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Mineralogical and geochemical feature of the disseminated ores of the southern part of the Noril'sk 1 deposit

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Abstract. The new data on the composition of disseminated sulphide ore in the southern part of the Noril'sk 1 deposit are obtained. It was found that a sulfur-poor assemblage: as Fe-rich (cubanite, mackinawite) and Cu-rich (talnakhite, bornite, chalcocite, native copper) minerals due to the evolution of two different fractions of sulphide melt is characteristic of picritic gabbro-dolerite. It has been formed at relatively low sulfur activity ($lgfS_2$ range from -12 to -11). And a high-sulfur assemblage (monoclinic pyrrhotite, pyrite and Ni-rich pentlandite) formed at higher sulfur activity (lg/S_2 range from -10.5 to -10) due to the pyrrhotitechalcopyrite fractionation of the sulphide melt is characteristic of olivine gabbro-dolerite. The ratios of Ni/Cu in the rocks decrease from picritic (Ni/Cu = 1.24 average) to olivine gabbrodolerites (Ni/Cu = 0.69 average). But the Ni/Fe ratios in pentlandite are increasing down the cross-section due to increase of sulfur fugacity during the evolution of ore-forming system. The Pd-parageneses vary along the cross-section top down as follows: $Sn \rightarrow Pb \rightarrow As \rightarrow Bi(Te)$ in picritic gabbro-dolerite and Sn \rightarrow Sb \rightarrow As \rightarrow Te(Bi) in olivine gabbro-dolerite. There is a clear correlation between the sulfide and PGM assemblage and the type of the host rocks.

1. Introduction

Platinum-copper-nickel deposits of the Noril'sk region are located in the northwestern part of the Siberian platform and are associated with flood-basalt of Perm-Triassic age [1-3]. The Noril'sk 1 deposit is located in the northern part of the same name intrusion, confined to the Noril'sk-Kharaelyakh fault in the Noril'sk Trough. Intrusion of Noril'sk I breaks the Carbon-Permian terrigenous deposits of the Tungusska Series and basalts of the Upper Permian-Lower Triassic age [2].

Numerous works are devoted to the ores of the Noril'sk 1 deposit [5,7-10]. Most of the works devoted to the massive ores or low-sulphide horizons, and only some of them are considering the disseminated ore of the Main Ore Horizon composed of picritic, taxitic, and lower olivine gabbrodolerites [7,11,12]. The features of sulfide mineralization in each unit have been characterized previously [2], however the task of establishing a correlation between the types of the host rocks and the chemical and mineral composition of ores is still relevant [3].

The new data on the composition of disseminated sulphide ore in the southern part of the Noril'sk 1 deposit are obtained on the basis of the samples study of the PH-14 borehole (figure 1). This borehole crosses all the rocks, alternating in a certain stratigraphic sequence which have been described earlier [1,2]. We studied samples of the lower part of the intrusion Noril'sk 1, composed of picritic and lower olivine gabbro-dolerites containing the disseminated Cu-Ni sulphide with the minerals of platinum group elements (PGM). The zoning (changes of geochemical feature, mineral parageneses and compositions of sulfides) from picritic gabbro-dolerite (821.2-902.0 m) to olivine gabbro-dolerite (902.0-938.1 m) and to the contact with siltstones has been established. The more common contact rock of the Noril'sk 1 intrusion is taxitic gabbro-dolerite. But the lower olivine gabbro-dolerire instead

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of taxitic gabbro-dolerite occur in this cross-section of the PH-14 borehole that is similar to the Northern intrusive body (OM-14) of the Maslovsky deposit (figure 1) [3].



Figure 1. The scheme of location of ore-bearing intrusions and deposits of Noril'sk region

2. Result

2.1. Variations of ore elements

The absolute concentrations of Ni and Cu almost in the whole interval of the investigated cross-section do not exceed of 0.5 % in total (figure 2): the average content of Cu is 0.22 % in picritic gabbro-dolerite and 0.25 % in olivine gabbro-dolerite; the average content of Ni is 0.24 % and 0.17 %, respectively. But there is the single anomalies reaching 2-3% of Cu and Ni, which coincide with the presence of veins of sulphides. Content of Ni predominates over Cu (Ni/Cu is 1.24 average) in picritic gabbro-dolerite, but there are several horizons, where Ni/Cu <1, which coincide with the Pt-Pd anomalies. In olivine gabbro-dolerites, on the contrary, content of Cu prevails over Ni (Ni/Cu is 0.69 average). In general, Ni/Cu ratios vary considerably along section, gradually decreasing to contact with the host rocks (figure 2).

The concentrations of PGE vary in range: 0.11-3.80 % (Pt) and 0.27-7.36 % (Pd) in picritic gabbro-dolerite; 0.06-1.94 (Pt) and 0.15-5.80 (Pd) in olivine gabbro-dolerite; the total of Pd and Pt reach up to 10 ppm in massive ores (figure 2). The ratio of Pd/Pt as a whole increases downward along the cross-section: Pd/Pt = 2.50 (on average) in the upper part of picritic gabbro-dolerite (with CrSp), 2.79 - in the lower part of them, 3.08 - in olivine gabbro-dolerite, and 4.42 - in massive ores. It is consistent with the evolution of sulphide melt and fractionation of ore elements during its deposition to the bottom of the magmatic chamber [1,13].

2.2. Sulphide mineralization in picritic gabbro-dolerites

A considerable variety of ore minerals are characteristic of picritic gabbro-dolerite: pyrrhotite, chalcopyrite, pentlandite, cubanite, talnakhite, chalcocite, bornite, native copper, magnetite and ilmenite, which are spread unevenly. It is noticed that the amount of pyrrhotite, chalcopyrite and pentlandite decreases with the increase of cubanite (figure 3 a). But in the upper horizons (up to 840 m) the pyrrhotite is the most common. The prevalence of S-poor assemblage: as Fe-rich (cubanite, mackinawite) and Cu-rich (talnakhite, bornite, native copper) minerals are a typomorphic feature of the sulphide assemblage of picritic gabbro-dolerite. Chromspinels are common in the upper part of picritic gabbro-dolerites – "chromite horizon" of the thickness about 40 m (figure 2).

The drople-like, irregular and interstitial sulphide patches (aggregates) up to 5 mm are characteristic of picritic gabbro-dolerite (figure 4). Pyrrhotite is found in intergrowths with chalcopyrite, pentlandite and cubanite. Pentlandite occurs often as lamellas in the marginal parts of pyrrhotine grains (figure 4 d) due to decomposition of solid solution. Chalcopyrite is represented by small grains, often in association with bornite (figure 3c). Native copper occurs as the veins in sulphide aggregates (figure 4 a) and rims over sulphides and oxides. Chromspinels and magnetite

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occur as irregular impregnation in silicates, occasionally in association with sulphides (figure 4 f). Cubanite and chalcopyrite in the sulphide aggregates begin to dominate lower in the profile of the picritic gabbro-dolerite (figure 2), in which minor sphalerite, galena, native gold and PGM are included. The lamellae of cubanite are characteristic of chalcopyrite grains.





Figure 3. The variations in the amount of sulphides (%) along the cross-section of borehole PH-14: a – in picritic gabbro-dolerite, b – in olivine gabbro-dolerite. Po – pyrrhotite, Cp – chalcopyrite, Pn – pentlandite, Cb – cubanite, Bn – bornite, Py – pyrite, Ml – millerite

2.3. Sulphide mineralization in olivine gabbro-dolerite

Sulfides are represented by a high-sulfur association composed of chalcopyrite, pyrrhotite and pentanedite, as well as pyrite, which is occurs more often in the lower part of this interval (figure 3 b). Chromspinels and copper-rich minerals are absent in this interval. A positive correlation appears between amounts of chalcopyrite and pentlandite and a negative correlation of both these minerals with amount of pyrrhotite in olivine gabbro-dolerite (figure 3 b), which also distinguishes olivine gabbro-dolerites from picritic ones.

Chalcopyrite is the predominant sulphide in disseminated and vein-disseminated ores of olivine gabbro-dolerite (figure 3 b, figure 4 h). It together with other sulfides compose the xenomorphic interstitial aggregates of various sizes (figure 4 g-i). Pyrrhotite composes their internal parts and it is bordered by chalcopyrite. The pyrrhotite is almost completely replaced by pyrite-marcasite-magnetite aggregates and pentlandite – by violarite on some horizons of the lower part of olivine gabbro-

dolerites (figure 3 b). Millerite and unnamed phase of $(Fe,Ni)_2S_3$ occur in this assemblage (figure 5 a). Ilmenite and magnetite occur as uneven impregnation in silicates. Magnetite is also found as a secondary phase. Disseminated ores of olivine gabbro-dolerite change on the horizon of 839.8 m by massive sulphide ores, mainly pyrrhotite composition (85%), in which chalcopyrite and pentlandite are in a subordinate amount.



Figure 4. Photomicrographs in reflected light of the sulphide minerals of the picritic (a-f) and olivine (g-i) gabbro-dolerites.

2.4. Compositions of sulphides in picritic and olivine gabbro-dolerites

2.4.1. Fe(+Co) - S - Ni system

The compositions of sulfides in picritic and olivine gabbro-dolerites differ in sulfur and copper contents (figure 5). But in each unit they change with a depth. The pyrrhotite is close to troilite (FeS); pentlandite is Fe-rich (figure 5 a) and contains a minor Co (1.2-2.4 wt%); makinawite $[(Fe_{5.67}Ni_{2.84}Co_{0.21})S_{8.28}]$ is common at the upper horizons of *picritic gabbro-dolerite*. Below in the section, the compositions of pentlandite vary considerably from makinwite $(Fe_{5.37}Ni_{3.19}Co_{0.13})S_{8.31}$ to Fe-rich pentlandite $(Fe_{4.88}Ni_{3.53}Co_{0.12})S_{8.47}$. The Co content decreases to 0.60 wt.%. Below in the cross-section of picritic gabbro-dolerites the pyrrhotite is enriched in sulfur and pentlandite is enriched in nickel. And at the lowest horizon (896.7 m) pentlandite is represented by a nickel variety $(Ni_{4.54}Fe_{3.82}Co_{0.27})S_{8.37}$. The Fe content predominates over Ni and there is an Co as minor element (up to 6.2 wt.%) in the pentlandite on the upper horizons of *olivine gabbro-dolerite*. The compositions of the pentlandite are shifted to the nickel-rich chart area below in the section: $Ni_{4.76}Fe_{3.20}Co_{0.52}S_{8.32}$ (figure 5 a). In this case the pyrrhotite is most enriched in sulfur $Fe_{0.90}S_{1.10}$ (monoclinic species), and contains Ni < 1 wt.%; troilite is absent.

2.4.2. Fe(+Ni, Co) - S - Cu system

Compositions of Cu-minerals include chalcopyrite, cubanite, talnakhite, chalcocite and native copper in *picritic gabbro-dolerite* (figure 5 b). In this case, Fe predominates over Cu in chalcopyrite, and it occur as solid solutions with cubanite (figure 5 b). While the chalcopyrite becomes the less ferruginous, cubanite is not found, and pyrrhotite is the most enriched in sulfur (monoclinic species) in *olivine gabbro-dolerite* compared to the upper horizons.



Figure 5. The compositions of Fe-Ni (a) and Cu-Fe sulfides in picritic and olivine gabbro-dolerites.



Figure 6. The compositions of Fe-Ni (a) and Cu-Fe sulfides in picritic (a-c) and olivine (d-f) gabbro-dolerites. Po - pyrrhotite, Cp - chalcopyrite, Pn - pentlandite, Ap - apatite, Au - gold.

PGM are the smallest single- and two-phase inclusions in all sulphides, silicates and on their contacts. The intergrowths PGM with gold (Au) observed often (figure 6). Sperrylite is found in all types and horizons of rocks (figure 7). The compounds of Pd with Sn and Pb [paolovite Pd₂Sn, atokite (Pd,Pt)₃(Sn,As,Sb), unnamed (Pd,Ag)₅Pb₃] are typical for the upper horizons *of picritic gabbro-dolerite* (figure 7 a) which are changed by arsenides of PGE and As-containing PGM [hollingworthite RhAsS, majakite PdNiAs, As-paolovite Pd₂(Sn,As)] and further by Pd-Bi(Te) minerals [sobolevskite PdBi and michenerite PdBiTe] on the lower horizons (figure 7 b). The stannides and antimonides of PGE [paolovite Pd₂(Sn,As), atokite (Pd,Pt)₃Sn, mertieite II Pd₈Sb₃] of the upper horizon *of olivine gabbro-dolerite* are changed by the Pd arsenides [menshikovite Pd₃Ni₂As₃, vincentite Pd₃As and unnamed Pd₅As₂], and finally, by Pd tellurides [kotulskite PdTe and Pd(Te,Bi)] on contact with massive ores (figure 6c). PGM are represented by PtFe in massive ores.



Figure 7. The ratio of PGM in different rocks: a – picritic gabbro-dolerite (chromite horizon), b – lower part of picritic gabbro-dolerite (horizon 891.8 m), c - olivine gabbro-dolerite; n - number of analyzes.

3. Discussion

Thus, the following mineralogical-geochemical regularities are observed in the disseminated ores of the southern part of the Noril'sk 1 deposit. The Ni/Cu ratios are decreasing in the rocks with depth: Ni/Cu is more than 1 in picritic gabbro-dolerite, whereas Ni/Cu is less than 1 in olivine gabbrodolerite. The Ni/Fe ratio in the pentlandite increases with depth.

Iron-nickel ratios in pentlandite reflect the activity of sulfur (lg/S_2) during its formation [14,15]. As the $lgfS_2$ increases, the concentration of Ni in the pentlandite increases as well. The variation of k = Ni/(Ni+Fe) in pentanedite varies in the range 0.33 - 0.47 in picritic gabbro-dolerite that corresponds to the lg/S_2 from -12 to -11. Whereas variation of k in pentlandites from olivine gabbro-dolerite varies from 0.49 to 0.57, therefore they crystallized under conditions of $lgfS_2$ corresponding to an interval from -10.5 to -9. Thus, two different sulphide assemblage are characteristic of picritic and olivine gabbro-dolerites. In the first case, the "low-sulfur" minerals sequence is due to the evolution of the sulphide Cu-rich melt fraction separated from Fe-rich melt in the pre-crystallization time [5]. The following parageneses are formed during fractionation of mss and iss: $Po_{(h>tr)}+Cp+Pn_{(Fe>Ni)} \rightarrow Cp+Pn_{(Fe>Ni)}$ $Po_{(h>tr)}+Cp+Cb+Pn_{(Fe>Ni)} \rightarrow Cb\pm Cp+Pn_{(Fe>Ni)}\pm tr \rightarrow Th+Cb+Pn\pm Bn$ [1]. This agrees with the investigated parageneses in picritic gabbro-dolerite of PH-14 borehole. But disseminated ore hosed by picritic gabbro-dolerite has a Ni/Cu ratio >1. It means that the Cu-rich melt fraction was enriched in Ni also largely because the Ni tends to be an incompatible element in all plausible sulfide magma compositions [16]. The evolution of mineral parageneses in olivine gabbro-dolerite is: $Po_{(m>h)}+Cp+Pn_{(Fe<Ni)} \rightarrow Cp+Po_{(m+h)}+Pn_{(Fe<Ni)}$. It agrees with the experimental data on directional crystallization of melts [17] and is due to the pyrrhotite-chalcopyrite fractionation in conditions of increased sulfur fugacity.

A positive correlation between sulfur and copper for all types of rocks (figure 8 a) and a gradual increase in the concentrations of ore elements and sulfur towards the towards the bottom intrusion (see figure 2) is in agreement with the evolution of sulphide melt and fractionation of ore elements during its deposition [13]. So, there is a clear genetic relationship between the sulfide assemblages in disseminated ores and the type of the host gabbro-dolerites. A sulfur-poor and Cu-rich sulphide assemblage which has been formed at low sulfur activity is characteristic of picritic gabbro-dolerite. And a high-sulfur assemblage (monoclinic pyrrhotite, pyrite and Ni-rich pentlandite) formed at higher sulfur activity. Binary diagram of Cu versus Pd (figure 8 b) shows a difference in trends: a poorly defined linear for olivine gabbro-dolerite and indeterminate for picritic gabbro-dolerite.

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Figure 8. Binary diagrams of S versus Cu (a) and Cu versus Pd in 100% sulfides

4. Conclusions

Thus, on the basis of mineralogical and geochemical features it is established that:

- Ni/Cu ratios are decreasing in rocks from picritic to olivine gabbro-dolerites and toward the massive ores, that agreed with the increase of the chalcopyrite in this direction;

- Ni/Fe ratios in pentlandite are increasing from picritic to olivine gabbro-dolerites and to massive ores which indicates an increase in sulfur fugacity in mineral parageneses down the section of borehole;

- There is a clear correlation between the sulfide assemblages and the type of the host gabbro-dolerites: picritic gabbro-dolerites are characterized by a low-sulfur and Fe- and Cu-rich sulphide assemblage; olivine gabbro-dolerite is characterized by a high-sulfur assemblage of sulfides.

- The change of the compounds of Pd with semimetals is observed along the section: $Sn \rightarrow Pb \rightarrow As \rightarrow Bi(Te)$ in the picritic gabbro-dolerite and $Sn \rightarrow Sb \rightarrow As \rightarrow Te(Bi)$ in olivine gabbro-dolerite. The difference in evolutionary trends is due to the different schemes of fractionation of sulphide melt.

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