Factors affecting distribution of precious metals in rocks of the South Sopchinsky massif and the ‘Moroshkovoe Lake’ target (southern framing of the Monchegorsk pluton, Kola Peninsula): experience of applying statistical methods

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Abstract. Three types of vein bodies are developed within the southern framing of the Monchegorsk pluton, in metapyroxenites of the South Sopchinsky massif: 1) plagioclase-pyroxene; 2) quartz-feldspar, and 3) amphibole-plagioclase composition. PGM mineralization is related to sulfide-oxide dissemination in these vein bodies (they are also found in the neighboring ‘Moroshkovoe Lake’ target) and mainly occurs as tellurides, arsenides, bismuthides, and Pt and Pd sulfides. A correlation analysis of non-ferrous and precious metal contents in the veins and metapyroxenites enclosing them was carried out using the Spearman’s rank correlation nonparametric coefficient. It showed an inhomogeneous distribution of Cu, Ni, Pt, and Pd in these bodies. In conjunction with geological observations and petrochemical studies, the implementation of this statistical method allowed drawing a conclusion about a possible mechanism of formation of the low-sulfide PGM mineralization in rocks of the South Sopchinsky massif.

1. Introduction
Layered intrusions of mafic-ultramafic rocks of the Kola Peninsula are an important source of platinum group elements (PGE) in the Arctic area. One of such intrusions is the layered mafic-ultramafic Monchegorsk pluton (2.5 Ga). Within it, there are multiple deposits and PGE ore occurrences such as the Vurechuaivench deposit, the “Horizon 330” ore occurrences of the Sopcha massif, bottom deposits of the Nittis-Kumuzhya-Travyanaya massif, and ore occurrences of the South Sopchinsky massif, to which this paper is devoted. A low-sulfide PGM ore occurrence of the South Sopchinsky massif was found in its north-west part during prospecting and exploration works on the cusp of the 20s and 21st centuries (Ivanchenko, Davydov, 2009). The South Sopchinsky massif (SSM) is located in the southern framing of the Monchegorsk pluton within its contact with the Monchetundra intrusion (Figure 1). The massif stretches for 6 km to the north-west, where the thickness is ca. 600 m and the width is up to 1.5 km (Ivanchenko, Davydov, 2009; Chashchin et al., 2016). There are two zones in the SSM section. The lower zone with the thickness of 250–300 m is typically composed of metapyroxenites, and the upper zone is mainly composed of leuco-mesocratic coarse-grained maculose metagabbro-norites. The PGM mineralization is confined to the lower zone, which is referred to as “layered” and contains lenticular bed bodies of low-grade (1-5%) sulfide disseminations, where the content of Pt is 0.3-1.71 to 9 g/t and of Pd is 0.71-4.25 to 9 g/t. (Ivanchenko, Davydov, 2009).
Figure 1. Geological map of the southern framing of the Monchgorsk pluton in the contact zone with the Monchetundra intrusion (modified after Pripachkin et al., 2016). A red frame shows localization of the map A within the Monchegorsk pluton: MI - Monchetundra intrusion; NKT – Nittis-Kumuzhya-Travyanaya massif; DB - Dunite Block; SM - Sopcha massif; N-P - Nude-Poaz massif; SSM - South Sopchinsky massif; G-10 - Gabbro-10 massif; VN - Verhny Nude block; VM - Vurechauivench massif; IV - Imandra-Varzuga structure.

Two major rock types can be defined within the SSM and the adjacent “Moroshkovoe Lake” (ML) target: fine- to medium-grained metapyroxenites (metanorites) and coarse-grained metagabbronorites. The ML target is mainly composed of fine- to medium-grained metanorites. In the contact area of metapyroxenites (metanorites) and coarse-grained metagabbronorites, there is a magmatic breccia, where fragments of the metapyroxenites are cemented by the metagabbronorites (Rundkvist et al., 2016; Pripachkin et al., 2016; Figures 2A, 2B).

Coarse-grained vein bodies of complex morphology (Miroshnikova, Pakhomovsky, 2015; Miroshnikova et al., 2019) were found in the SSM and ML fine- to medium-grained metapyroxenites (metanorites) remote from the contact zone. They were divided into three types: 1) plagioclase-pyroxene vein bodies (Figure 2C); 2) quartz-feldspar veins; 3) amphibole-plagioclase veins. It is significant that the last two types of veins were defined based on their mineral composition, so they can be combined into one type.

The sulfide, oxide, and PGE mineralization is related to plagioclase-pyroxene vein bodies of the first type (Rundkvist et al., 2011; Figure 2D). The sulfide mineralization occurs as the bornite-millerite-chalcopyrite, pentlandite-chalcopyrite-pyrrohotine, or chalcopyrite-pyrrohotine types, which are closely spatially associated with the magnetite-ilmenite, or magnetite, type. There is a mineralization of precious metals on the contact of sulfides and oxides with silicate minerals, which also occurs as
inclusions in sulfides. Tellurides and arsenides prevail over bismuthides and Pt and Pd sulfides within minerals of platinum metals (Miroshnikova et al., 2019). The low-grade ore mineralization of the second and third type vein bodies composed of amphibole-plagioclase and quartz-plagioclase rocks occurs as the pyrite-chalcopyrite type, which is closely associated with the ilmenite type.

Figure 2. Relationships between rocks of the South Sopchinsky massif and the “Moroshkovoe Lake” target: A – contact of metapyroxenites (P) and coarse-grained metagabbro-norites (GN); B – fragments of metanorites (N) and metapyroxenites (P) cemented by a coarse-grained metagabbro-norite (GN); C – plagioclase-pyroxene veins (cN) intersecting fine- to medium-grained metapyroxenites (P); D – vein rock with sulfide-magnetite dissemination (photo of a large sample of ore).

This work attempted to study factors of non-ferrous and precious metal distribution in the SSM and ML rocks using mathematical methods of correlation analysis.

2. Method
Analyses of Ni, Cu, Pt, Pd, Au, and S contents in the SSM and ML rocks were carried out using the atomic absorption method at the Chemical-Analytical Laboratory of the Geological Institute, Kola Science Centre, Russian Academy of Sciences. A sulfide liquid of non-ferrous metals is considered to be a phase, which the most frequently affects contents of chalcophilic elements during magmatic processes (Barnes S.-J., Gomwe T.S., 2011). To evaluate whether the sulfide liquid affected distribution of non-ferrous and precious metals in the SSM and ML, dependencies between the content of Ni, Cu, Pt, Pd, Au and the sulfur content in these rocks were studied, and Harker’s binary variation diagrams were constructed in the Microsoft Excel program (Figure 3). A correlation analysis was
carried out for Cu, Ni, and PGE by the Statistica program, and a linear dependency was calculated using the Spearman’s rank correlation non-parametric coefficient.

A correlation analysis is a statistical study of stochastic dependency (i.e., dependency between random variables, which is an alteration of conditional distributions of any variable after an alteration in values of other variables) between random variables \{Xi\} and \{Yj\} (Mathematical methods…, 2008). Objectives of correlation analysis are sample estimation of pair correlation coefficients, sample estimation of multiple correlation coefficients, test of statistical significance of sample correlation coefficients, and estimation if a revealed relationship could be linear.

If the dependency between \(X_i\) and \(Y_j\) is linear, it is possible to characterize not only strength of relationship, but its direction. A relationship is called direct (positive) if values of one variable increase (decrease), values of other variable sustainably increase (decrease). In this case, a pair correlation coefficient is positive. A negative correlation shows an inverse relationship of \(X\) and \(Y\) variables, which a sign of pair correlation coefficient.

Correlation of ordinal geological data is a next higher level of description of geological objects features. Measurement are taken using order scales, which allows subsuming any observation under a certain category (class), as well as arranging these categories, i.e., sort observations as a succession, \(x_1, x_2, \ldots\), in ascending or descending order based on the degree of intensity (manifestation) of the measured property. A typical special feature of order scales is absence of data on the magnitude of differences between its gradations.

An example of order scales in geological studies are semi-quantitative (approximate estimation of contents of chemical elements: "a great amount", "a big amount", "little", "traces", "not detected", etc.) and approximately quantitative (distances between neighboring gradations are not determined precisely) spectral analyses. Differences in degree of detail of measurement of chemical elements contents for these two types of analyses are rather sufficient. It is a reason for a separate consideration of correlation measures of semi-quantitative and approximately quantitative data. The semi-quantitative data are called categorized ordered data. The approximately quantitative data can be easily ranked, so they are called rank data.

A ranking procedure is a positioning of values of a variable in ascending order and determination of ranks for each value as its number in this ordered row. An average rank is assigned for duplicate values. A rank measure of association between \(X\) and \(Y\) (\(X\) and \(Y\) are ranked variables) can be determined as:

\[
r_c = \frac{1}{N} \sum_{i=1}^{N} \frac{R_{Xi} R_{Yi} - R_X R_Y}{S_X S_Y},
\]

where \(R_X\), \(R_Y\) are arithmetic means of the ranks, and \(S_X, S_Y\) are mean quadratic deviations of these ranks. This is a simplified version of the formula after transformations:

\[
r_c = 1 - \frac{6}{N^3 - N} \sum_{i=1}^{N} (R_{Xi} - R_{Yi})^2.
\]

This measure of relationship strength is called the Spearman’s correlation rank coefficient. Significance of this rank coefficient is estimated by comparison of its random value with the threshold limit value \(r_a\), which is regulated by a number of observations and the significance level of \(a\). There are tables of exact distribution of the Spearman’s correlation rank coefficient, yet, they are rather inconvenient to use. The Spearman’s correlation rank coefficient changes within the range of \(-1\) to \(1\) reaching extreme values if both \(X\) and \(Y\) rows are either highly consistent or inconsistent (Mathematical methods…, 2008).

3. Results
The study of non-ferrous and precious metal distribution in different types of the SSM and ML rocks using the Spearman’s coefficient (R) indicated its inhomogeneity. The highest contents of these elements are found in plagioclase-pyroxene vein rocks, the lowest contents are in metagabbrororites and quartz-plagioclase and amphibole-plagioclase vein rocks, which significantly supports geological and mineralogical observations.

Copper shows statistically significant strong positive correlation with S (Figure 3a) for samples from plagioclase-pyroxene veins (correlation coefficient R=0.84) and from fine- to medium-grained metapyroxenites and metanorites (R=0.84), where the significance level is below 0.05, statistically significant strong correlation for samples of quartz-plagioclase and amphibole-plagioclase vein rocks (R=0.74) and weak correlation for samples of coarse-grained metagabbrororites (R=0.31), where the significance level is below 0.10.

In case of correlation of Ni with S (Figure 3b), there is a positive correlation for all rock: very weak for metapyroxenites and metanorites (R=0.15) and stronger for coarse-grained metagabbrororites (R=0.40) and quartz-plagioclase and amphibole-plagioclase veins (R=0.62), which is statistically significant if the significance level is below 0.10. There is also a positive correlation between these elements in plagioclase-pyroxene vein rocks (R=0.56), where the significance level is below 0.05.

Pd, Pt, and Au show a positive correlation with S in samples of all rock types (Figures 3c-e). There is a statistically significant positive correlation R(Pd)=0.73, R(Pt)=0.69, R(Au)=0.55) for samples from plagioclase-pyroxene veins, where the significance level is below 0.05. For metapyroxenites and metanorites, correlation of contents of these elements is also positive, statistically significant for Pd and Pt (R=0.48 and R=0.47, relatively), and insignificant for Au (R=0.32). For coarse-grained metagabbrororites and quartz-plagioclase and amphibole-plagioclase vein rocks, there is a weak correlation of these elements (R(Pd)=0.26, R(Pt)=0.37, R(Au)=0.3 and R(Pd)=0.10, R(Pt)=0.42, relatively), where the significance level is below 0.10. The Pd/Pt graph in relation to Pd (Figures 3g) shows that Pd/Pt ratios in samples of coarse-grained metagabbrororites, quartz-plagioclase and amphibole-plagioclase vein rocks and fine- to medium-grained metapyroxenites and metanorites vary from 0.2 to 13 and change according to the Pd content. Compared to these ratios, values of plagioclase-pyroxene vein rock samples vary from 3.1 to 13.1 and do not change according to the Pd content.

4. Discussion

Different correlation of copper with sulfur for various rock types indicates that the Cu content in these rocks was affected when the sulfide liquid component mixed with another component containing very little Cu. This component might be silicate and not contain Cu (Barnes S-J., Gomwe T.S., 2011).

The positive correlation of nickel and sulfur for all rock types can be interpreted as a sign that the sulfide liquid affected Ni in these rocks. Ni and MgO show a statistically significant negative correlation, where the significance level is below 0.10 (Figure 3f). It suggests that Ni might not be affected by changes in contents of plagioclase and orthopyroxene in these rocks.

The different correlation of precious metals in various rock types suggests that the sulfide liquid accumulated Pd, Pt, and Au in these samples. These observations allow assuming that PGE accumulation by the sulfide liquid would be enough to enrich rocks with the high Pd/Pt ratio with Pd, Pt, and Au, whereas other additional processed might be required to enrich rocks with a lower Pd/Pt ratio with these elements.

5. Conclusion

The implemented studies of correlation of non-ferrous and precious metals with sulfur in the SSM and ML rocks led to the following conclusions:

1. There is a positive correlation of Cu with S in all rocks. It indicates that the Cu content might have been affected when the sulfide liquid component mixed with another component (possibly silicate), which contained little Cu.
Figure 3. Binary variation diagrams for the South Sopchinsky massif and the “Moroshkovoe Lake” target rocks:
1 – fine- to medium-grained metapyroxenites and metanorites;
2 – plagioclase-pyroxene vein;
3 – coarse-grained metagabbro-norites;
4 – quartz-feldspar vein;
5 – amphibole-plagioclase vein.
2. There is also a positive correlation of Ni with S in all rocks. It can be interpreted as a sign that the sulfide liquid affected Ni in these rocks.

3. In samples of all rock types, Pd and Pt show a positive correlation with S, which suggests that the sulfide liquid accumulated Pd and Pt in these samples. Yet, correlation between these elements and sulfur are stronger and statistically more significant in plagioclase-pyroxene vein rocks and medium-grained metapyroxenes and metanoritites, whereas they are weaker and statistically less significant in coarse-grained metagabbronorites and quartz-plagioclase and amphibole-plagioclase vein rocks. These observations might be related to a small data set for the last two rock types. However, these conclusions confirm differences in average contents of Pd and Pt, which are significantly higher in plagioclase-pyroxene vein rocks and some samples of medium-grained metapyroxenites (metanoritites).

4. Dependency of Pd/Pt in relation to Pd suggests that plagioclase-pyroxene vein rocks and medium-grained metapyroxenes could be enriched with Pd, Pt, and Au by only PGE accumulation the sulfide liquid, whereas other additional processes might be required to enrich the rest of the rock types with these elements.

A sulfide liquid separated from the parental metagabbronorite melt might have absorbed PGE from surrounding rocks. Later, the sulfide liquid enriched in chalcophilic elements mixed with a residual silicate melt, which further intruded into metapyroxenites (metanoritites) and formed plagioclase-pyroxene veins with the increased content of PGE.

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References
[1] Barnes S-J Gomwe T S 2011 The Pd-deposits of the Lac-des-Illes Complex, north-western Ontario Review in Econ. Geol. 17 351-370
[2] Chashchin V V et al 2016 Low-Sulfide PGE ores in paleoproterozoic Monchegorsk pluton and massifs of its southern framing, Kola Peninsula, Russia: Geological characteristic and isotopic geochronological evidence of polychronous ore magmatic systems Geol. of Ore Deposits 58(1) 37-57
[3] Ivanchenko V N, Davydov P S 2009 PGM deposits and prospects in the Southern part of the Monchegorsk mineral area: general features of the geological structure An Interreg-Tacis Project N KA-0197 (Apaitity, KSC RAS) 2 70-78
[4] Martynov E V 2008 Mathematical methods used to model parameters of geological processes and phenomena: A study guide for the program 130100 Geology and mineral resources prospecting (Murmansk: Publishing House of the MSTU) p 136
[5] Miroshnikova Ya A et al 2019 Platinum-metal mineralization of the Yuzhnosopchinsky-I locality (Monchegorsk ore district, Kola Peninsula) ZRMO 148(1) 38-48
[6] Miroshnikova Ya A, Pakhomovsky Ya A 2015 Vein bodies in the Moroshkovoe Lake target (Monchegorsk area) and related mineralization Vestnik of MSTU 18(2) 280-286
[7] Pripachkin P V et al 2016 Geological structure and ore mineralization of the South Sopchinsky and Gabbro-10 massifs and the Moroshkovoe Lake target, Monchegorsk area, Kola Peninsula, Russia Miner. Depos. 51(8) 973-992
[8] Rundkvist T V et al 2011 Geological structure and features of localization of PGE mineralization in the eastern part of the South Sopchinsky mafic-ultramafic massif (Kola Peninsula) Ores and Metals 5 58-68