifices are composed of nonstoichiometric minerals primarily represented by two-phase djurleite–anilite associations with the subordinate Cu-poor sulfides of the geerite–covellite

Table 5. Composition of copper sulfides in sediments of the Logatchev-1 field (based on EPMA data)

Sample no.	Location	Analysis no.	Cu	Fe	Ca	S	Total	Formula	Minerals (based on XRD data)
918-5	Station 918, interval 57–62 cm	4	80.54	–	0.30	21.37	102.21	$Cu_{1.90}S$	Roxbyite with an admixture of djurleite
	»	5	75.82	1.35	0.14	21.45	98.78	$Cu_{1.78}Fe_{0.04}S$	»
	»	6	76.95	0.21	0.43	21.50	99.09	$Cu_{1.80}S$	»
	»	8	76.97	0.52	0.25	22.54	100.29	$Cu_{1.72}Fe_{0.01}S$	»
	Average of 4		77.57	0.52	0.28	21.71	100.08	$Cu_{1.80}Fe_{0.01}S$	»
918-5	Station 918, interval 57–62 cm	1	78.36	–	0.20	20.10	98.66	$Cu_{1.97}S$	Djurleite
»	»	2	80.26	–	0.25	20.63	101.15	$Cu_{1.96}S$	»
»	»	3	79.01	–	–	20.60	99.61	$Cu_{1.94}S$	»
	Average of 3		78.512	0.164		20.597	99.273	$Cu_{1.95}S$	»
918-2	Station 918, interval 35–37 cm	9	78.63	0.21	0.19	19.53	98.56	$Cu_{2.03}S$	Chalcocite
»	»	11	78.39	–	–	19.65	98.03	$Cu_{2.01}S$	»
	Theoretical composition of chalcocite		79.86	–		20.14		Cu_2S	
	Composition of djurleite (Roseboom, 1966)		79.53	–		20.47		$Cu_{1.96}S$	
	Composition of roxbyite (Mumme *et al.*, 1988)							$Cu_{1.74–1.82}S$	

Table 6. XRD data on djurleite–anilite associations in ores of the Logatchev-1 field (crystals on chimney walls)

Djurleite (Roseboom, 1966)		Synthetic anilite Cu_7S_4 (Morimoto *et al.*, 1969)		Djurleite-anilite associations from the Logatchev-1 field (Station 12)			
				djurleite prevails		anilite prevails	
I	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*I*	*d*, Å
1	4.28						
1	3.89						
2	3.752						
2	3.586						
5	3.386	20	3.36	2	3.3475	1	3.4267
1	3.35	17	3.32			1	3.3669
3	3.282						
		57	3.20			7	3.2000
3	3.192			1	3.1652		
2	3.100						
3	3.04						
3	3.01			2	3.0026	2b	3.0337[2]
2	2.89						
2	2.87			2	2.8707		
1	2.82	65	2.77			8b	2.7894
1/2	2.73	6	2.75				
1	2.69	14	2.69				
1	2.654			5	2.6290	1	2.6523[2]
1/2	2.595	29	2.59				
1	2.557	31	2.54			1	2.5397
1/2	2.514			2	2.5184		
1	2.477						
1/2	2.41						
9	2.387	10	2.39	8	2.3890	3	2.3984[2]
1/2	2.289						
		39	2.16			5	2.1543
1/2	2.142	15	2.13	3	2.1322[1]		
1/2	2.107						
1	2.069						
1/2	2.047	5	2.05	1	2.0353	1	2.0619
9	1.964						
9	1.957	100	1.956	10	1.9479[1]	10	1.9598
10	1.871	10	1.873	9	1.8634	4	1.8742[2]
		3	1.847				
1	1.693						
1	1.683	35	1.677	4	1.6754[1]	4b	1.6837[2]
				3	1.6315		

Note: [1] Anilite lines or common lines of djurleite and anilite; [2] djurleite lines or lines intensified by djurleite.

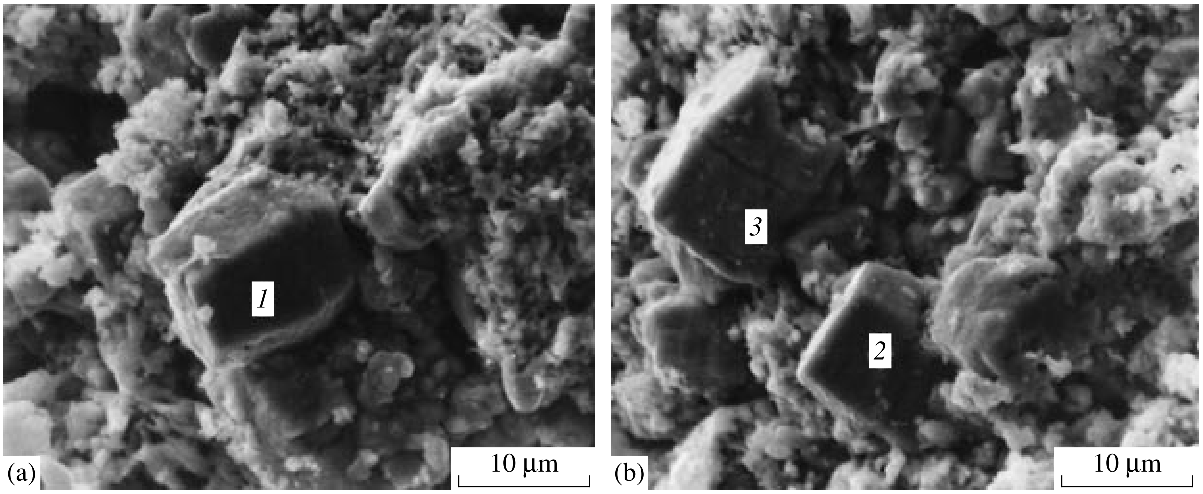

Fig. 6. Copper sulfide crystals on walls of an active chimney of the Logatchev-1 field (SEM image). (a) Hexagonal bipyramid of copper sulfide crystal $Cu_{1.86}S$ (*1*); (b) fractured and corroded hexagonal copper sulfide crystals: compositions of the lower (*2*) and upper (*3*) crystals match formulas $Cu_{1.56}S$ and $Cu_{1.49}S$, respectively.

series and the minor roxbyite. Prevalence of nonstoichiometric minerals and replacement structures in the sulfide edifices indicates the disintegration of copper sulfides located in constant contact with seawater immediately after their precipitation. Under the influence of seawater, they begin to loose Cu and give way to Cu-depleted sulfides of the Cu–S system. The abundance of anilite in these ores is related to its good preservation in cold seawater (anilite is stable up to 30°C). Thus, anilite can be considered a typomorphic mineral of oceanic hydrothermal edifices (Gablina *et al.*, 2000).

In sediments of the Logatchev-1 field, copper sulfides are present both in sulfide edifice fragments submerged in the mud (Station 813) and in authigenic sulfide accumulations scrutinized at Station 918. It is evident from Fig. 3 that the lumpy-isometric sulfide concretions include compact intergrowths of hexagonal crystals that often make up pseudomorphs after organic remains. Their shape and structure indicate authigenic formation. The abundance of paramorphoses of copper sulfides after the hexagonal chalcocite testifies to high temperatures of their formation, probably, from thermal fluids percolating in the unconsolidated sediment. The copper sulfides could partly represent colloidal lumps that also began to recrystallize at high temperatures (>103°C is the lower stability limit for hexagonal chalcocite). The sulfide concretions are almost completely composed of copper sulfides with rare relict inclusions of pyrite, chalcopyrite, bornite, and sphalerite. The sulfides are confined to dark-colored organic-rich units. The overlying red-colored layers include iron hydroxides and atacamite $Cu_2Cl(OH)_3$, while the underlying layers are enriched in iron hydroxides. Hence, sulfides were formed during diagenesis in a reductive environment of organic-rich bottom sediments. Such mechanism of ore formation is known for ancient cupriferous shales in Central Europe (Permian Mansfeld, Lubin-Seroshovitse, and other deposits), United States (White Pine deposit in Late Proterozoic shales of the Nonsach area), Africa, and other regions (White, 1971; Lur'e and Gablina, 1972; Lur'e, 1988; Gablina, 1997; and others). In both scenarios, sulfides presumably accumulate at the biogeochemical reductive barrier represented by the organic-rich black bottom sediments. However, cupriferous shales are formed during the discharge of cold or warm metalliferous subsurface waters in the coastal zone of continental and marginal-marine basins, whereas ore-bearing sediments are accumulated on the seafloor in zones of active hydrothermal activity at high temperatures and pressures. The physicochemical barrier developed under such conditions is characterized by a sharp contrast of all parameters. Therefore, high-temperature sulfides (hexagonal chalcocite and cubic digenite) accumulated in the course of intense hydrothermal activity are transformed soon after the termination of the hydrothermal activity. At lower temperatures, the hexagonal chalcocite is transformed into the monoclinic modification, whereas the high-temperature digenite is transformed into the low-temperature pseudocubic modification, anilite, or anilite–djurleite associations. Their further transformations are related to the impact of the ambient interstitial water.

Modern sulfide ores in oceanic sediments are primarily composed of roxbyite and djurleite. Chalcocite, anilite, and digenite are the subordinate minerals. Chalcocite is preserved as monomineral patches in the inner zone of dense clusters that are not altered by interstitial waters. The surface of sulfide concretions is intensely dissolved and destroyed by interstitial waters, probably, with the participation of oxidizing microorganisms (Fig. 4). This is accompanied by the transformation of chalcocite into nonstoichiometric copper sulfides (with oxidized Cu); the replacement of sulfides by atacamite, aragonite, and other carbonates; and the concentration of organic carbon. Roxbyite is among the most widespread products of the initial oxidation of chalcocite in sediments. This feature is the most prominent distinction of the diagenetic transformation of copper sulfides (in the sediment) from their supergene alterations on the seafloor (at the contact with seawater). As was emphasized above, anilite is an indicator of the supergene process.

Differences in the mineral composition of products of the alteration of primary chalcocite are probably related to physicochemical constraints of the environment. Roxbyite is a common product in experiments with the chemical and electrochemical leaching of Cu from chalcocite at room temperature (Cavalotti and Salvago, 1969; Flamini *et al.*, 1973; Brage and Lamache, 1979; Koch and McIntyre, 1976). It has been experimentally established that sulfides with a lesser amount of Cu are more stable at room temperature (~25°C) under conditions of higher acidity and oxidizing potential of the medium. This is caused by the oxidation of a portion of Cu up to the bivalent state. In experiments with the synthesis of copper sulfides at low temperatures close to those in the oxidation zone, Rickard (1973) reacted Na_2S with Cu_2O and obtained djurleite in an alkaline medium ($pH > 7.65$) and covellite in a more acid medium ($pH < 7$). In experiments with the leaching of Cu from djurleite contained in copper concentrates of the Olympic Dam deposit with the help of H_2SO_4, the roxbyite-type phase is the first transitional product in the djurleite–covellite series (Mumme *et al.*, 1988). The reaction duration and solution concentration are very important. Kosyak *et al.* (1980) reacted the natural chalcocite with 5%-HCl solution and obtained the chalcocite–djurleite association after 1 day, djurleite after 2 days, the djurleite–anilite association after 3 days, anilite after 4 days, and covellite after 36 days. Whiteside and Goble (1986) performed experiments with the leaching of Cu from synthetic chalcocite and digenite by acid solutions of iron sulfate of different concentrations. The dissolution of synthetic digenite produced first anilite and then metastable polymorphs of geerite, spionkopite, yarrowite, covellite, and CuS_2 with structures based on the cubic close packing of sulfur atoms. Two scenarios of Cu leaching were observed in the course of chalcocite dissolution (Fig. 7). In a strongly diluted solution ($\leq 10^{-2}$ M), the dissolution proceeded slowly in the following way: chalcocite–tetragonal $Cu_{1.96}S$–digenite–anilite–geerite–covellite-type metastable phases (with cubic sublattice of sulfur) that do not exist in nature. Tetragonal $Cu_{1.96}S$ is formed here as a transitional structure between chalcocite (with a hexagonal close packing of sulfur) and digenite (with cubic sublattice of sulfur). In the case of rapid leaching due to high concentration of the solvent ($>10^{-1}$ M), chalcocite was never transformed into structures based on the cubic close packing. The mineral was first transformed into djurleite and then into spionkopite and yarrowite without the transitional phases (digenite, anilite, and geerite), the formation of which requires a structural rearrangement of the anionic sublattice. The intermediate product between djurleite and Cu-poor sulfides (spionkopite and yarrowite) was represented by a roxbyite-type phase with the composition approximately corresponding to ≈ $Cu_{1.9}S$ with the characteristic reflection 1.93 (Whiteside and Goble, 1986).

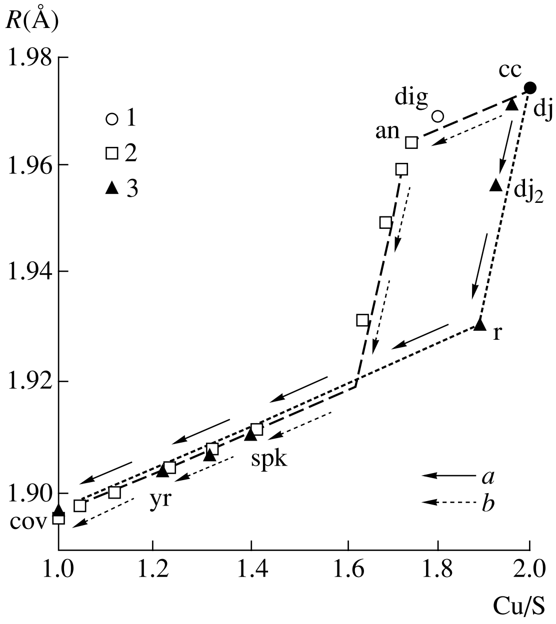

Fig. 7. Composition vs. *d* relationship during the dissolution of digenite and chalcocite grains (Whiteside and Goble, 1986). (1) Starting material; (2) leaching phases with the main structures based on the cubic close packing; (3) leaching phases with structures based on the hexagonal close packing. Arrows show two trends of chalcocite leaching: (*a*) rapid leaching at high concentration of solvent; (*b*) slow leaching at weak concentration of solvent. Abbreviations: (cc) chalcocite, (dig) digenite, (dj_1) djurleite with composition matching $Cu_{1.96}S$, (dj_2) djurleite with composition matching $Cu_{1.93}S$, (r) roxbyite-type phase, (spk) spionkopite, (yr) yarrowite, (cov) covellite.

Thus, the abundance of roxbyite in sediments and its extremely rare occurrence in seafloor sulfide concretions of the Logatchev-1 field are probably related to different concentrations of solutions that react with the primary chalcocite. Interstitial waters are more concentrated than the seawater, primarily, owing to the continuous exchange reactions between the liquid and solid phases of the sediment in the course of diagenesis. In addition, the sediments, presumably, inherit to a certain extent physicochemical parameters of primary hydrothermal solutions characterized by a salinity of as much as 26 wt % NaCl equiv (Bortnikov *et al.*, 2004) and a pH value of 3.35–3.9 (Gurvich, 1998). Equilibrium between the newly formed sulfides and the ambient medium is disturbed under the influence of the descending seawater after the termination of hydrothermal activity and the consequent decrease in temperature and pressure of hydrothermal fluids. The diagenetic dissolution of hydrothermal sulfide concretions follows a scenario of the rapid leaching of Cu from chalcocite and the formation of nonstoichiometric copper sulfides based on the hexagonal sublattice of sulfur. Sediments of the Logatchev-1 field in the study area could be affected by oxidative fluids that gradually replaced the metalliferous hydrothermal solutions. This is indirectly suggested by the hematitization of basic and ultrabasic rocks of the substrate.

The newly forming sulfides are in immediate contact with seawater on the seafloor. The seawater is a diluted reagent characterized by the salt concentration of not more than 4 wt % NaCl equiv, low-alkaline reaction (pH 7.8), low temperature (2–5°C), and presence of dissolved oxygen (Gurvich, 1998). Chalcocite and djurleite are slowly dissolved in the seawater. Leaching products may contain nonstoichiometric sulfides with the cubic anionic sublattice (anilite and geerite), the transition to which is accompanied by a prolonged rearrangement of the hexagonal close packing of sulfur anions into the cubic version.

The rate of Cu and S oxidation during diagenetic alterations of sulfides in the sediments can also be fostered by the presence of microorganism colonies on the disintegrating sulfides (Fig. 4). Yakhontova and Nesterovich (1984) experimentally demonstrated that the oxidation of natural chalcocite at room temperature in acid and oxygenated solutions (pH 3.7, Eh > +0.5) is accompanied by the more rapid transfer of Cu (relative to S) into the solution. The presence of oxidative carbothionic bacteria considerably accelerates this process. The participation of microorganisms in the oxidation of reduced compounds in modern hydrothermal edifices and fluids leading to the formation of the chemically synthesized organic matter is indicated in (Gal'chenko, 2002; Lein, 2004; and others).

The presence of roxbyite in hydrothermal solutions is a reliable indicator of diagenetic alterations after the hydrothermal activity. Among the Cu-rich copper sulfides, roxbyite is a unique mineral that forms only as the product of dissolution. This mineral is unknown in exsolution products of the high-temperature digenite that grades into the low-temperature digenite or breaks down into anilite and djurleite at a lower temperature (Flamini *et al.*, 1973; and others). Roxbyite is produced by the chemical and electrochemical synthesis at room temperature. At 50–70°C, this mineral is transformed into digenite (Flamini *et al.*, 1973; Mumme *et al.*, 1988). The transition is irreversible, because the high-temperature digenite is transformed into the low-temperature modification, while roxbyite is not reduced (Flamini *et al.*, 1973). Thus, roxbyite can be considered an indicator of initial stages of the diagenesis of cupriferous sediments at ordinary (<50°C) temperatures. Later transformations lead to the sequential replacement of this mineral by Cu-poor sulfides, such as spionkopite, yarrowite and (or) covellite, and atacamite. Upon drying in air, the sediments are coated with the newly formed brochantite ($CuSO_4$), testifying to the fact that the interstitial water contains an appreciable amount of Cu^{+2} that is transferred into the solution due to the processes described above.

CONCLUSIONS

(1) The association of copper sulfides is confined to black reduced interlayers of ore-bearing sequences in the modern Logatchev-1 hydrothermal field.

(2) The association is mainly composed of nonstoichiometric copper sulfides dominated by roxbyite ($Cu_{1.72–1.86}S$) that is an indicator of the low-temperature (<50°C) oxidation of chalcocite in an aggressive physicochemical environment.

(3) The formation of the modern mineral composition of sulfide concretions during the diagenesis of enclosing rocks can be subdivided into two stages: (a) the precipitation of high-temperature sulfides, such as the hexagonal chalcocite (Cu_2S) and, probably, cubic digenite ($Cu_{1.8}S$) from the high-temperature hydrothermal metalliferous solution in organic-rich bottom sediments that served as a biogeochemical barrier; (b) low-temperature transformations of primary copper sulfides after the termination of the hydrothermal activity according to the following scheme: hexagonal chalcocite–monoclinic chalcocite (Cu_2S)–djurleite ($Cu_{1.93–1.96}S$)–roxbyite ($Cu_{1.72–1.86}S$)–spionkopite ($Cu_{1.4}S$)–yarrowite ($Cu_{1.1}S$)–covellite (CuS)–copper sulfides + copper chlorides.

(4) The transformation of copper sulfides in the course of diagenesis is more rapid in sediments than in sulfide edifices on the seafloor.

(5) Oxidative microorganisms play a significant role in the diagenetic transformation of sulfides.

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