

Experimental modeling of pentlandite-bornite ore formation

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Abstract

For experimental modeling of the formation of pentlandite–bornite ore during fractional solidification of sulfide magma, we performed directional quasi-equilibrium crystallization of a melt containing (mol%) 17.19 Cu, 19.05 Fe, 19.66 Ni, and 44.10 S, from which pentlandite and bornite can cocrystallize. Based on the results of measurement of the average composition of the solid phase, the distribution curves of the components in the ingot were constructed and the change in the melt composition during directional solidification was calculated. The obtained data show that the crystallized sample consists of six zones, each of which has characteristic phase and chemical compositions. In the Cu–Fe–Ni–S composition tetrahedron, the melt composition path is a broken spatial curve, each segment of which corresponds to a point showing the average composition of one of the zones. These points form a disordered set, indicating a complex fractionation process. Investigations of characteristic microstructures along the ingot, using data on its average chemical composition, made it possible to determine the probable set of primary phases crystallizing from the melt (bornite solid solution bnss, three types of pentlandite with different cation compositions: cfpn, npn, and cnpn, and quaternary solid solution tss) and to establish the sequence of separation of these phases and their associations from the melt in six zones: cfpn (zone I) / cfpn + bnss (zone II) / cfpn + bnss + npn (zone III) / tss + bnss (zone IV) / cnpn + bnss (zone V) / npn + bnss (zone VI). A scheme of phase reactions along the crystallization path has been compiled and it has been shown that high-temperature pentlandite forms have a significant effect on the fractionation process. These results are consistent with previous data on the fractional crystallization of multicomponent sulfide melts and the theoretical features of this process. In previous studies, samples with a small number of zones were obtained. In this study we first obtained a sample containing six zones. The zoning observed in the sample belongs to the complex second type of low-sulfur zoning of orebodies. The same data confirm the possibility of different types of zoning within the major two types of zoning of copper-nickel orebodies.

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Introduction

Most experts believe that massive orebodies of magmatic copper-nickel deposits formed as a result of fractional crystallization of sulfide magma in intrusive cavities. This process is accompanied by a regular change in the composition of the melt and the average composition of the crystalline rock and leads to a zonal structure of the orebody. In the process, different phase associations sequentially crystallize from the melt, with the transition from one association to another being very abrupt. The sequence of associations forms the mineral zoning of the orebody, and the regular change in the chemical

composition within each zone is commonly referred to as latent zoning (Distler, 1994; Distler et al., 1988; Genkin et al., 1981; Naldrett, 2004).

The results of geochemical studies of natural copper-nickel sulfide ores indicate the existence of two types of zoning of massive ores. Zoning of type I resulted from the crystallization of high-sulfur ($\Sigma\text{Me}/\text{S} < 1$) sulfide magmas and corresponds to the change from pyrrhotite ores to pyrrhotite-chalcopyrite and chalcopyrite. Magmas with $\Sigma\text{Me}/\text{S} > 1$ crystallize to form zoning of type II, which is characterized by more complex sequences of mineral assemblages. Usually, they contain sulfur-deficient chalcopyrite minerals (haycockite, talnakhite, mooiohoekite) and pentlandite. Zoning of type II is observed in copper-rich ores of the Oktyabr'skoe and Talnakhskoe deposits of the Norilsk ore field. Detailed descriptions of the mineral composition of copper-nickel sulfide ores suggest the

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existence of zoning subtypes which have slightly different sequences of mineral assemblages but which can be assigned to the major types I or II.

The zoning of massive orebodies is explained by invoking current theoretical concepts of the fractional crystallization of multicomponent melts (Ariskin and Barmina, 2000; Barnes et al., 2006; Distler et al., 1988; Kosyakov and Sinyakova, 2012; Li and Naldrett, 1994; Naldrett, 2004; Naldrett et al., 1997; Nathan and Van Kirk, 1978). It is known that copper-nickel ores contain more than 30 geochemically significant components, but it is reasonable to assume that the main features of the behavior of this complex system can be understood by considering the directional crystallization of a Cu–Fe–Ni–S quaternary melt (Fleet, 2006; Kosyakov et al., 2012; Naldrett, 2004).

In real orebodies, the thickness of the transition region between two zones is substantially less than the length of these zones, i.e., it can be argued that after complete crystallization of one of these zones, crystallization of the adjacent zone begins virtually instantaneously. This property is inherent in quasi-equilibrium directional crystallization which satisfies the following assumptions: (a) the melt is homogeneous in composition, (b) mass transfer in solid phases is absent, (c) at the crystallization front, the melt is in thermodynamic equilibrium with the solid phases crystallized from it, (d) crystallization occurs in a conservative system which does not exchange components with the external environment. In this case, the crystallization process is uniquely determined by the equilibrium melting diagram and the composition of the initial melt. The results of this process can be represented as the distribution of the phases and components along the sample using the single coordinate g —the fraction of crystallized melt—and depicted by the paths of the melt composition and solid phases in the concentration simplex (Kosyakov and Sinyakova, 2012).

Consider the current understanding of the structure of the phase diagram of the Cu–Fe–Ni–S system. In their fundamental paper, Craig and Kullerud (1969) have shown that the sulfur-intermediate portion of the phase diagram of the quaternary system contains primary crystallization regions of monosulfide ($\text{Fe}_z\text{Ni}_{1-z}\text{Cu}_{1-z-u}\text{S}_{1+\delta}$ (mss), intermediate ($\text{Fe}_x\text{Cu}_{1-x}\text{Ni}_{1-x-y}\text{S}_{1-z}$ (iss), and bornite $\text{Cu}_{5\pm x}\text{Fe}_{1\pm x}\text{S}_4$ (bnss) solid solutions and schematically plotted tie-lines between these solutions and sulfide melt (L). In later studies, fragments of this quaternary system have been investigated using high-temperature isothermal annealing and DTA, with the equilibrium between mss and sulfide melt being studied most thoroughly (Ballhaus et al., 2001; Ebel and Naldrett, 1997; Fleet and Pan, 1994). Fleet and Pan (1994) plotted mss–L tie-lines in the temperature range 850–1180 °C at a sulfur content of 52.5–50.0 mol%. The importance of these data is due to the fact that mss is released from the melt at an early stage of fractional crystallization of sulfide magmas, and the zone of pyrrhotite ore is present in nearly all solid orebodies of magmatic copper-nickel deposits. In describing the fractional crystallization of the Cu–Fe–Ni–S system, it is assumed that iss intermediate solid solution crystallizes

after mss (Craig and Kullerud, 1969). However, there is experimental evidence for the existence of a phase in the phase diagram that is intermediate in composition between mss and iss and close in stoichiometry to cubanite CuFe_2S_3 (Fleet and Pan, 1994). A region of high-temperature (Ni, Cu, Fe) $_{3\pm x}\text{S}_2$ quaternary solid solution extending from the heazlewoodite solid solution in the Fe–Ni–S system to the intermediate solid solution in the Cu–Fe–S system was detected in (Peregoedova and Ohnenstetter, 2002; Peregoedova et al., 1995).

New unique qualitative and quantitative data on the structure of the melting diagram of the Cu–Fe–Ni–S system have been obtained by quasi-equilibrium directional crystallization combined with DTA experiments. It has been shown that pentlandite in this system can be formed as a result of solid-state reactions and directly from the melt (Sinyakova and Kosyakov, 2015). Two-phase eutectics of mss + iss, mss + bnss, and bnss + pnss (pentlandite solid solution) and a three-phase eutectic of mss + bnss + ($\text{Ni}_z\text{Fe}_{1-z}$) S_2 (vaesite solid solution) have been found (Kosyakov and Sinyakova, 2011; Sinyakova and Kosyakov, 2007b, 2012). It has been shown that the three-phase region of L + mss + iss in the Cu–Fe–Ni–S diagram is divided into two subregions: a nickel-rich region, in which the peritectic reaction $\text{L} + \text{mss} \rightarrow \text{iss}$ occurs, and a copper-rich region, in which the eutectic reaction $\text{L} \rightarrow \text{mss} + \text{iss}$ occurs (Kosyakov and Sinyakova, 2012; Sinyakova and Kosyakov, 2012). The obtained experimental data indicate a more complex structure of the Cu–Fe–Ni–S system in the region $x_S \sim 0.5$ and its behavior during fractional crystallization. It is obvious that new data on the phase relations in the system are needed to simulate the fractional crystallization of natural sulfide magmas.

Primary zoning of a directionally crystallized sample formed during melt crystallization is readily determined by chemical analysis. During cooling, the primary phases completely or partially decompose into secondary phases, resulting in secondary zoning (Kosyakov and Sinyakova, 2010), so that the experimental samples consist of decomposition products. Mineralogical and geochemical data on the structure of orebodies also contain information only about their secondary zoning. To understand the processes of fractional crystallization of laboratory melts or natural sulfide magmas, it is necessary to reconstruct the formation of the primary zoning from these data (Kosyakov et al., 2012; Sinyakova and Kosyakov, 2007a,b, 2012, 2014; Sinyakova et al., 2016).

In this work, we carried out directional crystallization of a melt of the following composition (mol%): Cu = 17.19, Fe = 19.05, Ni = 19.66, and S = 44.10. As a result, a new complex type of zoning in the Cu–Fe–Ni–S system was found.

Experimental technique

Samples were prepared using especially pure Cu, Fe, and Ni (99.99%) and analytically pure sulfur (99.9999%) which was further purified from moisture by distillation under

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