Partizansky Base-Metal Skarn Deposit, Dal'negorsk Ore District, Russia: Stages of Ore Formation, Mineral Assemblages, and Typomorphism of Fahlore

L. F. Simanenko

Far East Geological Institute, Far East Division, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

Received March 13, 2006

Abstract—As indicated by mineralogical, geochemical, and structural–textural data, the base-metal skarn ore at the Partizansky deposit was formed during two stages (base-metal skarn and silver-sulfosalt), which were separated by intrusion of basaltic dikes. The bulk of the base-metal ore was deposited at the first stage, which comprises four sequential mineral assemblages: skarn–silicate, quartz–arsenopyrite, productive galena– sphalerite, and pyrrhotite–pyrite–chalcopyrite. The mineralization of the second stage was mainly confined to the upper margins of orebodies and pertains to the sulfosalt–galena–chalcopyrite assemblage, which was superimposed on minerals of the first stage. The vertical mineralogical–geochemical zoning of the deposit is telescopic (related to the formation of the late silver-sulfosalt mineralization) and facies (typical of the early skarn and base-metal assemblages). The zoning of the skarn–silicate assemblage is expressed in the metasomatic replacement of skarn by quartz and calcite in the uppermost zone of skarn bodies and is emphasized by variation of the mineral composition throughout the skarn column, for instance, by the distinct updip enrichment of hedenbergite in manganese. The vertical zoning of the productive assemblage is emphasized by variations in the ratio of sphalerite to galena (the Pb/Zn ratio in the ore increases upward from 0.1 to 1), changes in mineral assemblages, and compositional variation of major ore-forming and minor minerals. In particular, galena from the deep levels is extremely enriched in Bi and Ag, while that from the upper levels is almost completely devoid of isomorphic admixtures. Fahlore displays updip enrichment in Sb, Ag, and Fe and corresponding depletion in Cu and Zn. The vertical chemical variations in fahlore are caused by the specific geological setting of ore deposition, the composition of the ore-forming solutions, and the physicochemical conditions of their transportation and ore deposition.

DOI: 10.1134/S1075701506040040

INTRODUCTION

The base-metal skarn deposits of the Dal'negorsk ore district have been known since the 19th century and remain of economic value. Significant attention has been paid to systematic variations in the typomorphic features of skarn silicate minerals and major ore-forming sulfides (Mozgova, 1957; Shadlun and Dobrovol'skaya, 1986; Blagodareva et al., 1974; Koreneva and Kolesnikov, 1987; Dobrovol'skaya, 1989; Dobrovol'skaya et al., 1993; Ratkin et al., 1994; Simanenko, 1998). New data on the formation sequence, structure, and mineralogy of the skarn orebodies were obtained from deep levels of orebodies that became accessible in the last decade. The spatial variations in the chemical composition of fahlore are of special interest.

GEOLOGY OF THE DEPOSIT

The Dal'negorsk district is a part of the Pacific ore belt and is located in the Taukha Terrane, a fragment of an Early Cretaceous accretionary prism (Golozubov and Khanchuk, 1995). Terrigenous rocks, including olistostrome and turbidite sequences of this terrane, are deformed into a system of tightly compressed linear folds, which strike in the NE direction and are overlain by a gently dipping sequence of Late Cretaceous intermediate-to-acid volcanic rocks of the East Sikhote-Alin belt (Fig. 1). Middle–Upper Triassic limestones considered fragments of paleoguyots are often associated with high-Ti subalkali basalts (Khanchuk et al., 1989).

The Partizansky deposit is located in the town of Dal'negorsk, on the right bank of the Rudnaya River. The ore-hosting mixtites of the olistostrome complex are made up of a terrigenous, mainly silty matrix containing varisized blocks, clasts, and sheets of Lower Cretaceous sandstone, Triassic–Jurassic siltstone, and Middle to Upper Triassic limestone. Individual sheets are as large as 2–4 km long and 200– 800 m thick.

Most skarn orebodies of the Partizansky deposit are localized at the contacts of a large steeply dipping lime-

Address for correspondence: L.F. Simanenko. E-mail: fegi@online.marine.su

Fig. 1. Schematic geological map of the central Dal'negorsk ore district, modified after V.V. Golozubov and B.I. Kuznetsov. (1) Quaternary alluvium; (2) Late Cretaceous (a) volcanic rocks and (b) granodiorite; (3) bedded sandstone, siltstone, and flysch sediments; (4) mixtite; (5) sinistral strike-slip fault; (6) axis of antiform; (7, 8) allochthonous blocks: (7a) limestones and (7b) basalts as fragments of Middle–Late Triassic guyots, (8a) banded cherts and (8b) Triassic–Jurassic cherty–clayey rocks conformably overlain by Lower Cretaceous turbidites; (9) base of cherty–terrigenous allochthons; (10) Partizansky deposit.

stone olistolith with siltstone and sandstone. The position of the orebodies is clearly controlled by faults. Some orebodies are localized at the contact of limestone with overlying Late Cretaceous volcanic rocks. Ore lodes are variably dipping veins, lenses, and pipelike bodies made up of skarn with sulfide mineralization. They are crossed by underground workings spaced at intervals of $35-70$ m down to a depth of $~600$ m. Below, at a depth of 800 m, the ore zones pinch out and grade into almost unaltered limestone, while aluminosilicate rocks are replaced by quartz, sericite, and biotite.

COMPOSITION OF MINERAL ASSEMBLAGES AND SEQUENCE OF THEIR DEPOSITION

The skarn bodies of the Partizansky deposit consist mainly of hedenbergite, garnet, ilvaite, and axinite, with minor wollastonite, vesuvianite, fluorite, quartz, and calcite.

Sphalerite and galena are the major ore minerals. Chalcopyrite, arsenopyrite, luzonite, pyrite, marcasite, pyrrhotite, acanthite, fahlore, Ag–Pb–Sb and Bi sulfosalts, intermetallic compounds and native elements (allargentum, bismuth, silver, gold), Bi tellurides and sulfotellurides (hedleyite, Se-bearing joseite A), and iron oxides (magnetite, hematite) occur in subordinate and minor amounts.

The ores have medium- to coarse-grained texture and massive, mottled, pocket–disseminated, and stringer–disseminated structure. Druses of sulfides associated with calcite, quartz, fluorite, and zeolites often fill cavities regarded as a result of hydrothermal karst.

Two stages of endogenic mineralization, (I) basemetal skarn and (II) silver-sulfosalt, were recognized on the basis of relationships between orebodies and structural–textural features of skarn and ore. The basemetal skarn stage comprises the following assemblages (in order of formation): skarn–silicate, quartz–arsenopyrite, galena–sphalerite, and pyrite (pyrrhotite)– marcasite–chalcopyrite. The late silver-sulfosalt stage was marked by the formation of the sulfosalt–galena– chalcopyrite assemblage (Simanenko, 1997).

The absence of deformation and crosscutting relations between skarn silicate minerals and younger ore mineral aggregates of the first stage allows us to consider them as consecutive mineral assemblages that were derived from a common hydrothermal system.

The mineral aggregates of the silver-sulfosalt stage postdate the local brecciation of base-metal skarn orebodies, which are crosscut by mineral aggregates of the second stage. The late mineralization was separated from the mineral aggregates of the first stage not only by tectonic movements but also by emplacement of basaltic dikes. Pustov (1990) described the superposition of the silver-sulfosalt assemblage on postmineral (with respect to base-metal ore) dikes of porphyritic basalt dated at 57 ± 5 Ma.

The four mineral assemblages of the first stage are widespread in all orebodies of the deposit and occur in close proximity to one another. The silver-bearing assemblages of the second stage are developed at the flanks of the deposit, beyond the orebodies, or as cutting veinlets and superimposed pocketlike aggregates in the uppermost parts of the orebodies. In the latter case, the products of the second stage are spatially juxtaposed with the mineral complex of the first stage. The skarn orebodies of the first stage demonstrate a gradual change in mineral assemblages and chemical composition of particular minerals with depth.

The mineral assemblages are briefly described in the next section in the order of their formation.

Base-Metal Skarn Stage

Skarn–silicate assemblage. Thick skarn zones developed along the fracture systems at the contact of limestone with aluminosilicate rocks owing to intense circulation of hydrothermal solutions. The vertical range of skarnification amounts to 600–700 m. At a depth of ~1 km, skarn zones give way to slightly greisenized aluminosilicate rocks that contain topaz, fluorite, muscovite, and tourmaline.

The skarn–silicate assemblage is composed of hedenbergite; garnet; axinite; ilvaite; and less abundant wollastonite, vesuvianite, fluorite, quartz, and calcite. In the Levoberezhny (left bank of the Rudnaya River) area, the early skarn–silicate assemblage at the basemetal skarn deposits (Verkhny, Pervy Sovetsky, and Nikolaevsky) also contains ore minerals (Dobrovol'skaya and Balashova, 1993; Mozgova and Borodaev, 1995). The possibility of simultaneous skarn and ore formation was confirmed by experimental studies (Ezhov, 1994). The Levoberezhny deposits are commonly composed of alternating bands of sulfides and silicate minerals. However, the Partizansky deposit does not show such structural relations between skarn and sulfides. As can be seen in hand specimens, only some intergranular segregations of Zn and Pb sulfides, chalcopyrite, pyrrhotite, and iron oxides may be regarded as syngenetic with respect to silicate aggregates. Although skarn and ore at the Partizansky deposit were closely related to each other in time, they did not form simultaneously, and most sulfides were superimposed on skarn bodies.

The metasomatic skarn column reveals a zonal arrangement of mineral assemblages.

The number of minerals in skarn reaches a maximum at the base of the lode, mainly composed of hedenbergite with less abundant ilvaite, garnet, fluorite, quartz, and calcite and minor vesuvianite and wollastonite. Axinite is contained in skarn close to the contact with terrigenous rocks. In the middle zone, the orebodies consist of predominant hedenbergite skarn with subordinate garnet, axinite, and quartz; no ilvaite is detected. In the upper zone of the orebodies (the pinching zone), the amount of silicate skarn minerals sharply decreases up to their complete disappearance, giving way to the preore veinlike quartz–calcite metasomatic bodies.

The vertical zoning of skarn is accentuated by variations in hedenbergite composition. The hedenbergite with the highest Fe content was found in the root zones of the orebodies. Updip, the Fe content in hedenbergite gradually decreases and the Mn content increases from 3 wt % (the level of -135 m) to 12 wt % (the level of +145 m). A similar but less contrasting trend is demonstrated by the variation of Fe and Al contents in garnet, represented by andradite in the lower zone and enriched in the grossular end member in the upper zone.

The quartz–arsenopyrite mineral assemblage predated the deposition of base-metal ore. Arsenopyrite associated with quartz forms scattered disseminations or pocketlike aggregates of skeletal and hypidiomorphic crystals both in skarn and in quartz–calcite preore metasomatic rocks at the upper levels of the deposit. The early crystallization of arsenopyrite I is evident because other sulfides and sulfosalts replace this mineral and fill fissures in its dismembered aggregates, cementing and corroding the fragments (Figs. 2a, 2b, 3a). The chem-

Fig. 2. Microstructure of ores from the upper and middle zones of the Second Contact orebody. (a, b) Replacement of arsenopyrite I (3) from the quartz–arsenopyrite assemblage with sulfide minerals of the productive galena–sphalerite assemblage: (1) sphalerite, (2) galena; black fields are silicates: (a) $+285$ m level, sample 536/1, magn. 100; (b) $+215$ m level, sample 612/2, magn. 100; (c) freibergite (1) in galena I (2) (productive galena–sphalerite assemblage), +145 m level, sample 539/2, magn. 800, immersion specimen; (d) disseminated freibergite (1) in galena II (2) from the upper zone of the orebody (sulfosalt–galena–chalcopyrite assemblage), +285 m level, sample 536/4, magn. 200.

ical composition of arsenopyrite varies with depth: the As content decreases from 47.49 wt % at the lower levels to 45.65 wt % at the upper levels. In addition, arsenopyrite at the upper levels is enriched in Sb (up to 0.24 wt %).

Minerals of the productive *galena–sphalerite mineral assemblage* were precipitated later than those of the quartz–arsenopyrite assemblage. Their formation was preceded by the brecciation of arsenopyrite, and the late minerals filled fractures and cemented brecciated arsenopyrite grains and aggregates. The galena– sphalerite orebodies exhibit vertical zoning (Ratkin et al., 1991, 1994), which is reflected in variations in mineral composition, the percentage of sphalerite and galena (the Pb/Zn ratio increases upward from 0.1 to 1), and the chemical composition of major and minor ore minerals. The root zones of the orebodies are largely composed of sphalerite (up to 95%), which occurs as pocketlike and massive aggregates in hedenbergite, hedenbergite–ilvaite, and hedenbergite–garnet–ilvaite

Fig. 3. Microstructures of ore from the root zone of the Second Contact orebody at the level of –135 m. (a) Replacement of arsenopyrite I (3) (quartz–arsenopyrite assemblage) with a fine-grained aggregate of Ag–Bi-bearing galena and cosalite (2) (productive galena–sphalerite assemblage), sphalerite (1), microinclusions of native Bi (4) in arsenopyrite; black fields are silicates; sample 571/3, magn. 200; (b) intergrowth of Zn–Fe tetrahedrite (1) and native Bi (2), sphalerite with chalcopyrite emulsion (3), sample 571/15, magn. 400; (c) inclusions of Zn–Fe tetrahedrite (1) in sphalerite (2); tetrahedrite contains disseminated arsenopyrite II (3) and chalcopyrite (4), sample 571/13, magn. 300; (d) disseminated native Bi (1) and tetrahedrite (2) in sphalerite, sample 571/15, magn. 200.

skarn. The Fe content in sphalerite from this assemblage is not higher than 2 wt %. Other ore minerals, including widespread Bi minerals (Simanenko, 1998), are second in abundance, making up fine disseminations or pocketlike polymineral segregations in sphalerite.

Finely disseminated galena occurs as veinlets and reticulate aggregates in sphalerite or, more rarely, as pockets in aggregates of silicate minerals or sphalerite grains. Galena occurs in tight intergrowths with Ag−Pb–Bi sulfosalts. As follows from microprobe results, galena is enriched in Ag and Bi, revealing a variable Bi/Ag ratio (Fig. 4).

Fahlore was detected in sphalerite as small monomineral inclusions (Fig. 3d) or polymineral aggregates intergrown with chalcopyrite, arsenopyrite II, and native Bi (Figs. 3b, 3c).

In addition to major galena and sphalerite, minor chalcopyrite and fahlore were found in this assemblage in the middle and upper zones of orebodies. The percentage of sphalerite and galena changes in these parts of the orebodies, with an insignificant predominance of

Fig. 4. Compositions (at %) of galena from the galena–sphalerite assemblage plotted on the Pb–Bi–Ag diagram. (1) Root zone (−135 m level) of the Second Contact orebody; (2) Bol'nichny ore lode (+75 and +145 m levels).

sphalerite over galena. No corrosion textures are observed in their intergrowths, testifying to nearly simultaneous crystallization (Figs. 2a, 2b). Embayments of galena in sphalerite indicate that sphalerite precipitated first and continued to precipitate together with galena. The upper zones of orebodies are composed largely by galena, where this mineral was formed later than sphalerite. Sphalerite in the galena–sphalerite mineral assemblage has a somewhat higher Fe content, which increases up to 3.5 wt % in the middle and up to 5 wt % in the upper zones of orebodies.

As was established by emission and atomic absorption spectroscopy, galena of this assemblage is depleted in admixtures. In particular, galena from the middle levels contains 0.023–0.033 wt % Ag, 0.048–0.060 wt % Sb, and 0.036–0.075 wt % Bi, and only 0.0008 wt % of these admixtures were detected in the upper parts of orebodies. Occasionally, galena contains disseminated fahlore (Fig. 2c). Minor amounts of chalcopyrite occur as a fine emulsion or microveinlets in sphalerite.

The pyrite (pyrrhotite)–marcasite–chalcopyrite mineral assemblage replaces the minerals of the productive galena–sphalerite assemblage. Fe disulfides and sulfides and chalcopyrite II are the major minerals. The variation in mineral composition of this assemblage accentuates the zoning of orebodies, where pyrrhotite largely occurs at deep levels and pyrite and marcasite at the middle and upper levels.

Silver-Sulfosalt Stage

The mineral aggregates of the silver-sulfosalt stage are widely developed at the uppermost level (+285 m) of the Second Contact orebody, where the early basemetal ore was overprinted by the *sulfosalt–galena– chalcopyrite assemblage*, which fills fissures and intergranular spaces in aggregates of the early sulfides and cements fragments of brecciated base-metal ore.

The characteristic feature of the sulfosalt–galena– chalcopyrite assemblage is the occurrence of abundant disseminations of Ag minerals (pyrargyrite, stephanite, acanthite) in galena II and chalcopyrite III as major sulfides. Chalcopyrite III and galena II also contain abundant and finely disseminated freibergite (Fig. 2d).

In my opinion, small quartz veins and stringer–disseminated zones reported by Garbuzov et al. (1983) from the Nikolaevsky deposit may be also referred to the second stage. They are spatially separated from the base-metal skarn bodies and contain disseminated Ag– Pb sulfostibnites (pyrargyrite, miargyrite, freibergite, boulangerite, andorite, diaphorite). These veins cut postmineral (with respect to base-metal skarn ore) gabbroids and pinch out at a shallow depth. At a depth of 100 m from the surface, the sulfosalt–silver–stibium ore veins give way to sphalerite–arsenopyrite–pyrite ore, which is significantly enriched in Bi but depleted in Ag, unlike the ore exposed at the surface.

The aforementioned data on the mineralogy of skarn and associated ore highlight a distinct zoning of the orebodies. The most pronounced mineralogical–geochemical zoning was revealed in the Second Contact orebody, the only one accessible for examination at six levels. The zoning of this orebody is characterized by the following attributes.

The root zone consists of garnet–ilvaite–hedenbergite skarn with subordinate fluorite, axinite, wollastonite, quartz, and calcite. Pyroxene contains more than 80% hedenbergite end member with an $Fe^{3+}/(Fe^{3+} +$ $Fe²⁺$) ratio of 0.14 on the basis of Mössbauer data. The ore in this zone is characterized by a prevalence of Zn over Pb (Pb/ $Zn < 0.5$), and sphalerite is the major ore mineral; matildite-galena solid solution, arsenopyrite, tetrahedrite, chalcopyrite, magnetite, Ag–Pb–Bi sulfosalts, Bi tellurides and sulfotellurides, native Bi, and pyrrhotite are also detected.

The middle zone of the lode is mainly composed of hedenbergite skarn. The hedenbergite is enriched in Mn and contains 51.5–60.6% hedenbergite end member, with an Fe³⁺/(Fe³⁺ + Fe²⁺) ratio of 0.7–0.11 based on Mössbauer data. The ore largely consists of galena and sphalerite (Pb/Zn \sim 0.8).

In the upper zone of the lode, skarn is almost completely replaced by quartz–calcite rock. The ore consists of sphalerite and galena (Pb/Zn > 0.1). Chalcopyrite, freibergite, stephanite, pyrargyrite, acanthite, pyrite, and marcasite are common minerals.

As was established previously, the zoning, similar in all orebodies, is polygenetic and reflects spatiotemporal variations in the temperature and physicochemical regime of skarnifying and ore-forming hydrothermal solutions (Ratkin et al., 1994).

MODE OF OCCURRENCE AND CHEMICAL COMPOSITION OF FAHLORE

In the root and middle zones of the orebodies, the major ore-forming sulfides of the productive assemblage pertaining to the first stage typically contain finely disseminated fahlore. The fahlore is most abundant in the upper zone of the First, Second, and Fifth Contact orebodies, where the spatial juxtaposition of the two mineral stages resulted in the development of complex Ag–Sb–Pb–Zn ore. Fahlore was detected both in the productive galena–sphalerite assemblage of the first stage and in the mineral assemblage of the second stage. In the Bol'nichny ore lode, fahlore as rounded and elongated inclusions of 10–50 µm in size occurs in sphalerite and chalcopyrite of the sharply dominant productive galena–sphalerite assemblage.

Twenty fahlore grains from 14 samples were taken from different levels of several orebodies for microprobe analysis (Tables 1, 2). In the Second Contact orebody, minerals from the upper zone (the level of $+285$ m), the middle zone (the level of $+5$ m), and the root zone (the level of –135 m) were analyzed. The First and Fifth Contact orebodies were sampled only at the upper level (+285 m). The Bol'nichny lode was sam-

pled at two levels of $+145$ and $+75$ m. The studied samples were subdivided into three groups (Table 1, I–III) in accordance with their position in the vertical section (from top to bottom). Samples from the Bol'nichny lode with less pronounced zoning were placed into the separate group IV (Table 1).

The chemical compositions of all analyzed fahlore grains are satisfactorily recalculated for their crystallochemical formulas (Tables 1, 2): $Me_{10}^{1+}Me_2^{2+}X_4^{3+}Y_{13}^{2-}$, where $Y = S$ and Se; $X = As$, Sb, Bi, and Te; $Me^{1+} = Cu$ and Ag; and Me^{2+} = Fe, Zn, Cu, Hg, Cd, Sn, and Pb (Mozgova and Tsepin, 1983; Spiridonov, 1985). In addition to major mineral-forming elements (Cu, Ag, Fe, Zn, Sb, As, S), fahlore also contains less typical elements: up to 6.77 wt $\%$ Bi and up to 2.76 wt $\%$ Pb (Table 1). The content of the major mineral-forming elements in the studied fahlore varies widely: 0.56– 33.06 wt % Ag, 13.39–40.23 wt % Cu, 2.68–5.92 wt % Fe, 0.22–5.43 wt % Zn, and 20.27–27.16 wt % Sb, with the content of As ranging from below the detection limit to 5.15 wt % (Fig. 5). The Ag/(Ag + Cu) ratio varies from 0.01 to 0.59; i.e., fahlore varieties where Ag prevails over Cu are present. The $Fe/(Fe + Zn)$ ratio ranges from 0.43 to 0.97 with a prevalence of Fe over Zn in most analyzed samples. Sb is predominant among semimetals; the Sb/As ratio as expressed in the fahlore number ($N_{\text{fahl}} = f.u.$ Sb/(f.u. Sb + f.u. As) \times 100) varies within 71–100%.

The chemical composition of fahlore significantly varies with depth, remaining similar at one level (Fig. 6). High-Ag fahlore, freibergite, occurs at the upper levels. The wide variation in Ag content throughout orebodies is clearly expressed in the $Ag/(Ag + Cu)$ ratio, which equals 0.01–0.09 in the root zone and 0.44 in the middle zone and reaches the highest value of 0.51–0.59 at the upper levels (Table 2, Fig. 7). The Fe content of fahlore also varies with depth. High-Zn fahlore (Fe/(Fe + Zn) = 0.43–0.49) was found at the deepest levels. This ratio increases up to 0.71 in the middle zone and reaches 0.86–0.97 in the uppermost zone, thus demonstrating a notable prevalence of Fe over Zn (Table 2, Fig. 8).

The Sb content in the studied fahlore tends to increase insignificantly from bottom to top. The Bi content decreases in the same direction: tetrahedrite from the Second Contact orebody at the level of –135 m contains $0.15-6.77$ wt % Bi (the average Bi content of six samples is 3.21 wt $\%$), whereas freibergite from the upper and middle zones typically contains no more than 0.4 wt % Bi (Table 1).

The vertical compositional variation in fahlore from the Bol'nichny ore lode is less significant, which is consistent with only a slight variability of sulfides.

The Zn and Bi contents in fahlore from the Bol'nichny lode are comparable with those from the deep levels of the contact orebodies. However, fahlore is characterized by a wide range of the Fe/(Fe $+$ Zn)

Fig. 5. Compositions of fahlore (at %) plotted on the metals (Me)–semimetals (SMe)–sulfur (S) diagram. (1) Root zone of the Second Contact orebody (–135 m level); (2) middle zone of the Second Contact orebody (+5 m level); (3) upper zone of the Second, First, and Fifth Contact orebodies (+285 m level); (4) Bol'nichny ore lode (+75 and +145 m levels). Numbers of points correspond to analysis numbers in Table 1.

ratio, from 0.49 to 0.90 (Tables 1, 2; Fig. 8). The $Ag/(Ag + Cu)$ values in fahlore from the Bol'nichny lode are transitional between the lowest-Ag fahlore from the root zone of the Second Contact orebody and the fahlore with moderate Ag content from the middle part of this orebody (Fig. 8).

CRYSTALLIZATION CONDITIONS OF FAHLORE

The chemical composition of fahlore testifies to the absence of significant differences in the composition of the ore-forming solutions and formation conditions between the productive assemblage (stage I) and the sulfosalt–galena–chalcopyrite assemblage rich in freibergite (stage II), in contrast to some other multistage deposits that experienced more complex evolution reflected in significant variations in contents of Sb, Cu, and other components (Spiridonov, 1985, 1987; Kovalenker et al., 1980). Many volcanic-hosted deposits, which were formed under abrupt changes in temperature, pressure, and redox conditions, contain fahlore markedly differing in ratios of semimetals. The early fahlore at these deposits typically shows a prevalence of As over Sb and is represented by tennantite, while the late fahlore is enriched in Sb and fits tetrahedrite in composition. Tellurium is the main semimetal in the latest fahlore, where S is partially substituted by Se; therefore, this fahlore is referred to as Se goldfieldite. The late fahlore generations are enriched in Bi in addition to Ag (Spiridonov, 1987).

Fahlore from most plutonogenic deposits, formed under a gradual decrease in temperature and pressure, demonstrates a slight enrichment in Sb and Ag from the early to the late generations (Spiridonov, 1985). In fahlore grains of the same generation, the rims are enriched in Sb, thus indicating an increase in the $Sb/(Sb + As)$ ratio during crystallization. In addition, during ore dep-

Fig. 6. Compositions of fahlore (at %) plotted on the Cu–Ag–Sb diagram. (1) Root zone of the Second Contact orebody (–135 m level); (2) middle zone of the Second Contact orebody (+5 m level); (3) upper zone of the Second, First, and Fifth Contact orebodies (+285 m level); (4) Bol'nichny ore lode (+75 and +145 m levels). Numbers of points correspond to the analysis numbers in Table 1.

osition, the Zn content in fahlore typically decreases, while the Fe content increases (Spiridonov, 1987).

No drastic changes in physicochemical conditions of mineral formation are recorded in the chemical variations of fahlore from the Partizansky deposit, apparently indicating an evolutionary spatiotemporal trend of the ore-forming fluid.

The composition of fahlore is known to depend on many parameters of ore deposition. Therefore, the established differences in proportions of components in the studied fahlore could be caused by a combination of different factors. It was suggested that a change in the salt, e.g., NaCl, content in the solution can shift the Ag/(Ag + Cu) ratio in fahlore (Sack and Loucks, 1985). This conclusion is based on the assumption that Ag and Cu are transported with hydrothermal solutions as chloride complexes of different stoichiometry. The exchange reactions between tetrahedrite and chloride complexes of Ag and Cu in solution, as well as between tetrahedrite and chloride complexes of Fe and Zn,

 $Cu_{10}Fe_2Sb_4S_{13} + 6AgCl^{-2}$ $= Ag_6Cu_4Fe_2SbS_{13} + 6CuCl⁰ + 6Cl⁻$, $0.5Cu_{10}Fe_2Sb_4S_{13} + ZnCl_4^{-2}$ $= 0.5Cu_{10}Zn_2Sb_4S_{13} + FeCl^+ + 3Cl^-$

are shifted to the right with a decrease in Cl activity in the solution and promote an increase the in $Ag/(Ag +$ Cu) and Fe/(Fe $+$ Zn) ratios in tetrahedrite.

The model of fractional crystallization of fahlore from hydrothermal solution (Hackbarth and Petersen, 1984) also deserves attention and explains the variations of the Sb/As and Cu/Ag ratios in these minerals. In terms of this model, the early fahlore, which was precipitated in proximity to the source of the solution, is enriched in Cu and As owing to their preferable incorporation in fahlore relative to Ag and Sb. During crystallization, the solution becomes depleted in Cu and As and enriched in Sb and Ag. This brings about the precipitation of fahlore containing more Ag and Sb.

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 4 2006

Fig. 7. The Ag content of fahlore (wt %) versus the fahlore number. (1) Root zone of the Second Contact orebody (–135 m level); (2) middle zone of the Second Contact orebody (+5 m level); (3) upper zone of the Second, First, and Fifth Contact orebodies (+285 m level); (4) Bol'nichny ore lode (+75 and +145 m levels).

According to the proposed model, the composition of fahlore precipitated at various depth levels and, thus, during various periods of mineral formation depends on the chemistry of the initial solution (the proportions of Cu, Ag, Sb, and As) and the coefficients of element partition between the liquid and solid phases, which depend on the temperature, pressure, and activities of the components in the solution.

According to published data (Bortnikov et al., 1987; Gamyanin and Bortnikov, 1989), an increase in the Fe content in fahlore is caused by a decrease in the temperature and sulfur activity of the ore-forming fluid rather than by a significant increase in the concentration of this element in the solution. Therefore, even high-Fe solutions can precipitate low-Fe fahlore at a high S activity, with incorporation of excess Fe into iron sulfides (pyrite at a high S activity and pyrrhotite and arsenopyrite at a relatively low S activity). This conclusion was drawn taking into account the correlation between Fe and Zn in coexisting fahlore and sphalerite. Since

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 4 2006

the Fe content in sphalerite is a function of temperature and sulfur activity, it is logical to suggest that these parameters control the Fe/(Fe $+$ Zn) ratio in fahlore (Gamyanin and Bortnikov, 1989). The study of homogenization temperatures in fluid inclusions in sphalerite coexisting with fahlore showed that a decrease in mineral formation temperature in the vertical section of the hydrothermal column with time (Ratkin et al., 1994) explains the low Fe contents in fahlore and sphalerite at the deep levels of the Second Contact orebody even at a high Fe content in the solution. In addition, there is evidence of an insignificant decrease in sulfur activity at the final stage of formation of the Partizansky deposit, when most freibergite had already been precipitated. Freibergite from the sulfosalt–galena–chalcopyrite assemblage (stage II) has the highest Ag and Fe contents and is associated with Ag sulfoantimonite characterized by a deficiency of sulfur.

Table 1. Chemical composition of fahlore from the Partizansky deposit (results of microprobe analysis, JXA-5A), wt %

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 4 2006

300

SIMANENKO

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 4 2006

PARTIZANSKY BASE-METAL SKARN DEPOSIT, DAL'NEGORSK ORE DISTRICT, RUSSIA 301

Fig. 8. The Fe/(Fe + Zn) ratio of fahlore versus the fahlore number. (1) Root zone of the Second Contact orebody (–135 m level); (2) middle zone of the Second Contact orebody (+5 m level); (3) upper zone of the Second, First, and Fifth Contact orebodies (+285 m level); (4) Bol'nichny ore lode (+75 and +145 m levels).

CONCLUSIONS

1. The Partizansky base-metal skarn deposit was formed during two stages (base-metal skarn and silversulfosalt), which were separated by intrusion of basaltic dikes. The first stage comprised four sequential mineral assemblages: skarn–silicate, quartz–arsenopyrite, productive galena–sphalerite, and pyrrhotite–pyrite–chalcopyrite. The mineral aggregates of the second stage are composed of the sulfosalt–galena–chalcopyrite assemblage, which is mainly confined to the uppermost portions of the orebodies.

2. The ore composed of the productive assemblage reveals a vertical zoning, which is expressed in variations of the sphalerite-to-galena ratio, changes in the composition of mineral assemblages, and a variable chemical composition of the ore-forming and minor minerals.

3. It was established that the distinct compositional variability of fahlore, which is expressed in an increase in Sb, Ag, and Fe and a decrease in Zn, Bi, and Cu from the bottom to the top of orebodies, is caused by the changing composition of ore-forming solutions and the evolution of physicochemical conditions during their transportation and ore deposition.

ACKNOWLEDGMENTS

I thank V.V. Ratkin and N.S. Bortnikov for their constructive advice and comments and V.I. Sapin for his assistance in studying the chemical composition of fahlore.

REFERENCES

- 1. N. S. Blagodareva, I. N. Govorov, E. D. Lagovskaya, and S. P. Slavkina, "Contributions to Mineralogy of the Sadovoe Lead–Zinc Deposit," in *Mineralogy, Magmatism, and Mineralization in the Far East* (Far East Sci. Center, Acad. Sci. USSR, Vladivostok, 1974), pp. 78–92 [in Russian].
- 2. N. S. Bortnikov, A. D. Genkin, and V. A. Kovalenker, "Mineralogical and Geochemical Indicators of Hydro-

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 4 2006

thermal Ore Formation Conditions," in *Endogenic Ore Regions and Deposits* (Nauka, Moscow, 1987), pp. 40–59 [in Russian].

- 3. M. G. Dobrovol'skaya, *Lead–Zinc Ore Mineralization (Ore Formations, Mineral Assemblages, Specific Features of Ore Deposition)* (Nauka, Moscow, 1989) [in Russian].
- 4. M. G. Dobrovol'skaya, S. P. Balashova, O. N. Zaozerina, and T. I. Golovanova, "Mineral Assemblages and Stages of Ore Mineralization at the Lead–Zinc Deposits of the Dal'negorsk Ore District, Southern Primorye)," Geol. Rudn. Mestorozhd. **35** (6), 493–519 (1993).
- 5. S. V. Ezhov, "Relationship between Skarn Formation and Sulfide Mineralization at the Base-Metal Deposits in Altyn-Topkan Ore District, Central Asia," Geol. Rudn. Mestorozhd. **36** (3), 237–249 (1994).
- 6. G. N. Gamyanin and N. S. Bortnikov, "Chemical Composition of Fahlore from Gold Deposits of Different Types in Eastern Yakutia," Geol. Rudn. Mestorozhd. **31** (2), 50–62 (1989).
- 7. S. P. Garbuzov, G. P. Vasilenko, and V. I. Taskaev, "Mineralogy and Geochemistry of Silver at a Base-Metal Skarn Deposit in Primorye," Tikhookean. Geol. **14** (2), 109–114 (1983).
- 8. V. V. Golozubov and A. I. Khanchuk, "Taukha and Zhuravlevka Terranes (Southern Sikhote-Alin)—Fragments of the Early Cretaceous Asian Margin, Tikhookean. Geol. **14** (2), 13–25 (1995).
- 9. C. J. Hackbarth and U. A. Petersen, "A Fractional Crystallization Model for the Deposition of Argentian Tetrahedrite," Econ. Geol. **79** (3), 448–460 (1984).
- 10. A. I. Khanchuk, A. P. Nikitina, I. V. Panchenko, et al., "Paleozoic and Mesozoic Guyots of the Sikhote-Alin and Sakhalin," Dokl. Akad. Nauk SSSR **307** (1), 186– 190 (1989).
- 11. L. I. Koreneva and V. N. Kolesnikov, "Some Mineralogical and Geochemical Features of Base-Metal Skarn Mineralization of the Bol'nichny Lode (Dal'negorsk Ore District)," in *New Data on Mineralogy of the Far East* (Far East Division, Acad. Sci. SSSR, Vladivostok, 1987), pp. 85–88 [in Russian].
- 12. V. A. Kovalenker, N. V. Troneva, and V. V. Dobronichenko, "Specific Compositional Features of Major Ore Minerals from Pipelike Orebodies at the Kochbulak Deposit," in *Methods of Research of Ore-Forming Sulfides and Their Assemblages* (Nauka, Moscow, 1980), pp. 140–164 [in Russian].
- 13. N. N. Mozgova, "Relationship between a Porphyritic Diabase Dike and Mineralized Skarn at the Verkhny

Rudnik Deposit (Tetyukhe, Primorsky Krai)," Izv. Akad. Nauk SSSR, Ser. Geol., No. 1, 25–31 (1957).

- 14. N. N. Mozgova and Yu. S. Borodaev, "Texture, Mineralogy and Genesis of Base-Metal Skarn Deposits in the Dal'negorsk Ore District," Geol. Rudn. Mestorozhd. **37** (5) , 437–444 (1995).
- 15. N. N. Mozgova and A. I. Tsepin, *Fahlore* (Nauka, Moscow, 1983) [in Russian].
- 16. Yu. K. Pustov, Candidate's Dissertation in Geology and Mineralogy (Moscow, 1990).
- 17. V. V. Ratkin, L. F. Simanenko, and P. I. Logvenchev, "Mineralogical and Geochemical Zoning of Skarn and Vein Base-Metal Deposits in the Dal'negorsk Ore District as the Basis for Local Forecasting of Ore Mineralization Spreading to a Depth," in *Ore Deposits of the Far East:Mineralogical Criteria of Forecasting, Exploration, and Evaluation* (Far East Division, Acad. Sci. USSR, Vladivostok, 1991), pp. 34–35 [in Russian].
- 18. V. V. Ratkin, L. N. Khetchikov, V. A. Pakhomova, and L. F. Simanenko, "Composition and Physicochemical Conditions of Sphalerite Crystallization as Reflection of Zoning at the Partizansky Base-Metal Skarn Deposit," Tikhookean. Geol. **13** (3), 72–82 (1994).
- 19. R. O. Sack and R. R. Loucks, "Thermodynamic Properties of Tetrahedrite–Tennantites; Constraints on the Interdependence of the Ag \longrightarrow Cu, Fe \longrightarrow Zn, and As \rightarrow Sb Exchange Reactions," Am. Mineral. 70 (11/12), 1270–1289 (1985).
- 20. T. N. Shadlun and M. G. Dobrovol'skaya, "New Data on Sulfide Typomorphism at Lead–Zinc Deposits of Different Types," in *Typomorphism of Minerals and Mineral Assemblages* (Nauka, Moscow, 1986), pp. 69–78 [in Russian].
- 21. L. F. Simanenko, Candidate's Dissertation in Geology and Mineralogy (Vladivostok, 1997).
- 22. L. F. Simanenko, "Bismuth and Bismuth-Bearing Minerals in Base-Metal Ores of the Dal'negorsk Ore District," in *New Data on Magmatism and Metallogeny of the Far East* (Dal'nauka, Vladivostok, 1998), pp. 51–82 [in Russian].
- 23. E. M. Spiridonov, "Fahlore Facies and Variety and Rational Nomenclature of Minerals from This Group. Some Comments on the Origin of Fahlore," Tr. Mineral. Muz. Akad Nauk SSSR, No. 33, 128–146 (1985).
- 24. E. M. Spiridonov, "Typomorphic Specific Features of Fahlore from Some Plutonogenic, Volcanogenic, and Telethermal Gold Deposits," Geol. Rudn. Mestorozhd. **29** (6), 83–92 (1987).