

Zonality of talnakh copper-nickel ores (experiment and physicochemical explanation)

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Introduction

Hypothesis of fractional crystallization. To date, geological structure of the Noril'sk-Talnakh and Sudbury magmatic copper-nickel deposits well studied [Naldrett, 2004; Distler *et al.*, 1988; Distler, 1994]. An investigation of chemical and mineral composition of massive orebodies indicated that they are divided into zones with different phase associations. The mineral composition of zones includes practically all known crystalline phases of the Cu-Fe-Ni-S system. Dimensions of transitional layers between zones are very small compared with typical dimensions of zones; therefore you can talk about discontinuous crossing from one zone to the next. In addition, chemical composition of any zone is also heterogeneous. The components distribute regularly in the volume of the orebody. These features are connected presumably with fractional crystallization of sulfide melts [Naldrett, 2004; Distler *et al.*, 1988]. If this process occurs in nearly quasi-equilibrium regime, so the components behavior are determined by the Fe-Cu-Ni-S phase diagram. It was founded that the average composition of Noril'sk magmatic sulfide deposits lies in the field of primary crystallization of monosulfide solid solution (mss) (i.e. pyrrhotite, doped nickel and copper). So the melt and solid compositions change during crystallization and the melt is progressive enrichment of copper. At the end of mss crystallization intermediate solid solution (iss) is formed melts [Naldrett, 2004; Distler *et al.*, 1988].

Primary and secondary zonality. Sequential deposition of basic minerals from the melt results in formation of the primary zones in orebodies. It can be identified from the distribution of main ore components in the volume of ore body. The average chemical composition of ores changes step-wise from one zone to another. The concentrations of components should gradually change inside zone from one its boundary to another. A chemical heterogeneity within zone often called hidden zonality [Distler, 1994]. However, the majority of primary minerals decay at cooling, in accordance with the subsolidus Cu-Fe-Ni-S phase diagram. For example, it was found that sulfur solubility in Fe-rich mss decrease at cooling the Fe-Ni-S system. An excess of this component precipitates in view pentlandite inclusions in mss matrix [Kosyakov and Sinyakova, 2005]. Another example is the decomposition of the iss into chalcopyrite group minerals [Vaughan and Craig, 1981]. A manner of the decay of primary solid solutions depends on their composition. This leads to formation of the secondary (mineral) zonality of orebodies [Kosyakov and Sinyakova, 2010].

Geological setting of Talnakh ores. Talnakh ore field consists from a system of ~ 25 orebodies, connected by veins [Naldrett, 2004]. These bodies are surrounded by veined-impregnated and breccia ores localized mainly in sedimentary-metamorphic rocks of exocontact stratified intrusions (fig. 1a). The orebodies of the first group show hidden zonality of pyrrhotite ores. The orebodies of the second group has a strong mineral zoning (fig. 1b) [Distler, 1994]. It is plausible to assume that such construction of the ore field may be realized consequently of an integrated solidification of magma massif. The mineral and chemical composition of the system of orebodies must be formed during the solidification and following cooling.

The objective. Traditional approach to experimental investigation of zonality is based on studying of the phase relation of the Cu-Fe-Ni-S system in the region of ore composition. A great number of the samples with different composition are needed to study even for crude understanding of the process.

It is necessary to note that available data is deficient to build of adequate simulation of zonality. Quantitative model of the phase diagram are necessary for calculating of phase and chemical composition of

orebody [Kosyakov, 1998; Ariskin and Barmina, 2000]. In the other hand experiments on the fractional crystallization of sulfide melts well simulate zonality of the crystallized samples [Sinyakova and Kosyakov, 2009]. In this work the directional crystallization of sulfide melt is used to investigate behavior of main ore components at fractional crystallization.

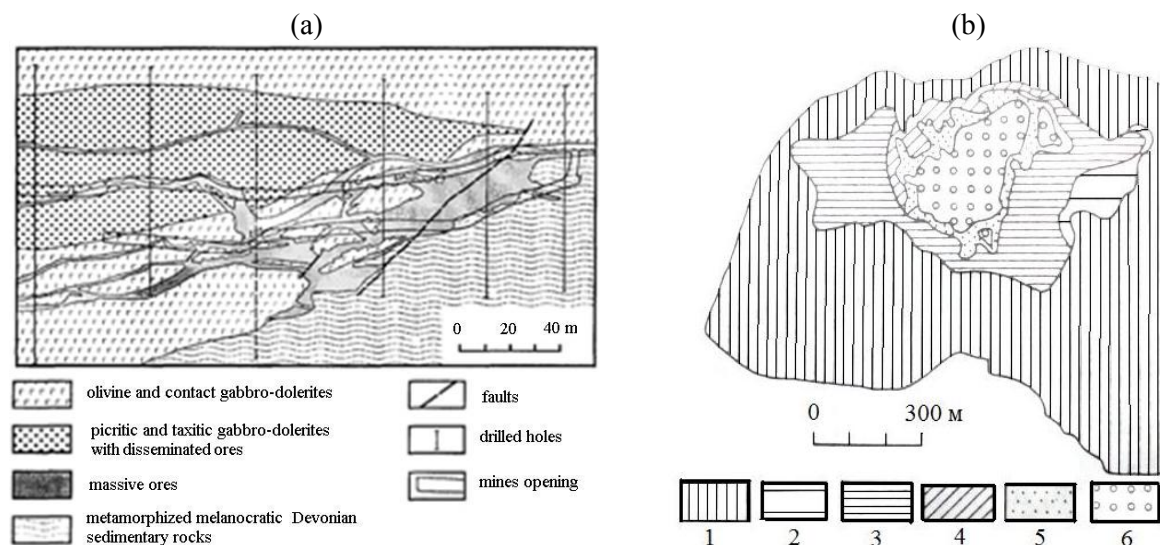


Fig. 1. Geological setting of Oktyabr'sky main. (a) Vertical section through southern part of the main [Naldrett, 2004]. (b) Mineral assemblages in massive orebody (1 – pyrrhotite and pyrrhotite-chalcopryrite, 2 – cubanite-troilite-pyrrhotite-chalcopryrite, 3 – chalcopryrite-cubanite, 4 – troilite-cubanite-chalcopryrite, 5 – cubanite-mooihoekite, 6 – mooihoekite) [Distler, 1994].

Experiment

Used melt composition is simulated of natural sulfide copper-nickel magma. Sample A with composition Fe 32.90, Cu 10.70, Ni 5.40, S 51.00 at.% similar to pyrrhotite-chalcopryrite type of massive sulfide ores. Composition of the sample B (Fe 33.76, Cu 15.98, Ni 1.50, S 48.76 at.%) is richer copper and poorer nickel and sulfur so it is similar to pyrrhotite-mooihoekite type.

One-dimensional quasi-equilibrium crystallization of the melt was carried out by Bridgman method [Kosyakov and Sinyakova, 2005]. The ampoule with homogenous melt has been dropped from the hot zone to the cold one with $2.3 \cdot 10^{-8}$ m/s rate. Length of cylindrical specimens was 70 and 90 mm and their diameter were 7 mm and 8 mm, respectively (fig. 2). They were cut into 24 (sample A) and 30 (sample B) parts perpendicular to the longitudinal axis, and each sample was weighed. The samples were examined with optical and electronic microscopic, X-ray diffraction and electron microprobe analyses. The melt composition and partition coefficient of the components were calculated from material balance equation.

Results

Primary zonality. The mss is formed at the first stage of the solidification of the both samples, and after that the iss is crystallized (fig. 2). The distribution curves of Fe and Cu in the sample A are shown in fig. 3. The transition from zone I to zone II may be interpreted as a bivariant phase reaction: $L + mss \rightarrow iss$. The partition coefficients ($k_{mss/L}$) for the samples vary in following limits: $k(Ni) = 0.94 \div 1.6$, $k(Fe) = 1.2 \div 1.4$, $k(Cu) = 0.19 \div 0.28$, $k(S) = 1.04 \div 1.08$. During iss crystallization in sample A Cu and Fe are concentrated in this phase, while Ni is enriched of sulfide liquid, and $k(S_{iss/L})$ is ~ 1 . In the sample B $k(Fe, Cu, \text{ and } S)$ between iss and L are close to 1, while $k(Ni)$ is $\sim 0.6-0.7$. So Ni is accumulated in the melt. Thus, the sequence of mss and iss crystallization from the melts and variation of their chemical composition reflect primary chemical and mineral zoning as in the samples so in orebodies.

Secondary mineral zoning. A cooling of the samples results in decomposition of the primary mss and iss and formation of secondary mineral zones [Kosyakov and Sinyakova, 2010]. Zone I breaks on two subzones. In subzone Ia ($0 < g < \sim 0.03$) of the sample A hexagonal mss is transformed into monoclinic mss. In subzone Ib ($\sim 0.03 < g < \sim 0.68$) mss transforms into low-temperature hexagonal modification. Excess of Cu gathers in lamellar of tetragonal chalcopryrite (fig. 2). Primary iss is completely decomposed at cooling with formation of tetragonal (cp^t) and cubic (iss^c) chalcopryrite, bornite (bn), and Ni-rich pentlandite. Subzone Ia ($0 < g < \sim 0.13$) of the sample B consists of hexagonal mss^h matrix with izocubanite inclusions.

Subzone Ib ($\sim 0.13 < g < \sim 0.4$) contains also the pentlandite micro grains. Two subzones are formed from iss. Subzone IIa ($\sim 0.4 < g < \sim 0.7$) is formed from haycockite and pentlandite, and subzone IIb ($g > \sim 0.7$) contains of mooihoekite, pentlandite, and bornite.

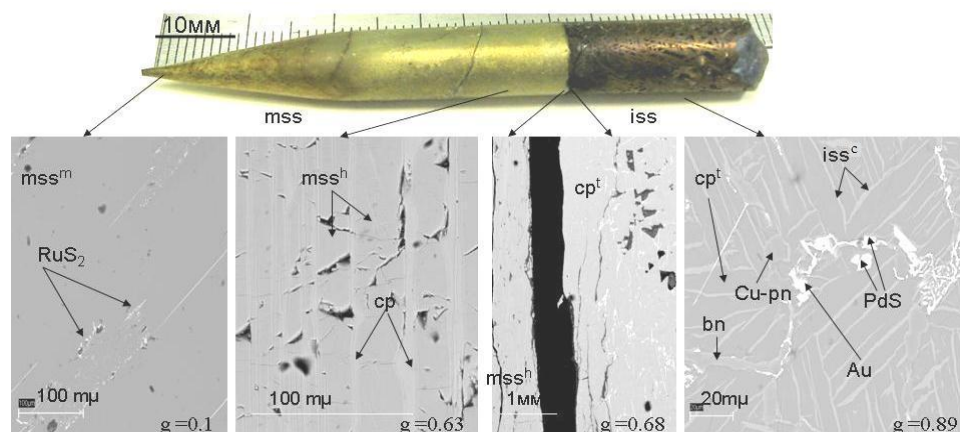


Fig. 2. A sample A obtained by the directional crystallization (above) and its microstructure (below). Left part of the ingot corresponds to subzones Ia and Ib. Right part shows zone II. A crack corresponds to boundary between zones I and II.

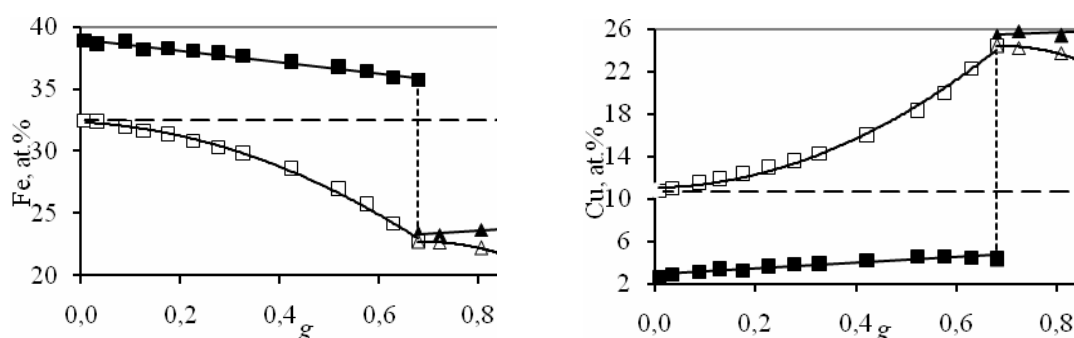


Fig. 3. Distribution of Fe and Cu in the solid phases (close squares and triangles) and in the melt (open squares and triangles) in the sample A. The horizontal dashed line shows the concentration of the component in the initial melt.

Discussion

Examined samples belong to Fe-rich area of a middle part of the Cu-Ni-Fe-S phase diagram, where fields of primary crystallization mss and iss present [Craig and Kullerud, 1969]. Obtained data conform to literature information, and agree with our results on experimental modeling of the fractional crystallization of sulfide melts [Sinyakova and Kosyakov, 2007]. Initial composition of the charges belongs to the field of the mss crystallization. The sample A is enriched with sulfur and nickel, and is depleted with copper as compared to the sample B. The composition of both samples is changed similarly. One may conclude that solidification processes carried out likely in a common part of the diagram. Measured partition coefficients of components between mss and sulfide melt conform to published information [Naldrett, 2010]. During iss crystallization, the concentration of sulfur increases in the melt and decreases in solid solution. This result is supported by our experimental data in the Cu-Fe-S system [Sinyakova and Kosyakov, 2009].

A mixture of fine-grained phases presents in the end part of the samples. Consequently the described zoning of the samples belongs to an initial stage of the crystallization process. Early it was shown theoretically that the process had to finish by forming of four-phase eutectic mixture.

Available data on distribution of components between the iss and melt are absent. According to above data the partition coefficients vary in the range: $k(\text{Fe}) = 0.88 \div 1.03$, $k(\text{Ni}) = 0.59 \div 0.64$, $k(\text{Cu}) = 0.96 \div 1.15$, $k(\text{S}) = 0.99 \div 1.02$. Values of $k(\text{iss/L})$ for Fe, Cu, and S are equal ~ 1 , but for Ni < 1 . Therefore the melt is enriched in Ni during iss crystallization, while the distribution coefficients of the other elements are near 1.

The obtained regularities can be used to reconstruct the history of Talnakh ore field formation. At first

the system of the voids and channels in the rocks was filled up sulfide magma. The magma crystallization began in colder voids of the first group. As a result massive of pyrrhotite and chalcopyrite ores was formed. A residual melt prolonged to solidify in the channels and the voids of the second group. Such talnakhite and mooihoeite orebodies occurred.

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