# **Mineralogical and Geochemical Zoning and Genesis of Massive Sulfide Ores at the Oktyabr'sky Deposit**

**N. S. Gorbachev**

*Institute of Experimental Mineralogy, Russian Academy of Sciences, Institutskaya ul. 4, Chernogolovka, Moscow oblast, 142432 Russia* Received June 16, 2005

**Abstract**—Fractional crystallization and emanation differentiation of sulfide magma and related mineralogical and geochemical zoning are exemplified in massive sulfide ores of the Oktyabr'sky deposit, Noril'sk district. The mineralogical zoning is expressed in the change of mineral types of ore from pyrrhotite (Po) to chalcopyrite (Cp) (from the flanks to the center of the ore lode). In terms of geochemistry, the Cu content, Cu/(Cu + Ni) ratio, and contents of noble metals incompatible with Mss (Pt, Pd, and Au) increase in this direction, while the S and Fe contents decrease. The distribution of elements compatible with Mss (Ir, Os, Rh, and Ru) is more complex. Their contents decrease from Po to high-Cu Cp ore, although there is a second maximum for Cb-type ore. The distribution of ore elements in the vertical and horizontal sections of massive ores at the deposit is different. The upper outer contact zone and frontal parts of massive ore lodes are enriched in all ore elements and a light sulfur isotope. The succession of enrichment is correlated with the relative affinity for sulfur and remains independent of the affinity of these elements for Mss (Pd–Rh, Os–Au). The possible role of liquid immiscibility of sulfide magma in the development of the mineralogical and geochemical zoning of massive ore is discussed.

**DOI:** 10.1134/S1075701506060031

# INTRODUCTION

The main mineral resources are concentrated in giant deposits, which are not numerous. The Talnakh

Corresponding author: N.S. Gorbachev. E-mail: gor@iem.ac.ru

and Oktyabr'sky deposits of the Talnakh ore field in the Noril'sk district are among the world's largest sulfide deposits of nickel and platinum metals. The deposits are hosted in the Talnakh layered mafic–ultramafic intrusion, the formation of which is related to trap mag-



Fig. 1. Mineralogical zoning of massive ores from the MSL, after Stekhin (1994). (1) Po, Po–Cp; (2) Cb–Po–Cp; (3) Cp–Cb; (4) Po–Cp–Cb; (5) Cb–Mh; (6) Mh.



**Fig. 2.** Major ore-forming mineral contents (vol %); Ni, Fe, and S contents (wt %); and Cu/(Cu + Ni) ratio (%) in massive sulfide ores versus Cu content, after Distler (1994) and Dodin et al. (2000). Ore types: (I) Po, (II) Po–Cp, (III) Cb, (IV) Cp.

matism of the Siberian Platform. These deposits are characterized by a high sulfide content and remarkably variable mineral and chemical composition of ore mineralization. Godlevsky (1959, 1968) was the first to study mineral zoning of the Noril'sk sulfide ores and its relationship with crystallization of sulfide melt. His inferences on fractionation of sulfide melt with separation of hydrothermal fluid and the implications of this fractionation for the development of mineralogical zoning of sulfide ores remain significant even now. Later on, different aspects of the mineral and chemical composition of sulfide ores and their genesis were considered in many papers, collections of articles, and monographs (Genkin et al., 1981; Distler et al., 1988; *Platinum of Russia*, 1994, 1995, 1999; Dodin et al., 2000; Krivtsov et al., 2001; Naldrett, 1993). Despite the intense study of these deposits, many genetic problems, including the specific features and nature of the mineralogical and geochemical zoning of sulfide mineralization, remain a matter of debate.

In this regard, the high-grade massive ores that make up several lenticular lodes at the base of the intrusion and in its outer and inner contact zones attract special interest. The Main (Kharaelakh) sulfide lode (MSL) of the Oktyabr'sky deposit is the most remarkable owing to its large size  $(4 \times 2 \text{ km})$  and great thickness (up to 50 m) together with the perfection and scope of its mineralogical and geochemical zoning. Geological data indicate a temporal break between the formation of the intrusion, which contains syngenetic sulfide disseminations, and the emplacement of sulfide melt that crystallized as lodes of massive sulfide ore. This provides grounds to assert that emplacement and crystallization of a special sulfide magma was responsible for the formation of massive ores and determined their mineral

Ore type	Cu, wt $%$	Ni, wt $\%$	Pd, mg/t	Au, mg/t	Pt, mg/t	Ir, $mg/t$	Os, mg/t	Ru, mg/t	Rh, mg/t
Po	2.02	6.27	5982	32.43	1056.03	190.61	124.05	481.88	1718
Po	2.72	5.62	6452.17	29.39	1457.53	15.77	10.26	3.99	347.05
Po	2.87	6.00	6925	33.39	1263	288	186.37	527.83	2357
Po	3.32	4.49	6696	88.65	1242	27.62	16.55	64.34	417.2
$Po$ - $Cp$	3.88	5.58	5256.57	43.96	1002.66	120.74	88.12	247.57	1285
$Po$ - $Cp$	6.94	5.31	15595.68	193.95	3209.19	20.63	17.23	20.44	295
$Po$ - $Cp$	12.01	5.36	17835.11	755.53	4244.14	21.35	24.25	16.21	203.61
Cb	12.76	3.75	17376.56	766.36	3690.40	1.89	4.60	3.00	42.84
Cb	13.63	3.79	15269.67	1460.67	4206.68	64.49	42.78	142.17	509.16
Cb	17.40	3.04	33078.46	1928.60	8832.79	78.60	63.17	160.02	831.89
$Cb$ - $Cp$	19.35	3.53	43196.60	2255.34	12706.75	31.57	24.17	62.86	233.32
Cp	20.19	2.56	52604.01	3091.12	14960.54	36.24	58.60	83.51	158.29
Cp	26.67	1.83	37654.23	363.46	12145.56	0.88	14.95	1.48	8.92
Cp	31.31	3.80	41557	4368	27382	3.11	17.98	37.87	17.67

Chemical composition of high-grade massive sulfide ores from the Oktyabr'sky deposit (recalculated for 100% sulfides)

and chemical composition, as well as the composition and zoning of the outer halo. In order to understand the behavior of ore elements in the course of magma crystallization and development of mineralogical zoning, the distribution of Cu, Ni, Au, and PGE in the vertical and horizontal sections of massive ores, represented by their major mineral varieties, is considered in this paper. Samples taken from exploration boreholes and underground workings of the Oktyabr'sky 1, Taimyrsky, and Komsomol'sky mines of the Oktyabr'sky deposit were analyzed with atomic absorption spectroscopy and instrumental neutron activation methods at laboratories of the University of Toronto and the Ontario Geological Survey, Canada (Asif and Parry, 1989). The analytical results were recalculated for 100% sulfides. Some of these data have been published elsewhere (Naldrett et al., 1992, 1998; Gorbachev et al., 1993, 2000).

### GEOLOGY, MINERALOGY, AND GEOCHEMISTRY

The Oktyabr'sky deposit is related to the Kharaelakh branch of the Talnakh intrusion, located in the Devonian terrigenous–sulfate–carbonate rocks to the west of the Noril'sk–Kharaelakh Fault. Sulfide ores comprise three morphological types: (1) disseminated ore hosted in the lower units of the intrusion, which are composed of picritic, taxitic, and contact gabbrodolerites; (2) massive ore at the base of the intrusion and in its inner and outer contact zones; and (3) disseminated, stringer–disseminated, and breccia ores in the inner and outer contact zones that make up the upper and lower ore units. Ores of the lower unit form a halo around the massive ore, while the upper ore unit occupies the upper outer and inner contact zones of the intrusion, mainly in its frontal part. According to contents of major ore-forming minerals, the following mineral types of ore are distinguished: pyrrhotite (Po), cubanite (Cb), chalcopyrite (Cp), and talnakhite (mooihoekite) (Tal–Mh). All ore types contain pentlandite (Pnt).

*Distribution of major minerals and ore-forming elements.* The central part of the MSL was characterized by distinct mineralogical zoning (according to published data (Valetov et al., 2000), this segment of the lode has been mined out to date). The mineralogical zoning was expressed in the successive replacement of the main mineral ore types (from the flanks to the center): pyrrhotite (Po)–cubanite (Cb)–chalcopyrite (Cp). The transition between these types was gradual via intermediate ore varieties: pyrrhotite–chalcopyrite, pyrrhotite–chalcopyrite–cubanite, and cubanite–chalcopyrite (Fig. 1).

In respect to major ore-forming elements, the mineral types of ores differ from one another mostly in the Cu content and  $Cu/(Cu + Ni)$  ratio, which vary from 2.5 wt % and 0.5 in pyrrhotite ores to 32 wt % and 0.9 in chalcopyrite ores, respectively. Such wide variations in Cu contents and  $Cu/(Cu + Ni)$  values allow use of these parameters as criteria of the fractionation degree of sulfide magma and the behavior of ore elements in this process. With reference to sulfide ores, the Cu content and  $Cu/(Cu + Ni)$  ratio play the same role as the Mg content and magnesian number (mg =  $Mg/(MgO +$ FeO)) in igneous petrology.

Variations of major ore-forming minerals and elements in massive ores are demonstrated in Fig. 2. Chalcopyrite and Cu contents increase from pyrrhotite to chalcopyrite ores, while pyrrhotite, Fe, and S contents decrease in the same direction. Cubanite ore is characterized by maximal Cb and minimal Po and Cp con-



**Fig. 3.** Contents of Ni, Fe, and S (wt %) and PGE and Au (mg/t) and Cu/(Cu + Ni) ratio (%) in massive sulfide versus Cu content. Ore types: (I) Po, (II) Po–Cp, (III) Cb, (IV) Cp.



**Fig. 4.** Correlation between Cu and PGE contents and their ratios in massive sulfide ores.

tents. Although pentlandite and Ni contents vary within relatively narrow limits, nevertheless, a negative correlation is seen between Ni, on the one hand, and Cu and  $Cu/(Cu + Ni)$ , on the other hand, with small maxima in pyrrhotite and cubanite ores.

*Distribution of PGE and Au.* The distribution of noble metals in ores of the MSL depending on the Cu content therein is presented in the table and Fig. 3. According to the correlation between metals and Cu, the noble metals are subdivided into the copper group, which includes Pt, Pd, and Au, and the iron group, which comprises Os, Ru, Rh, and Ir in addition to Ni.

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 6 2006

The contents of copper-group elements (Pt, Pd, and Au) increase with Cu content from pyrrhotite to chalcopyrite ores. A linear correlation of Pt, Pd, and Au with Cu and between each other is typical (Figs. 4, 5). The regression equations that describe the correlation of Pt, Pd, and Au with Cu determine the mineral type of massive ores and estimate the contents of these elements therein rather correctly. The distribution of irongroup elements (Os, Ru, Rh, and Ir) is more complex. Their concentrations decrease with the growth in Cu content from pyrrhotite to chalcopyrite–pyrrhotite ores, then increase in the cubanite variety, and decrease again toward the chalcopyrite ore type enriched in Cu.



**Fig. 5.** Ni and PGE contents in massive ores of the MSL in the field of the Oktyabr'sky Mine versus Cu content.

The correlation between Ni and other metals in massive ores from the central part of the MSL (Oktyabr'sky Mine) is shown in Fig. 6. The negative correlation between Ni and Cu and between Ni and other metals of the copper group (Au, Pt, and Pd) is seen, along with a positive correlation of Ni with Ir, Os, and Ru (Fig. 6).

It should be noted that, in geochemical diagrams demonstrating the distribution of elements in massive ores, their contents make up two isolated fields, the first corresponding to pyrrhotite and chalcopyrite–pyrrhotite ores and the second to cubanite and chalcopyrite ores (Figs. 3, 5, 6).

*Distribution of elements in the vertical section of the massive ore lode.* Figures 7 and 8 exhibit the distribution of ore elements in the vertical section of massive ores. The first distribution type (geochemical zoning of the first type) is established in the central part of the lode that is localized at the base of the intrusion in the area where the thicknesses of the intrusion and the massive ore are maximal (150 m or higher and up to 55 m, respectively). It is seen that the Cu, PGE, and Au contents decrease from the base of the sulfide lode toward its roof with further substantial enrichment of overlying contact gabbrodolerite in these metals (Fig. 7). This trend is accompanied by depletion of sulfides in a heavy sulfur isotope with further enrichment of sulfides contained in contact gabbrodolerite in 34S; this rock corresponds to the upper outer contact of the sulfide lode. The thickness of the zone with anomalously high concentrations of copper and noble metals at the upper outer contact zone of the MSL varies from 5–7 m for Os, Rh, and Ir and to 10–15 m for Cu, Au, Pd, and Pt. According to the degree of enrichment (*k*) of the anom-



**Fig. 5.** (Contd.)

alous zone relative to the massive ore, the following series is observed: Ni  $(k \approx 1)$  < Cu  $(k = 3-5)$  < Pd  $(k = 1)$ 5–10) < Rh (*k* = 10) < Pt (*k* = 10–15) < Ir (*k* = 15–20) < Ru (*k* = 20–30) < Os (*k* = 50–60) < Au (*k* = 100).

Another distribution type (geochemical zoning of the second type) is characteristic of the frontal part of the deposit, with a decreased thickness of the intrusion and massive ores. The sulfide lode is hosted here within the intrusion in contact gabbrodolerite. The zoning of this type is characterized by a growth in element contents from the base of the massive ore lode toward its roof without a concentration maximum in overlying rocks of the upper outer contact zone.

*Lateral distribution of ore elements in the sulfide lode.* The distribution of ore elements and the sulfur isotope composition from the base of the massive ore

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 6 2006

lode toward its roof in several sections (boreholes) along a profile extending from the central to the frontal part of the MSL is shown in Fig. 9. In order to eliminate samples belonging to different mineral types, the sampling profile crossed the marginal part of the MSL, composed largely of uniform chalcopyrite–pyrrhotite ore.

As follows from Fig. 9, the Ni content in the horizontal section of the MSL varies insignificantly from its frontal part to the center. The concentrations of copper and noble metals are more variable. The Cu, Pt, and Pd contents increase gradually from the central part of the lode toward its front, where the ore is substantially enriched in Cu and noble metals. In the same direction, sulfur in sulfides becomes depleted in a heavy isotope:  $\delta^{34}$ S decreases from 13.5 to 9.5‰. Kovalenker et al. (1974) was the first to note this trend.



**Fig. 6.** PGE and Au contents in massive ores of the MSL in the field of the Oktyabr'sky Mine versus Ni content.

## DISCUSSION

The formation of massive sulfide lodes is a result of crystallization of Fe–Ni–Cu–S sulfide melt. This process has been studied in experiments and considered in several publications (Naldrett, 1984, 1989, 2003). The mineralogical and related geochemical zoning of massive ore testifies to its development in the course of fractionation of sulfide melt with separation of its derivatives. The analysis of the parageneses of major ore-forming minerals of massive ores taking into account experimental data on the Cu–Fe–Ni–S system makes it possible to establish the successive stages in the formation of mineral ore types during crystallization of sulfide melt and to assess the number of degrees of freedom *f* for the respective equilibria. As is known,  $f = k + 1 - F$ , where *k* is the number of components and *F* is the number of phases. In our case,  $F = 4$  (m, Po, Cb, Cp) and  $k = 3$  (Fe, Cu, S). The addition of Pnt and related Ni does not change *f*. Thus, we have the following series:

sulfide melt, with  $f = 4 - m = 3$ ;

pyrrhotite ore, with  $f = 4 - (m + Mss) = 2$ ;

pyrrhotite–chalcopyrite ore, with  $f = 4 - (m + Mss +$  $Cpss = 1$ ;

chalcopyrite–pyrrhotite–cubanite ore, with  $f = 4$  –  $(m + Mass + Cpss + Cbss) = 0;$ 

cubanite ore, with  $f = 4 - (m + Mss + Cbss) = 1$ ;

cubanite–chalcopyrite ore, with  $f = 4 - (m + Mss +$  $Cbss + Cpss = 0$ ; and

chalcopyrite ore, with  $f = 2(1) = 4 - [m + Cpss]$  $(Mh + \text{Tail})$ ],

where m is sulfide melt; solid sulfide solutions: (Mss) monosulfide or Ni-pyrrhotite, (Cpss) chalcopy-

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 6 2006



**Fig. 6.** (Contd.)

rite, and (Cbss) cubanite; minerals: (Po) pyrrhotite, (Pnt) pentlandite, (Cp) chalcopyrite, (Cb) cubanite, (Mh) mooihoekite, and (Tal) talnakhite.

The obtained data show that, during the development of mineralogical zoning, the parageneses of the main mineral types of massive ores and their transitional varieties correspond to monovariant and nonvariant conditions, respectively. The appearance of sulfide melt with a new stable monovariant paragenesis in the course of crystallization is marked by the disappearance of one of the phases and by a change in the melt composition. Nonvariant parageneses (transitional ore types) formed under isothermal conditions, which were provided by the thermal field of the intrusion and fluid heat transfer from a deep chamber. This model is idealized; initial phase relationships in ore are actually modified by crystallization of intercumulus melt and by subsolidus transformations, which are thought to be responsible for the formation most of the pentlandite. Nevertheless, the minimal contents of minerals critical for a particular type of ore and the jumps in Cu content that separate the main mineral ore types in compositional diagrams are distinct (Figs. 2, 4, 6).

*Behavior of ore elements during fractionation of sulfide magma.* The different distribution patterns of noble minerals in ores during crystallization of sulfide melt revealed in C*i*–Cu diagrams are explained by the specific partition of metals between crystallizing solid solutions: Fe–Ni monosulfide (Mss), Fe–Cu chalcopyrite (Cpss), and cubanite (Cbss) solid solutions and sulfide melt (m). Noble metals differ in their affinity for Mss, which determines the partition coefficients *D* Mss/m between Mss and coexisting sulfide melt (Li et al., 1996; Fleet et al., 1993; Barns et al., 1997). The

# **GORBACHEV**



**Fig. 7.** Distribution of (a) ore elements and (b) sulfur isotope composition in the vertical section in the field of the Oktyabr'sky Mine. (a) (1) Intrusion, (2) host rocks, (3) massive ore; (b) (1) intrusion, (2) massive ore, (3) Cp, (4) Po.

elements compatible with Mss (Fe, Ir, Os, Rh, and Ru), with *D* Mss/m ranging (according to various estimates) from 3 to 10 or higher, concentrate in Mss. Because of this, the residual sulfide melt becomes depleted in these elements during crystallization, whereas the ore enriched in Mss cumulus, on the contrary, is enriched in these elements. Copper and other elements incompatible with Mss (Pt, Pd, and Au), with *D* mss/m of ~0.1–0.2, concentrate in the sulfide melt during crystallization and fractionation of Mss. Judging from the distribution of Au, Pt, and Pd in ore, crystallization of Cbss and Cpss does not exert a significant effect upon the distribution of these metals. A slight depletion in Au is noted only in the latest ore, enriched in Cu (up to 30 wt % or higher). This is probably caused by redistribution of Au to the fluid phase, which escapes from the residual sul-



**Fig. 8.** Distribution of Pt and Pd in the vertical section of massive ore in the MSL. Geochemical zoning of (a) frontal and (b) central parts of the lode.

fide melt enriched in volatile components and such fusible metals as Pb, Sn, Bi, Sb, and As (Godlevsky, 1968). In contrast, the second maximum of concentrations of the iron-group elements (Rh, Ru, Ir, and Os) in cubanite ore that is depleted in pyrrhotite and chalcopyrite indicates a relatively high affinity of these elements for the Fe-rich cubanite solid solution (Cbss).

Even small differences in affinities of PGE and Au to Mss are reflected in the distribution of these elements in ore. For example, positive [Au/(Au + Pd)]–Cu and



**Fig. 9.** Distribution of ore elements (a–c) and (d) sulfur isotope composition (Gorbachev and Grinenko, 1973) in massive sulfide ore of the MSL along a profile that extends from the frontal part of the lode to its central part. *L* is the distance from the frontal part (km).

negative  $[Pd/(Pd + Pt)]$ –Cu correlations indicate a higher affinity of Pd for Mss in comparison with Au and of Pt relative to Pd. (Of two elements, the residual sulfide melt is more enriched in that with higher incompatibility with Mss). Judging from negative  $[Ir/(Ir + Os)]$ –Cu and  $[Ru/(Ru + Os)]$ –Cu correlations, Ir and Ru have a higher affinity for Mss than does Os; maxima of the above ratios in Cb ore indicate their higher affinity for Cbss (Fig. 10).

*Separation of sulfide solution into immiscible Fe–Ni and Fe–Cu liquids and the possible role of immiscibility in the formation of contrastingly layered pyrrhotite and chalcopyrite ore types.* As was mentioned above, fractionation of the elements compatible and incompatible with Mss during crystallization of sulfide melt played an important role in the development of geochemical zoning of the sulfide lode. It cannot be ruled out that fractional crystallization was predated by separation of sulfide magma into immiscible Fe–Ni and Fe–Cu melts. This suggestion is supported by the experimental melting of sulfide-bearing peridotite in the presence of aqueous fluid. Separation of sulfide melt into two liquids, one enriched in Fe and Ni and the other in Fe and Cu, was confirmed by experimental results (Gorbachev and Nekrasov, 2004). A two-phase sulfide drop is shown in Fig. 11. The inner portion of this drop (quenched sulfide melt) is enriched in Fe, Ni, and S and corresponds to the Cu-bearing Fe–Ni monosulfide solid solution (Mss). The outer part of the drop is depleted in these elements and enriched in Cu and Pt; i.e., its composition corresponds to the Ni-bearing Cu–Fe solid solution (Cpss). This solution is oversaturated with Pt, as is evident from the occurrence of PtS inclusions. Fractionation of elements during separation of sulfide magma into two immiscible liquids is characterized by the partition coefficient *D* calculated as a ratio of the weight concentrations of the *i*th element in the Fe–Ni and Fe–Cu sulfide melts. Elements with  $D > 1$ (Ni, Fe, S) concentrate in the Fe–Ni sulfide melt (*D* Ni = 25, *D* Fe = 3, and *D* S = 1.3), and elements with  $D < 1$  (Cu, Pt), in the Fe–Cu liquid ( $D$  Cu = 0.08,  $D$  Pt < 0.01).

The obtained experimental results indicate that, in fluid-bearing silicate–sulfide systems, sulfide melt may be separated, under certain conditions (the presence of a supercritical fluid), into high-S, Cu-bearing, Fe- and Ni-rich sulfide liquid of Mss composition and low-S, Ni-bearing, Cu- and Pt-rich liquid of Cp composition. This process is accompanied by fractionation of compatible and incompatible elements with respect to Mss. In this regard, it may be assumed that the contrasting separation of sulfide ores into pyrrhotite and chalcopyrite varieties characteristic of the Noril'sk deposits and the discrete distribution of metals therein is related to immiscibility of two sulfide melts and the subsequent fractional crystallization of Fe–Ni and Fe–Cu liquids.

*Vertical and horizontal geochemical zoning of the sulfide lode and emanation differentiation of sulfide magma.* The vertical and horizontal geochemical zoning differs from the distribution of elements in the main mineral ore types related to fractionation of elements compatible and incompatible with Mss in the course of fractional crystallization of sulfide magma. The enrichment of the upper outer contact zone of the MSL and its frontal part in ore elements is independent of the affinity for Mss. For example, such pairs contrasting in geochemical properties as Pd–Rh and Os–Au, which have opposite affinities for Mss, are similar in the degree of enrichment in the upper outer contact zone. The absence of fractionation of elements compatible and incompatible with Mss indicates that vertical and horizontal geochemical zoning was developing before the mass Mss crystallization. The enrichment of the upper outer contact zone of the MSL with both compatible and incompatible elements may be explained by degassing of sulfide magma. Sulfide melt is characterized by a high vapor tension. In addition to sulfur and oxygen, the vapor is able to dissolve  $H_2O$ , Cl, F,  $H_2$ , and hydrocarbons and other fusible and volatile elements (K, As, Sb, Bi, Sn). The ability of sulfide melt to dissolve volatile elements is evidenced by the presence of graphite, apatite, djerfisherite, and hydrocarbon inclusions in sulfide ores, as well as by the development of reaction rims composed of biotite, amphibole, and anhydrite around sulfide drops in picritic gabbrodolerites. Finally, the available, although limited, experimental data on the solubility of volatile elements in sulfide melts confirm a high transporting ability of the fluid in the fluid–sulfide melt system with respect to ore elements and sulfur isotopes (Gorbachev, 1998; Konnikov, 1998). This suggestion is supported by the correlation between the degree of enrichment of the anomalous zone in metals *k* relative to massive ore and the affinity of these metals for sulfur, which is expressed as  $\log f_{S_2}$  of the equilibrium  $2/m \ M_nS_m = 2n/m \ M + S_2$ (Fig. 12). This correlation probably reflects emanation differentiation of sulfide melt, where the distribution of elements between the fluid and sulfide melt is controlled by the affinity of metals for sulfur rather than for



**Fig. 10.** Ratios of noble metal contents versus copper content in massive sulfide ores.

Mss. The increase in the concentrations of ore elements and a light S isotope in the horizontal section of the MSL toward its frontal zone is also unrelated to the fractional crystallization of sulfide melt. The transport of metals by fluids escaping during degassing of sulfide melt, along with probable purging of the melt column by fluid derived from a deep source, is the most plausible mechanism responsible for the development of horizontal geochemical zoning.



**Fig. 11.** Immiscibility of the (1) Fe–Ni and (2) Fe–Cu sulfide liquids in (a) experiment (two-phase sulfide drop, after Gorbachev and Nekrasov (2004)) and (b) in massive sulfide ore that determined mineralogical zoning (Fig. 1); (c) geochemical zoning in the MSL.

*Vertical zoning of sulfide magma and degree of intrusive body crystallization.* As was shown above, the vertical geochemical zoning in the central and frontal parts of the deposit is different. In its central part, gabbrodolerite that occurs in the upper outer contact zone of the MSL is enriched in Cu, Au, and PGE, whereas in the frontal part such enrichment is not observed. In my opinion, this may be explained by a different degree of intrusion consolidation by the moment of emplacement of the sulfide magma that formed the lode. The frontal part of the intrusion or, at least, its lower units were completely crystallized by that time and served as a firm screen preventing ore-bearing fluids from vertical migration. Precisely this factor explains the wide development of sulfide veins that fill fissures in the frontal part of the intrusion. In the central part of the deposit,

where the thickness of the intrusion is maximal, the rocks in its lower inner contact zone had crystallized only partly by the moment of the sulfide magma emplacement. The partially crystallized rocks at the base of the intrusion were permeable for the ore-bearing fluids that provided the supply of Cu, Au, and PGE into the lower contact zone.

Thus, the fractional crystallization of sulfide magma, probably, complicated by liquid immiscibility, resulted in the formation of the main mineral ore types with fractionation of noble metals according to their affinity for monosulfide Fe–Ni solid solution and, to some extent, for chalcopyrite Fe–Cu solid solution. Sulfide magma degassing (emanation differentiation) is responsible for the development of vertical and horizontal geochemical zoning, which was controlled by



**Fig. 12.** Affinity of ore elements for sulfur expressed as  $\log f_{S_2}$  of the equilibrium  $2/m (M_nS_m)_{\text{(solid)}} = 2n/mM_{\text{(solid)}} +$  $S<sub>2</sub>$  versus degree of enrichment of the upper outer contact zone of the MSL in ore elements.

the affinity of metals for sulfur and reflected their partition between the fluid and sulfide melt during its degassing. The degree of crystallization of the intrusion by the moment of sulfide magma emplacement was an important factor that determined the type of the vertical geochemical zoning.

### ACKNOWLEDGMENTS

I thank M. Asif, P. Lightfoot, and A. Naldrett for long-term cooperation in the study of the Noril'sk ore district; V.E. Kunilov and A.I. Stekhin for their assistance in conducting fieldwork, visiting mines, and sampling; and A.A. Marakushev for constructive criticism during preparation of the manuscript. This work was supported by the Russian Foundation for Basic Research (project nos. 03-05-64531 and 03-05-64549); by the Council for Grants of the President of the Russian Federation for Support of Leading Scientific Schools (grant no. NSh-1301.2003.5); and by Program no. 2-1114 of the Division of Earth Sciences, Russian Academy of Sciences.

#### REFERENCES

- 1. M. Asif and S. J. Parry, "Elimination of Reagent Blank Problems in the Fire Assay Preconcentration of the Platinum Group Elements and Gold with a Nickel Sulfide Bead Weighing Less than One Gram," Analyst **114**, 1057–1067 (1989).
- 2. S.-J. Barns, E. Makovicky, M. Makovicky, et al., "Partition Coefficients for Ni, Cu, Pd, Pt, Rh, and Ir between Monosulfide Solid Solution and Sulfide Liquid and the Formation of Compositionally Zoned Ni–Cu Sulfide

GEOLOGY OF ORE DEPOSITS Vol. 48 No. 6 2006

Bodies by Fractional Crystallization of Sulfide Liquid," Canad. J. Earth Sci. **34** (3), 366–374 (1997).

- 3. V. V. Distler, "Platinum Mineralization of the Noril'sk Deposits," in *Proceeding of the Sudbery-Noril'sk Symposium* (Geol. Surv. Spec. Publ., Ontario, 1994), No. 5, pp. 243–262.
- 4. V. V. Distler, T. L. Grokhovskaya, T. L. Evstigneeva, et al., *Petrology of Sulfide Magmatic Ore Formation* (Nauka, Moscow, 1988) [in Russian].
- 5. D. A. Dodin, N. M., Chernyshov, and B. A. Yatskevich, *PGM Deposits of Russia* (Nauka, St. Petersburg, 2000) [in Russian].
- 6. D. A. Dodin, L. V. Oganesyan, N. M. Chernyshov, et al., *Mineral Resource Potential of Platinum Minerals in Russia on the Turn of XXI Century* (Geoinformmark, Moscow, 1998)[in Russian].
- 7. M. E. Fleet, S. Chryssoulis, W. E. Stone, et al., "Partitioning of Platinum-Group Elements and Au in the Fe-Ni-Cu-S System: Experiments on the Fractional Crystallization of Sulfide Melt," Contrib. Mineral. Petrol **115** (1), 36–44 (1993).
- 8. A. D. Genkin, V. V. Distler, G. D. Gladyshev, et al., *Copper–Nickel Sulfide Ores of the Noril'sk Deposits* (Nauka, Moscow, 1981) [in Russian].
- 9. M. N. Godlevsky, *Traps and Ore-Bearing Intrusions of the Noril'sk District* (Gosgeolizdat, Leningrad, 1959) [in Russian].
- 10. M. N. Godlevsky, "Magmatic Deposits," in *Origin of Endogenic Ore Deposits* (Nedra, Moscow, 1968), pp. 7–84 [in Russian].
- 11. N. S. Gorbachev, "Sources and Formation Conditions of the Pt-Cu-Ni Deposits (Noril'sk Area)," Experiment in Geosci. **7** (1), 14–16 (1998).
- 12. N. S. Gorbachev, G. Brugmann, A. Naldrett, et al., "Oxidation-Reduction Conditions and Distribution of Platinum-Group Metals in Sulfide–Silicate Magmatic Systems," Dokl. Akad. Nauk **331** (2), 220–223 (1993).
- 13. N. S. Gorbachev and L. N. Grinenko, "Sulfur Isotopic Composition of Sulfides and Sulfates from Sulfide Ores of the Oktyabrsky Deposit (Noril'sk District) with Reference to Its Origin," Geokhimiya **11** (8), 1127–1136 (1973).
- 14. N. S. Gorbachev, A. D. Naldrett, V. E. Kunilov, and M. Azif, "The Fractional Crystallization and Fluid–Melt Differentiation of Sulfide Magma (Example from the Oktyabr'sky Platinum–Cooper–Nickel Deposit, Noril'sk District)," Dokl. Akad. Nauk. **371** (3), 362–365 (2000) [Dokl. Earth Sci. **371A** (3), 490–493 (2000)].
- 15. N. S. Gorbachev and A. N. Nekrasov, "Immiscibility of Fe–Ni–Cu Sulfide Melts: Experimental Studies and Geological Application, Dokl. Akad. Nauk **399** (4), 1–4 (2004) [Dokl. Earth Sci. **399** (9), 1256–1259 (2004)].
- 16. E. G. Konnikov, "Study of Ore-Forming Factors of Basic Ore-Magmatic Systems," Experiment in Geosci. **7** (1), 18–19 (1998).
- 17. V. A. Kovalenker, V. D. Gladyshev, and L. P. Nosik, "Sulfur Isotopic Composition of Sulfides from the Deposits of the Talnakh Ore Cluster in Regard to Their Se Content," Izv. Akad. Nauk SSSR, Ser. Geol., No. 2, 80–91 (1974).
- 18. A. I. Krivtsov, V. I. Kochnev-Pervukhov, O. M. Konkina, et al., *Cu–Ni–PGM Deposits of the Noril'sk Type* (TsNIGRI, Moscow, 2001) [in Russian].
- 19. C. Li, S.-J. Barnes, E. Makovicky, et al., "Partitioning of Ni, Cu, Ir, Rh, Pt, and Pd between Monosulfide Solid Solution and Sulfide Liquid. Effects of Composition and Temperature," Geochim. Cosmochim. Acta **60**, 1231–1238 (1996).
- 20. A. J. Naldrett, "Nickel Sulfide Deposits: Classification, Composition, and Genesis," in *Origin of Ore Deposits* (Econ. Geol., Seventy-Fifth Anniversary Volume 1905– 1980, Econ. Geol. Publ. Co., 1981; Mir, Moscow, 1984), Vol. 2, pp. 253–343.
- 21. A. J. Naldrett, *Magmatic Sulfide Deposits* (Oxford Univ. Press, New York, 1989).
- 22. A. J. Naldrett, *Magmatic Cu–Ni and PGM Sulfide Deposits* (St. Petersburg State Univ., St. Petersburg, 2003; Springer, Berlin, 2004).
- 23. A. Naldrett, M. Asif, N. Gorbachev, et al., "The Composition of the Cu–Ni Ores of the Noril'sk Region," Canad. Mineral. **30**, 494–495 (1992).
- 24. A. Naldrett, M. Asif, N. Gorbachev, et al., "The Composition of the Cu–Ni Ores of the Noril'sk Region," in *Proceedings of the Sudbury–Noril'sk Symposium* (Geol. Surv. Spec. Publ., Ontario, 1994), No. 5, pp. 357–372.
- 25. A. J. Naldrett, P. Lightfoot, N. S. Gorbachev, et al., "A Model for Formation of the Ni-Cu-PGE Deposits of the Noril'sk Region," in *Intern. Platinum* (Atheus., St. Petersburg, 1998), pp. 92–106.
- 26. *Platinum of Russia* (Geoinformmark, Moscow, 1994) [in Russian].
- 27. *Platinum of Russia* (Geoinformmark, Moscow, 1995), Vol. 2, Books 1, 2 [in Russian].
- 28. *Platinum of Russia* (Geoinformmark, Moscow, 1999), Vols. III, IV [in Russian].
- 29. A. I. Stekhin, "Mineralogical and Geochemical Characteristics of the Cu–Ni Ores of the Oktyabr'sky and Talnakh Deposits," in *Proceedings of the Sudbury–Noril'sk Symposium* (Geol. Surv. Spec. Publ., Ontario, 1994), No. 5, pp. 217–230.
- 30. A. V. Valetov, B. P. Badtiev, and V. A. Ryabikin, "Present-Day State of Resource Base of the Noril'sk Mining Company", Tsvetn. Metally, No. 6, 10–14 (2000).