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GEOLOGY

Petrological Model of the Formation of Sulfide Deposits

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Sulfide deposits differ from other ore deposits in their high Fe contents, which could not be provided by any other endogenic process except magmatism. Transmagmatic fluids with hydrogen sulfide and ore metals, which migrate from the core, serve as a link between the last process and sulfide ore formation. Under their influence, Fe-rich magmatic differentiates lose their stability and are subjected to sulfurization with the input of Cu and chalcophile metals, which make up the basis of sulfide ore formation. In terms of the composition of Cu-associated metals, sulfide ore formation is divided into copper–nickel and copper–zinc (massive sulfide) types. Such division is related to the universal mafic–ultramafic fractionation of primary mantle magmas and the consequent compositional differentiation of their ferruginous derivates (magnesian derivative in ultramafic settings and virtually Mg-lacking derivative in mafic environments). This process is responsible for different scenarios of their fluid sulfurization and can be defined as the following reactions of normative minerals:

$$MgFeSiO_4 + H_2S = FeS + MgSiO_3 + H_2O \text{ and}$$

$$Fe_2SiO_4 + 4H_2S = 2FeS_2 + 2(H_2O + H_2).$$

In the first case of monosulfide sulfurization of lower differentiates with normative hortonolite, the magnesian environment stimulates the accumulation of Cu in paragenesis with Ni, which has a high chemical affinity to Mg, and promotes the formation of copper–nickel ores with Pt and Pd.

Copper–nickel ores remain largely in intrusive position and only occasionally enter volcanic facies in basaltic komatiite complexes (perhaps, together with massive sulfide ores). This can be exemplified by the Precambrian Abitibi greenstone belt (North America), where copper–nickel sulfide ores in the basaltic komatiite association occur together with massive sulfide copper–zinc ores in acid-to-basic rhyolite–basalt complexes [1]. Copper–nickel ores of the Abitibi belt are characterized by the predominance of Ni over Cu (Cu 0.7 wt %, Ni 1.4 wt %). They are associated with magnesian komatiites (MgO 20–35%) with a high content of Cr (2 ppm). The massive sulfide ores are characterized by a high content of Zn (Cu 2.2 wt %, Zn 7.2 wt %). They occur in the contrasting association of alkaline (potassic) rhyolites and basalts, wt % (the alkali content is given in parentheses): SiO_2 75.68 (52), TiO_2 0.28 (2.29), Al_2O_3 11.27 (12.87), Fe_2O_3 2.65 (16.41), MnO 0.04 (0.25), MgO 0.62 (5.00), CaO 0.70 (7.18), Na_2O 0.94 (2.63), K_2O 7.79 (0.78), and P_2O_5 0.03 (0.57).

The copper sulfide deposits are confined to low-alkali mafic–ultramafic complexes (depleted in strong bases), in which tholeiitic basalts occur together with dunite–harzburgite intrusions (ophiolitic formations of Cyprus, Oman, California, the Urals, and others). In stratiform intrusions, the role of strong bases in ultramafic rocks increases from the bottom to the top in the harzburgite–lherzolite–wehrlite series. Combined with the Fenner's trend of increase in the Fe index of magmas, the process described above leads to the effective release of Fe from silicate structures according to the following reaction: ($MgFeSi_2O_6 + Ca(OH)_2 = CaMgSi_2O_6 + 0.25(Fe_3O_4 + Fe) + H_2O$). This reaction stimulates Cu–Ni sulfurization of melts and their Pt–Pd specialization.

In the case of disulfide sulfurization of normative fayalite differentiates, which virtually lack Mg, Cu is concentrated with Zn and other metals typical of the massive sulfide ore formation. Such differentiates reflect best the Fenner's trend of Fe accumulation, which is terminated in apical parts of magma chambers by the splitting of magma into ferrous (normative fayalite) and high-alkali silicate melts [2]. This fractionation is responsible for the typical occurrence of upper (apical) ferrous differentiates beneath acid rocks that

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crown the layered magma chambers. Sulfurization of these ferrous differentiates in magma chambers also fosters the regular development of massive sulfide ores in volcanic complexes after the eruption and intrusion of acid melts. Eruptions of fluid sulfide lavas are usually followed by calm periods that are reflected in sedimentary sections. The calm periods are followed, in turn, by effusions and explosions of basic magmas from deeper parts of magma chambers. Worth of mentioning is the reducing effect of disulfide sulfurization ($H_2O + H_2$), resulting in the hydrocarbon specialization of the latter process.

In the Sudbury layered intrusion (Canada) [3], the lower sublayer of ore generation produced large bottom deposits and ore offsets in underlying rocks. The sublayer is overlain by norites and magnetite-bearing quartz gabbro, which, in turn, underlie granophyres that crown the layered massif. The layer of magnetite-bearing quartz gabbro represents a poorly developed upper sublayer of ferrous differentiates enriched in F_2O_3 (up to 14%), TiO_2 (up to 3%), P_2O_5 (up to 1.4%), V, S, and Ba. The maximal contents of these elements complicate the general cryptic layered pattern of the massif with respect to all other components, the contents of which change monotonically in the norite-to-granophyre succession. In contrast to ferruginous differentiates of the lower sublayer, their counterparts from the upper sublayer avoided sulfurization. The Kiglapait Massif (Labrador) is another example of ferrous differentiates that avoided sulfurization. Ferruginous rocks of this massif contain virtually pure fayalite with a high Mn content (1.62%). During sulfurization of such melts, Mn is not concentrated in sulfide phases and is removed by fluids to form a peculiar association of Mn with pyrite ores. Zn, which is also concentrated in upper ferruginous differentiates, shows a different distribution pattern. It is intensely absorbed by sulfide melts, affecting the Zn specialization of massive sulfide ores. The Zn-rich titanomagnetite gabbro dolerites, which underlie apical granophyres in the Skaergaard intrusion (Greenland) [4], can serve as an example of Zn-bearing ferruginous rocks.

The sulfurization of ferruginous differentiates characterized by the above-mentioned reactions should lead to the prevalence of Cu, which represents the most sulfophile metal, over their chalcophile varieties. However, Zn usually prevails over Cu in the case of massive sulfide ore formation due to the influence of other additional factors that complicate sulfurization, which provides its copper profile. Such factors include, for example, hydrocarbon specialization of fluids due to the reducing effect of disulfide sulfurization ($H_2O + H_2$) of ferruginous differentiates expressed in the above-mentioned reaction. Owing to the latter effect, sulfurization was accompanied by reduction of carbon oxides and generation of hydrocarbons:

$$1.5Fe_2SiO_4 + 6H_2S + CO = 3FeS_2 + 1.5SiO_2 \\ + 4H_2O + CH_4 \text{ and } 3.5Fe_2SiO_4 + 14H_2S \\ + 2CO_2 = 7FeS_2 + 3.5SiO_2 + 11H_2O + C_2H_6.$$

This process should substantially influence the metallic effect of sulfurization. For example, oil fields [5, 6] always show substantial prevalence of Zn and Ni over Cu (ppm): Si 2.20, Cr 4.24, V 4.00, Ni 3.78, Ti 2.00, Al 1.15, Zn 0.87, Cl 0.80, Cu 0.39, B 0.28, S 0.11, Pb 0.08, Mn 0.06, W 0.02, Br 0.02, and Cd 0.01. Correspondingly, hydrocarbon specifics of sulfurization should reduce the role of Cu in both Cu–Zn and Cu–Ni evolution pathways. Association of hydrocarbon fluids with sulfurization of ferruginous melts is emphasized by frequent occurrence of sulfides together with hydrocarbons in fluid inclusions in diamonds and other minerals. The hydrocarbon specialization is frequently reflected in the subordinate role of massive sulfide deposits relative to carbonaceous formations (e.g., black shales). The massive sulfide ore of the Outokumpu deposit in Precambrian black shales of Finland is characterized by the significant prevalence of Zn over Cu [7]: SiO_2 38.6, Fe 28.3, Zn 23.5, Cu 3.8, and Au 1.0 wt %.

The present-day formation of massive sulfide deposits in mid-oceanic ridges is universally accompanied by hydrocarbon-producing hydrothermal activity. According to [8], fluid vents at the northern Juan de Fuca Ridge contain methane and many other heavier hydrocarbons, in addition to CO_2 and H_2O: C_2H_6, C_3H_8, C_4H_{10}, C_6H_6 (benzol), and C_7H_9 (toluol). Carbon of methane is characterized by an extremely low $\delta^{13}C$ value ranging from –50.8 to –54.3‰. Therefore, it differs principally from carbon of heavier hydrocarbons with $\delta^{13}C$ values ranging from –20.2 to –25.3‰ corresponding approximately to carbon in CO_2. The analogy between Paleozoic massive sulfide deposits in the Urals and recent deposits in oceans was noted in [9].

The study of trap formations clearly shows the alkaline trend of hydrocarbon specifics of ore formation and magmatism. Their development cycles begin usually with eruptions of tholeiitic basalts with minerals containing H_2O–CO_2 inclusions and are crowned by alkaline rocks usually with fluid inclusions of methane and other hydrocarbons [10]: C_2H_6, C_3H_8, C_4H_{10}, and C_5H_{12}. These contrasting volcanics are separated by sedimentary sequences that record calm volcanic periods of the evolution of magmatism at deep levels toward the intensification of its alkalinity and hydrocarbon specifics. Massive sulfide deposits fit this scenario of events: growth of alkalinity in them is reflected in the replacement of quartz–sulfide ores by more productive barite–sulfide varieties.

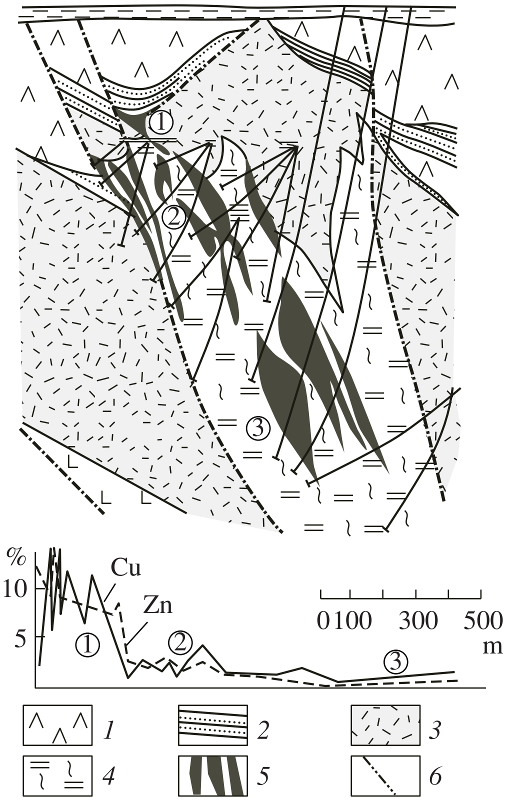

Fig. 1. Geological borehole-based section across the northern part of the Gai massive sulfide deposit in the Urals [12, pp. 35, 55]. The plot in the lower part illustrates contrasting Cu and Zn concentrations in the main conformable lode (1) and crosscutting (2, 3) bodies. (*1*) Basalts; (*2*) sedimentary rocks; (*3*) rhyolites; (*4*) metasomatic rocks; (*5*) massive sulfide ores; (*6*) faults. Encircled numerals: (1) main conformable lode of high-grade ores (main lens), (2, 3) low-grade sulfide orebodies steeply crosscutting rhyolites and accompanied by metasomatic rocks that mark conduits of the main lode.

Ore-generating cycles of volcanism begin with eruptions and extrusions of acid rocks corresponding to apical differentiates of magma chambers. This is followed by eruptions of high-grade Cu–Ni melts with their fractionation into zinc (upper) and copper (lower) layers. Their conduits are marked by crosscutting lodes of massive low-grade (massive sulfide) ores. The subsequent stage is marked by impregnated ores and metasomatites that replaced acid rocks underlying stratiform bodies of high-grade sulfide ores. The cycles are crowned by sedimentary sequences associated with effusive and explosive basic volcanics that correspond to deeper parts of parental magma chambers. Such succession is best developed in the classic Kuroko deposits of Japan [11]. It is also outlined in massive sulfide deposits of the Urals, where conformable bodies of high-grade ores are accompanied by crosscutting bodies of low-grade massive and impregnated ores and metasomatites confined to rocks beneath the stratiform high-grade ore lodes.

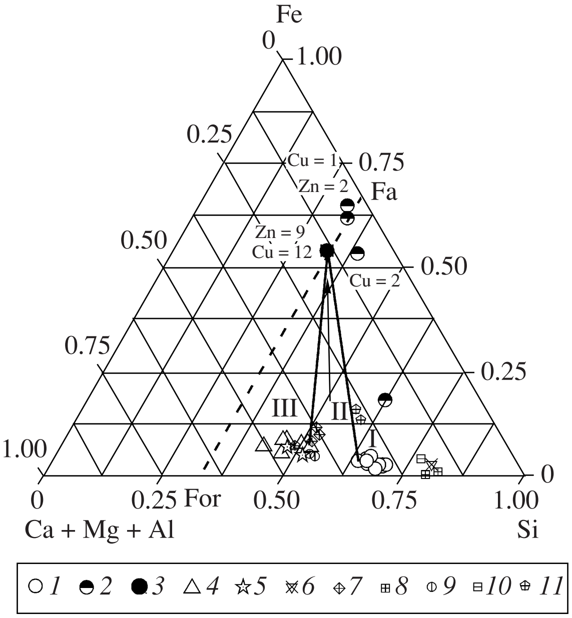

Fig. 2. Ore petrochemical diagram (atomic contents) of the Gai massive sulfide deposit in the South Urals. (*1*) Preore rhyolites and dacites; (*2*) metasomatic rocks and crosscutting bodies of low-grade impregnated and massive sulfide ores; (*3*) stratiform conformable body (main lode) of high-grade Cu–Zn ores differentiated into the copper (upper) and zinc (lower) zones; (*4*) conformably overlying sedimentary rocks and basalts; (*5*) dolerites (dikes crosscutting orebodies); (*6–11*) rocks enclosing conformable orebodies in other massive sulfide deposits shown for comparison: (*6, 7*) Uchaly (Urals) and (*8, 9*) Kuroko (Japan), respectively; *(10, 11)* the Galapagos Ridge of the Pacific. Analytical data were adopted from [2, 11–13]. See the text for explanation of Roman numbers. Cu and Zn contents in the diagram are given in wt %.

Figure 1 presents a latitudinal section of a borehole drilled in the Paleozoic Gai Cu–Zn deposit [12], the largest one in the Urals. The section is located in the weakly eroded northern part of the deposit, where the low-angle stratiform lode of high-grade ores (main lens) is retained. The ore lode is conformably overlain by sedimentary rocks and basalts. The underlying unit is composed of rhyolites intersected by steep bodies of low-grade sulfide ores subjected to substantial metasomatic alterations. The petrological formation model of this deposit (Fig. 2) reflects the above-mentioned relationships between rocks and ores. The arrow indicates the location of the main sulfide lode (II) governed by sulfurization of ferruginous (fayalite) differentiates, which separated apical acid (I) and underlying basic (III) differentiates in the magma chamber. For comparison and assessment of the general significance of the revealed relationships, the figure also presents data on compositionally contrasting rocks that enclose conformable sulfide lodes of other massive sulfide deposits.

The melt nature of stratiform lodes is substantiated by their layered patterns, including rhythmic layering at

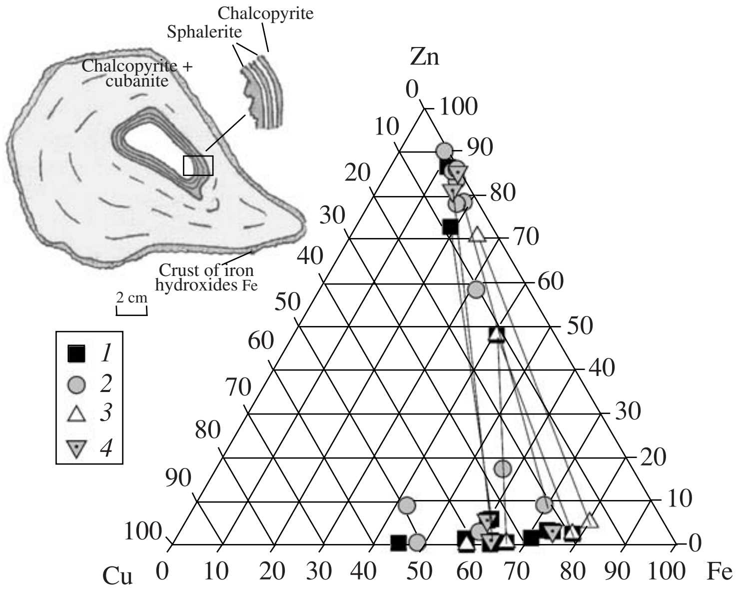

Fig. 3. Petrochemical formation model of rhythmically layered pipe-shaped sulfide body of inactive black smoker in the Rainbow field of the Atlantic (combined with the figure adopted from [13]). Tie lines join contrasting compositions of alternating copper and zinc ore layers that are traced from the apical part of the body to its base. (*1*) Base; (*2*) apical part; (*3*) inner zone; (*4*) external zone.

the boundary between the zinc (upper) and copper (lower) parts. The rhythmicity is observed in deposits of the Kuroko group (Japan) [11] and mid-oceanic ridges. For example, the rhythmic banded structure is typical of pipe-shaped lodes related to eruptions of fluid–sulfide melts in oceanic settings (Fig. 3). During these eruptions, huge masses of sulfides are dispersed in seawater or involved in sedimentation and only some portion of sulfides is involved in the formation of massive sulfide deposits.

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