Chemical Characteristics of Ore-Bearing Intrusions and the Origin of PGE–Cu–Ni Mineralization in the Norilsk Area

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Abstract: The composition of the parental magmas of Cu–Ni deposits is crucial for the elucidation of their genesis. In order to estimate the role of magma in ore formation, it is necessary to compare the compositions of silicate rock intrusions with different mineralization patterns, as observed in the Norilsk region. The rock geochemistry of two massifs located in the same Devonian carbonate rocks—the Kharaelakh intrusion, with its world-class platinum-group element (PGE)–Cu–Ni deposit, and the Pyasinsky-Vologochansky intrusion, with its large deposit—was studied. Along with these massifs, the Norilsk 2 massif with noneconomic mineralization intruded in the Ivakinskaya-Nadezhinskaya basalts was studied as well. Their settings allow the estimation of the parental magma composition, taking into account the possible assimilation of host rocks. Analyses of 39 elements in 97 samples demonstrated the similarity of the intrusions in terms of their major components. The Pyasinsky-Vologochansky intrusion contains the highest trace element contents compared with the Kharaelakh and Norilsk 2 massifs, evidencing its crystallization from evolved parental magma. No influence of host rocks on the silicate rock compositions was found, except for narrow (1–2 m) endo-contact zones. There is no correlation between the mineralization volume and the rock compositions of the studied intrusions. It is assumed that the intrusions were formed from one magma crustal source irregularly rich in sulfur (S). This source inhomogeneity in terms of the sulfur distribution resulted in deposits of varying sizes. The magmas served as a transporting agent for sulfides from deep zones to the surface.

Keywords: Norilsk deposits; geochemistry; statistical methods; assimilation

1. Introduction

The origin of Cu–Ni deposits related to mafic–ultramafic intrusions has been under discussion for several decades [1–19]. This problem encompasses numerous key points, such as metal and sulfur sources, mechanisms of sulfide formation and their contents, and platinum-group element (PGE) enrichment in sulfides. Primary magmas are also believed to play an important role in a deposit’s genesis. This suggestion has been reflected in several classifications taking into account both magma compositions and their tectonic settings [7,8,13,20,21]. However, the relation of the major and trace element contents in magmas with the formation of deposits is rarely considered in the models constructed for single ore-bearing intrusions such as Sudbury, Jinchuan and Voisey’s Bay [22–24]. The successive decision of this problem is possible through a comparison of the geochemistry of intrusions ranging in mineralization volume that are formed under similar tectonic conditions. Nevertheless, the geological opportunities for such studies are restricted worldwide. Therefore, the Norilsk region, which is characterized by the occurrence of
numerous multiscale deposits belonging to the Siberian traps province [25] plays an exceptional role in realizing the significance of magma in ore genesis.

Intrusions in the Norilsk region have been classified into several intrusive complexes based on their composition and internal structure. Ore-bearing massifs were combined into one Norilsk intrusive complex, the composition of which is usually compared with other complexes of this region [26,27]. The massifs are characterized by elevated MgO (10–12 wt.%) and Cr$_2$O$_3$ (up to 0.4 wt.%) contents, and low TiO$_2$ (<1 wt.%) contents compared with the gabbro sills widespread around the Siberian traps province. However, the mineralization of different intrusions within this complex varies dramatically: the volume of the trapped sulfides changes by several orders of magnitude from unique (Oktyabr’sky, Talnakh, and Norilsk 1) and large (Maslovsky and Vologochansky) deposits to subeconomic mineralization (Norilsk 2 and Bolshaya Bar’ernaya) and barren intrusions in the southern and eastern Norilsk regions. This variability has been justified by the magma assimilation of different host rocks [5,7,8,28–30]; for example, the Kharaelakh intrusion with extra-large sulfide orebodies is located in Devonian sulfate-carbonate rocks, the Talnakh intrusion with large orebodies lies in carbonate and terrigenous rocks, and Norilsk 1 with small orebodies is situated in terrigenous rocks and basalts. However, this conclusion was made based on the examination of only three deposits, while many ore-bearing intrusions of the Norilsk complex were out of the scope of this consideration. Including numerous mafic intrusions in an investigation fundamentally changes the abovementioned conclusion.

The assimilation of the surrounding rocks by magma must be recorded in the whole-rock chemistry of intrusions, particularly in massifs with a huge volume of sulfide ore in the deposits (sulfide ores account for 20% of the silicate rocks in the Oktyabr’sky deposit). Therefore, in order to unravel the probable connection between the parental magma composition and the volume of ore mineralization, it is necessary to consider the composition of intrusions that have graduated mineralization and are located in different rocks. Parental magma is the magma from which rocks and ores are crystallized in situ, i.e., it represents primary magma (originating from a source) that has undergone the possible assimilation. The estimation of parental magma compositions is mainly based on the average weighted composition of the intrusions. We use this approach coupled with other methods, including methods such as the composition of melt inclusions [31–33] or mathematical modeling [34], because it is very simple and productive if rocks have not been imprinted with essential hydrothermal activity and/or metamorphism.

In order to reveal the role of parental magma and assimilation in ore genesis, this study focused on the Pyasinsky-Vologochansky and Norilsk 2 intrusions—which are characterized by disseminated ores—along with the Kharaelakh intrusion, which includes unique massive ores. This work presents new geochemical data (X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), and emission spectrometry (ICP-AES)) on the three intrusions with different volumes of sulfides, hosted in different rocks: Devonian carbonate-terrigenous rocks, Permian coal-bearing rocks and Permian basalts. The silicate rock compositions are very similar for all of the intrusions despite their different geological settings and mineralization, and they demonstrate that assimilation did not play any role in the ore origin.

2. Geological Background

The Norilsk region is located on the northwestern edge of the Siberian platform, in the area of its junction with the Yenisey-Khatanga trough, i.e., within the ancient Norilsk-Igarka palaeorift zone (Figure 1).
There are two major structures in the Norilsk region: the Khantaysko-Rybninsky swell and the Norilsk-Kharaelakh trough, comprising the Iken, Kharaelakh, Norilsk and Vologochan synclines [36]. These structures are composed of carbonate-clastic Cambrian-Early Carboniferous and coal-bearing sediments (C₂–P₂, Tunguska series) with a total thickness of up to 10 km, overlapping with volcanic rocks (P₃–T₁, 3.5-km thick) (Figure 2).

The Cambrian-Devonian strata are mainly composed of dolomites, marls, limestones and mudstones with interbeds of salts and anhydrites formed in a shallow marine basin [36]. The Devonian and Permian deposits have attracted considerable interest as the host rocks of ore-bearing intrusions. Devonian rocks are subdivided into several formations, as shown in Figure 3. Meanwhile, the Zubovsky and Manturovsky formations are the richest in evaporites, with thick layers of anhydrite. The other formations (including Kurejsky and Razvedochninsky that host ore-bearing intrusions) mostly comprise terrigenous rocks, although sulfate and calcareous varieties also occur in sequence along the strike. After a slight break, the marine Devonian and Lower Carboniferous sediments overlapped with continental sediments of the Tunguska series, which is subdivided into several formations mainly composed of mudstones, siltstones and sandstones, with coal layers in the upper part of the section (Figure 3).
Figure 2. Schematic geologic map of the Norilsk area (after [37], with the authors’ corrections). Faults numbers: 1—Yenisey-Khatangsky, 2—Norilsk-Kharaelakhsky, 3—Mikchangdinsky, 4—Vologochansky.
The upper part of the stratigraphic sequence comprises tuffs and lavas divided into 11 formations [36]. The rocks of the lower formations (Ivakinskaya to Gudchikhinskaya) contain >1.5 wt.% TiO$_2$, while the upper formations (beginning from Khakanchanskaya; Figure 3) are poor in TiO$_2$ (<1.5 wt.%).

The Upper Permian–Lower Triassic intrusive rocks [2,25,35] are mainly mafic–ultramafic in composition, with normal alkalinity, though they may be locally subalkaline (Table 1).

All of the Norilsk district deposits are related to distinctly differentiated gabbro intrusions of the Norilsk intrusive complex, which are further classified into subcomplexes or types characterized by their specific composition and internal structure (according to the supposed formation time): the melanocratic Lower Talnakh, leucocratic Kruglogorsky, strongly differentiated Norilsk, and weakly differentiated Zubovsky deposits [36–38]. The world-class deposits (Talnakh, Oktyabr’sky and Norilsk 1) are all associated with the...
Norilsk complex. Although this division partly considers the composition of the primary magmas, it reproduces a structure of intrusive bodies that reflects their intra-chamber differentiation.

The intrusions of the Norilsk complex comprise gabbro–dolerites of varying compositions (from bottom to top): contact, taxitic, picritic, olivine, olivine bearing, and olivine free (we follow the rock nomenclature of Norilsk geologists that has been used in Russian and English publications [5,8,36,39–41]).

Table 1. Intrusive complexes of the Norilsk area (after [37]).

| Complex   | Type                          | Rocks                        | Av. MgO, wt% | Massif          | Deposit         | Deposit Size |
|-----------|-------------------------------|------------------------------|--------------|-----------------|-----------------|--------------|
| Daldykansky | -                             | dolerites                     | 7            | Daldykansky     | -               | -            |
| Morongovsky | -                            | Picritic gabbro–dolerites-gabbro-diorites | 10           | Morongovsky     | Pegmatitivy     | -            |
| Ogonersky | -                             | -                            | 7            | Ogonersky       | -               | -            |

Norilsk

| Norilsk | Picritic gabbro–dolerites-gabbro-diorites | 10–12 | Vologochansky, Pyasinsky | Vologochansky | L |
|--------|------------------------------------------|-------|-------------------------|--------------|---|
| Kharaelakh, Talnakh, Norilsk 1 | Oktyabr’sky, Talnakh, Norilsk 1 | Maslovsky, Norilsk 2 | Maslovsky, Norilsk 2 | Manturovsky |
| Kruglo-gorsky, leucogabbro | 8–9 | Kruglogorskoy | Bolshaya Bar’ernaya | S |
| Lower-Talnakh | Zelenaya Griva, Mikchangdinsky | Lower Talnakh | M |
| Ergalakhsky | - | Trakhy-dolerites | 4–5 | Ergalakhsky | - | - |

Note. Deposits: EL—extra-large (>1000); L—large (>100); S—small (10–50); and M—medium (50–100), mineralized intrusions (<10). In the brackets, the PGE reserves are given in tons [42].

Troctolites also occur along with the picritic gabbro–dolerites. The upper parts of the intrusions include a variable combination of leucogabbro, ferrogabbro, upper picritic and taxitic gabbro–dolerites, magmatic breccia, and upper-contact gabbro–dolerites.

The sulfides (pyrrhotite, chalcopyrite, pentlandite) are concentrated in the lower parts of the intrusive bodies in the form of disseminated ore in the picritic and taxitic gabbro–dolerites and troctolites, as well as in the underlying host rocks [43,44]. The ore volume varies from one intrusion to another. A low-sulfide mineralization often occurs in the upper parts [45].

3. Materials and Methods

In order to study the geochemical characteristics of ore-bearing intrusions, three massifs, i.e., Kharaelakh, Pyasinsky-Vologochansky, and Norilsk 2 (Figures 4–6), were selected (97 samples were analyzed; see Table S1 in Supplementary Materials). This assortment owes to their different positions and mineralizations (with extra-large and large PGE–Cu–Ni deposits, and noneconomic mineralization, respectively). In this work, we paid significant attention to the Pyasinsky-Vologochansky intrusion, which has been only briefly described earlier [46]. This intrusion is important for understanding ore genesis due to its setting, which is similar to that of the Kharaelakh intrusion in the
same Devonian rocks on the boundary of the Razvedochninsky and Kurejsky formations (Figure 3). Samples were taken from TG-21 and ZF-12 drillhole cores (in the Kharaelakh East and Kharaelakh West intrusions, respectively), and from the Pyasinsky-Vologochansky intrusion (drillhole cores OV-36 West, NV-12 Center and OV-37 East in the South Pyasinsky branch, and OV-29 in the Vologochansky branch). The third intrusion, Norilsk 2, occupies a higher stratigraphic setting, breaking through the Permian–Triassic volcanic formations (Ivakinskaya-Nadezhdinskaya). The samples were selected from the MP-18 drillhole core.

Figure 4. Cont.
Figure 4. Geologic map (a) and cross section (b) of the Kharaelakh intrusion (after the Norilskgeology Ltd. data, with the authors’ changes). This area is indicated as “1” in Figure 2.
Figure 5. Cont.
Figure 5. Geologic map (a), and cross sections (b,c) of the Pyasinsky-Vologanchsky intrusion (after Norilskgeology Ltd. data, with the authors’ corrections). The area is shown as “2” in Figure 2.
Figure 6. Geological map (a) and cross section (b) of the Norilsk 2 intrusion (after Norilskgeology Ltd. data, with the authors’ changes). The area is shown as “3” in Figure 2. Q—Quaternary deposits.

3.1. Analytical Methods

The major elements in the rocks were measured using X-ray fluorescence at the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences (IGEM RAS). The main analytical work was performed at the Geoscience Laboratories (Geo Labs) Sudbury, ON, Canada [47], as follows: the determination of the trace elements in the whole rock samples using inductively coupled plasma mass spectrometry; the study of the composition of the sulfide ores (Table S1; Supplementary Materials) using flame atomic-absorption spectrometry (FAAS), atomic emission spectrometry and ICP-MS; and the determination of the carbon and sulfur content
by infrared (IR) detection after combustion. The quality control of the analyses was ensured using blanks, duplicates (in part, analyzed by different methods) and reference materials (RM; international RMs AGV-2 and WMS-1a, and the in-house RM MRB-29).

3.1.1. Sample Preparation

The preparation of the 2-g samples for XRF included the determination of the loss on ignition (LOI) at 1000 °C, followed by fusion with lithium metaborate to produce a glass bead for analysis. The detailed measurement procedure is described in [48]. The sample preparation for ICP analysis included the acid decomposition of 1–2 g samples with a mixture of HF, HCl, HClO₄ and HNO₃ in closed beakers, which ensures that along with the removal of silicates there is greater decomposition due to better dissolution of some of the mineral phases at elevated temperatures [49]. Greater decomposition is especially important in the determination of trace elements, as well as Zr, Nb, Hf, Ta and some other elements contained in difficult-to-dissolve minerals. As, Sb, Se, Te, Tl, Au, Ag and Pt were leached from sulfides with aqua regia to measure their contents. Samples of the massive sulfide ores were transferred into a solution with a mixture of HF, HCl, HClO₄, and HNO₃ in open vessels to determine the contents of Cu, Ni, and Co by ICP-AES and FAAS.

3.1.2. Instrumental Analysis

The major and trace elements in the dissolved samples were determined using the ICP-AES [50] and ICP-MS techniques. Table S1 (Supplementary Materials) presents the limits of detection. The most challenging part of an ICP-MS analysis is the determination of the Cd, Mo, Tl and Sn, because errors of up to ±30% are possible when using acid decomposition in closed beakers. Better results can be obtained for Sb, As, Ba, Be, Cd, Cr and Pb, as well as Au, Ag, Pt, Se, Te, and Tl after aqua regia leaching. Of particular interest are the Au and Pt contents, but at the ppb level (near the detection limit of the method) these data can hardly be considered quantitative; we consider them indicative. However, because all of the samples are of a similar nature, the higher Au and Pt contents were used for the comparison between the samples.

3.2. Statistical Methods

A partial least-squares discriminant analysis (PLS-DA) was applied to compare the chemical composition of the samples from the three studied intrusions and their associations, following [51]. In a loadings and weights (qw*) biplot of two PLS-DA components, the correlations between the elemental variables and their relationships with the sample classes are illustrated. The elemental correlations detected in the qw* biplot control the distribution of the sample data points in the corresponding score scatter (t) plot. The variable importance on projection (VIP) is another parameter generated to depict the importance of an element in a sample classification by two PLS-DA components [52], such that the VIP values that are greater than or equal to 1 are the most significant for the classification. Variable contributions are metrics that can be used to diagnose the causes of shifts from one sample cluster to another in a latent variable space or from the origin of the score scatter plot. In order to overcome the closure of the compositional data, the data were transformed using the centered-log ratio prior to multivariate statistical analysis [51,53–55]. The censored values (values below the detection limits) were imputed by the R package compositions using the k-nearest neighbor function [51,56]. The elements with contents greater than 40% below the detection limits were excluded from the multivariate analysis.

4. Results

4.1. Geological Characteristics of the Studied Intrusions

4.1.1. The Kharaelakh Intrusion

This intrusion is located in the southeastern part of the Kharaelakh syncline. Its structure and mineral and chemical compositions have been described in many publications [7,13,36,57]. In plan, it has an irregular shape (Figure 4a) which is close to triangular.
The area’s length is approximately 8 km, and its width is up to 6 km. Despite the fact that it is usually characterized as a single intrusive body, its structure differs significantly from other ore-bearing massifs, and is more complex. There are several massive orebodies linked to separate intrusions, as shown in Figure 4b.

The eastern part of the deposit (Kharaelakh East; Figures 4a and 7a,b) was investigated in drillhole TG-21, which penetrates the intrusive body (160 m) and massive sulfide ore (1.5 m). The disseminated ores are concentrated in picritic and taxitic gabbro–dolerites (~40-m thick, Figure 7). The distinctive feature of this section is thick horizons of olivine-biotite and olivine gabbro–dolerites (60 m). The upper part of the intrusion is composed of leucogabbro. The distribution of MgO in the rocks in the vertical section demonstrates the internal structure of the intrusion (Figure S1a, Supplementary Materials). The rock-forming minerals constituting this intrusion have already been characterized [33]. The composition of olivine varies from Fo_{80.3} to Fo_{61.1}, whereas the mg# for clinopyroxene (Cpx) ranges within 71.1–82.7. Plagioclase also compositionally ranges from An_{84} to An_{53}. The chrome spinel (Cr–Sp) in picritic gabbro–dolerites contains 37-wt.% Cr_{2}O_{3}. The disseminated chalcopyrite–pyrrhotite ores are concentrated in picritic and taxitic gabbro–dolerites, with pentlandite as a subordinate mineral. The massive ore is 1.5-m thick, with the same composition.

The western part of the Kharaelakh intrusion (Kharaelakh West) is characterized by numerous thin intrusive bodies pinching out toward the west (Figure 4b). They differ in their internal structure from the eastern bodies. The thickest body (55 m, drillhole ZF-12) mainly comprises olivine gabbro–dolerites (Figure 7b and Figure S1a). A very thin layer (1 m) of picritic gabbro–dolerites is located in its central part, while a separate body of picritic gabbro–dolerites (22-m thick) is located 20 m above this intrusion, and is characterized by a lack of sulfides [58]. Taxitic gabbro–dolerites are the typical rocks of the eastern part of the intrusion, but are absent in the western part of the deposit area. The disseminated ores are concentrated in the horizon of olivine gabbro–dolerites, which are barren in the east. The massive ores are localized within the intrusive rocks (bodies of 1 m each) and at the boundary of silicate rocks with the host rocks (10-m thick orefbody). They have a pentlandite–chalcopyrite–pyrrhotite composition (3:35:60 vol.%, respectively), and the subordinate minerals are sphalerite, pyrite and magnetite; the rare minerals are sperrylite and Au–Ag alloys.

4.1.2. The Pyasinsky-Vologochansky Intrusion

The Pyasinsky-Vologochansky intrusion and the related Vologochansky deposit are located within the Vologochan syncline at the boundary between the Lower Devonian Kurejsky and Razvedochnsky formations (Figures 2 and 5), similarly to the Kharaelakh intrusion (Figures 2 and 4). The intrusion comprises two branches—South Pyasinsky and Vologochansky—traced for 15 km from east to west (Figure 5), and 1500 m in depth. The maximum thickness of the intrusion is 280 m. This intrusion had been considered a single body [28,58], but our studies identified its complex structure. Several distinct intrusive bodies occur in the two branches (Figure 5b,c).

The rock composition varies in the Pyasinsky-Vologochansky intrusion [46]: olivine gabbro–dolerites dominate, whereas other varieties (ophitic, poikilohytic, gabbro-ophitic, poikilitic, and prismatic-granular gabbro–dolerites) are subordinate (Figure 7c–f and Figure S1b,c). The major rock-forming minerals are olivine (Fo_{58–78}), plagioclase (An_{69–86}), clinopyroxene (Fs_{10–13}) and orthopyroxene (Fs_{25–35}). The accessory minerals include phlogopite, magnetite, apatite, biotite and titanomagnetite. By contrast, chromite and quartz occur in trace amounts in comparison with the Kharaelakh intrusion. Quartz and microcline form micropegmatite aggregates at the top of the intrusion. The secondary mineral assemblage comprises amphibole, serpentine, bowlingite, chlorite, hornblende, talc, albite, titanite and leucoxene.
The South Pyasinsky branch was studied in cores from drillholes OV-36 in the western part, and NV-12 and OV-37 in the eastern part (Figure 7 and Figure S1b,c). The thicknesses and internal structures of the intrusive rocks in these sections are almost identical. Those of the eastern part are slightly thicker than those in the western part (90 m compared with 60 m). Two horizons of high-magnesium rocks occur as picritic gabbro–dolerites (5-m thick) and troctolites (8-m thick) that are separated by a thin layer of olivine gabbro–dolerites (drillhole OV-36). Picritic gabbro–dolerites are found in the eastern part of the deposit (drillhole OV-37), where olivine, olivine-bearing and olivine-free rocks dominate (they compose 3/4 of the section). Some differences were found in the upper part of the intrusions: gabbro–diorites dominate in the western intrusion, whereas taxitic gabbro–
dolerites occur in the eastern one. A characteristic feature of the central part of the deposit (drillhole NV-12 in the eastern intrusive body) is the predominance of olivine-rich rocks, i.e., picritic and olivine gabbro–dolerites and troctolites (65-m thick).

The Vologochansky branch (eastern intrusion) was studied in drillhole OV-29 (60 m thick). Its internal structure is very similar to that of the South Pyasinsky branch and the eastern part of the Kharaelakh intrusion. The lower part of this section contains two horizons of high-magnesium rocks composed of troctolites and picrite gabbro–dolerites, separated by a 10-m layer of olivine gabbro–dolerites. The latter dominates in the upper part of the section (Figure 7) and overlaps with olivine-free gabbro–dolerites and gabbro–diorites. Gabbronorites occur at the contacts with sedimentary host rocks.

Sulfide mineralization occurs constantly at the bottom of intrusive bodies, but economic contents are only found locally. The geologists of Norilskgeology Ltd. identified four disseminated orebodies (Figure 5): Western (OV-36), Main (NV-12, OV-37), Central (OV-29) and Southern (not investigated in this study). The average amount of sulfides is 8–10 vol.%, and their aggregates range from 0.02 to 30 mm. The sulfide ores have relatively homogeneous mineral and chemical compositions, as well as structures and textures. The predominant textures are disseminated, veinlet-disseminated and nodular. A single vein of massive ores (11-cm thick) was detected in the eastern part of the deposit.

The ores have a pentlandite–chalcopyrite–pyrrhotite composition with a 15:30:55 ratio. Pyrite appears in the Western orebody (up to 60 wt.%), while mackinawite is a secondary mineral in the main orebody. The accessory minerals include cubanite and millerite, while the rare mineral assemblages comprise spherelite, galena, marcasite, bornite, argentopentlandite, violarite, Au–Ag alloys (Ag = 35–50 wt.%), and platinum-group minerals (PGM): sobolevskite, Te-sobolevskite, Te-insizvaite, maslovite, paolovite, zvyagintsevite, atokite, nigliite and guanglinite [28]. The oxide minerals represent different generations of magnetite (up to 16 wt.% Cr₂O₃), ilmenite, discrete chromite grains, ilvaite, titanite and hematite.

4.1.3. The Norilsk 2 Intrusion

The Norilsk 2 intrusion is located in the eastern part of the Norilsk syncline (Figures 2 and 6). As described in a previous study [59], Norilsk 2 significantly differs from the Kharaelakh and Pyasinsky-Vologochansky intrusions in terms of its morphology and geological setting. For example, it is hosted by a dike-like body (Figure 6). The massif extends in a northeasterly direction for approximately 10 km, with a width of 1 km. It penetrates into the Devonian rocks and Tunguska Group rocks, as well as into the volcanic rocks of lower formations, i.e., from the Ivakinskaya to Nadezhinskaya. Large blocks of volcanic rocks are included in the intrusive rocks (Figure 6b).

Borehole MP-18 demonstrates the internal structure of the Norilsk 2 intrusion. The distinguishable horizons in the intrusive body are as follows (from bottom to top): contact, olivine and olivine-bearing gabbro–dolerites. Disseminated chalcopyrite–pyrrhotite ores occur in the lower part of the body, and small (2–3 m) bodies of the massive pyrrhotite ores are exposed on the surface.

4.2. Chemical Composition of the Rocks

4.2.1. Major Elements

The diversity of the intrusive rock chemical compositions (Table S1) is controlled by proportions of the main rock-forming minerals, especially olivine content. A series of binary diagrams constructed for the three intrusions (Figure 8) shows the covariation of different elements versus MgO in the rock compositions, which contain 20–22 wt.% and 3–15 wt.% MgO, corresponding to picritic gabbro–dolerites and troctolites, as well as olivine-bearing and olivine-free gabbro–dolerites, respectively. This distribution is typical of the Vologochansky branch of the Pyasinsky-Vologochansky intrusion.
Figure 8. Diagrams of MgO vs. (a) SiO$_2$, (b) Al$_2$O$_3$, (c) TiO$_2$, (d) Fe$_2$O$_3$, (e) CaO, (f) P$_2$O$_5$, (g) Na$_2$O, and (h) K$_2$O for the rocks of the Norilsk intrusions.

Rare occurrences of rocks with intermediate MgO contents (13–17 wt.%), including taxitic gabbro–dolerites, have been detected in the Kharaelakh intrusion, which is characterized by the maximum variability of rock. This also applies to other oxides such as SiO$_2$, Al$_2$O$_3$ and TiO$_2$, etc. Although high-magnesium rocks are absent in the MP-18 section, they are widespread in the other sections of the Norilsk 2 intrusion [41] (Figure 6).
4.2.2. Trace Elements

Figure 9 shows the distribution of the trace elements in the rocks. All of the spider diagrams have common features typical of the intrusive and volcanic rocks of the Siberian traps province, which are characterized by distinct positive U and Pb anomalies, some Sr anomalies, and negative Ta–Nb anomalies. The spectra also have very steep slopes relative to the X-axis. These features are also emphasized by the element ratios reflecting both the whole-spectra inclination and the slopes of its parts (La/Yb, La/Sm, Gd/Yb), and by the value of the Ta–Nb anomaly (reflected in Th/Nb ratio) (Figure S2). However, some features are specific to each intrusion. A greater shift of the spectra relative to the X-axis occurs for the Kharaelakh intrusion, and partly for the Norilsk 2 intrusion, reflecting the degree of their differentiation on the basis of olivine distribution.

This differentiation occurs clearly for the Norilsk 2 intrusion, where the highest position of the spectrum corresponds to olivine-bearing gabbro–dolerites (sample MP-18/200) and the lowest belongs to picritic gabbro–dolerites (N-2/2). The spectra of the Pyasinsky-Vologochansky intrusion take similar positions: picritic gabbro–dolerites rich in olivine are located close to the X-axis, especially the rocks of the central part of the South...
Pyasinsky branch (NV-12, Figure 9e), and olivine-free rocks are located far from this axis (the Vologochansky branch, OV-29, Figure 9g).

The Kharaelakh intrusive rocks (Kharaelakh East) differ significantly from the others owing to high Pb contents, which indicate their high disseminated ore contents. These rocks host a large amount of disseminated sulfides compared with the other studied intrusions. They are also compositionally more variable, such that three of the spectra have higher contents of U than is typical of igneous rocks. The uppermost sample (drillhole TG-21, depth 1204), taken from the exocontact zone of the intrusion, comprises hornfels from Devonian sedimentary rocks, and reflects their compositions. Two samples also belong to the upper intrusive endocontact zone. The enrichments in uranium and other elements of these rocks can be explained by the assimilation of host rocks.

The (Gd/Yb)n–(La/Sm)n and (La/Yb)n–(Th/Nb)n diagrams (Figure S2) demonstrate negligible differences in the rock compositions within the studied intrusions. The points located behind the main field belong to varieties located in the upper or lower zones of the intrusions. These zones differ from the typical rocks of these intrusions, and they are very small (1–3-m thick, rarely 5–10 m, as in the upper Kharaelakh zone, drillhole TG-21).

4.3. Chemical Composition of the Ores

The data for the disseminated ores and a few analyses of the massive ores (due to their scarcity) are presented in Table S1. The contents of noble metals (Ag, Au, Pt, and Pd) determined by the analysis (see Section 3.1) are approximate, with the exception of those determined by mass spectrometry and published previously for the Kharaelakh and Norilsk 2 intrusions [38] that are included for comparison. Primary attention was paid to the ores from the Pyasinsky-Vologochansky intrusion, as their chemical composition was not previously presented. As shown in Section 4.1.2, the ores have similar pentlandite–chalcopyrite–pyrrhotite compositions.

Disseminated ores are found in three of the studied massifs. A positive correlation between the metals and sulfur contents occurs in all of the rocks (Figure S3a). The maximum Cu content (2.6 wt.%, i.e., 26,804 ppm, Table S1) was found in the Kharaelakh intrusion, while the value for the Norilsk 2 intrusion is 0.6 wt.%, and in the Pyasinsky-Vologochansky rocks it is 0.25 wt.%.

The Cu/Ni ratio is very stable in the disseminated ores from the three massifs, ranging from 0.9 to 2.4 (Table S1). The Ni contents demonstrate a rather weak correlation with sulfur (Figure S3b) due to its higher incorporation (up to 30%) into olivine than sulfides. The disseminated ores contain hundreds of ppb of Pt, and 2–3 ppm of Pd (the maximum value is 5.85 ppm, detected in a sample from Norilsk 2; Table S1). The Ag content significantly prevails over Au in all samples as the Ag/Au ratio varies from 11 to 60, with an average of 20. Higher values are typical of the Kharaelakh intrusion.

Two orebodies were studied within the South Pyasinsky branch, i.e., the Western and Main, and one—the Central orebody—in the Vologochansky branch. The ratios of Cu/Ni and Pd/Pt in these orebodies are very stable, and vary within the following limits: 1.6–1.8 and 4.2–4.4, respectively. The lack of extremely high Ni, Cu, and PGE contents in the Pyasinsky-Vologochansky intrusion is an indicator of the consistency of the chemical composition of the disseminated ores. The average contents of Pt and Pd in the main orebody (drillhole NV-12) are 1.1 ppm and 3.2 ppm, respectively. These contents vary through the section, and reach their highest values in the center of the picritic gabbro–dolerites, where the average sulfide content is 4.0 vol.%, with 0.55 wt.% Ni and 1.02 wt.% Cu. The metal contents remain low in the upper parts of the intrusion (average Cu + Ni = 0.8 wt.%, Pt + Pd = 0.15 ppm), and the low-sulfide mineralization typical of the Norilsk 1 intrusion [45] is absent.

The Se contents in many of the samples from silicate rocks are below the detection limits (D.L.) (Table S1). They vary from 1.7 to 15.8 ppm, and the S/Se ratio varies from 4000 to 12,000 in the disseminated ores from the different intrusions. The Sb, Co, Sn, Bi, Pb, and Te contents mostly depend on the S contents, but their correlation with S changes from very high to very low, as shown in a number of diagrams (Figure S4a–h). The most
significant correlations are recorded for Co (up to $R^2 = 0.99$, Figure S4b). For Sn (Figure S4c), a wide range of variations ($R^2 = 0.002–1.00$) is observed, which can be explained by either a lack of correlation with sulfur or a high correlation between them. The Sb contents do not exceed 0.5 ppm, except in three samples from the Kharaelakh intrusion with 3 ppm Sb (Figure S4a). However, these high Sb values are not related to the sulfur contents ($R^2 = 0.16$), as is observed for the lower contents. The same conclusion is true for Bi and Pb (Figure S4e–g). At the same time, it is remarkable that significant correlations are typical of the Pyasinsky-Vologochansky disseminated ores, while they are absent for the ores of the Kharaelakh intrusion. For the Bi–S pair, the dependence is clear—$R^2 = 0.31–0.98$—as well as for Te–S with $R^2$ close to 1 for all of the intrusions (Figure S4h). These variations reflect the forms of occurrence of the studied elements in the ores. First, the high correlations of the elements with sulfur suggest that their isomorphic forms exist in the main ore-forming minerals (for example, Ni in pentlandite and pyrrhotite), while poor correlations evidence the formation of individual mineral phases.

The available data on the composition of chalcopyrite–pyrrhotite massive ores are limited, and are absent for the Pyasinsky-Vologochansky intrusion (a single vein was not available for the analyses). Therefore, we can only draw the most general conclusions. The Pd/Pt ratio ranges from 2.8 to 11.6 in the Kharaelakh massive ore (drillholes TG-21 and ZF-12), and one value reaches 63 for the Norilsk 2 ores. The Ag/Au ratio is almost stable: it is 13–14 for the Norilsk 2 massive ore, and fluctuates from 14 to 43 in the Kharaelakh ore. The S/Se ratio in the massive ores (Se 0.5–1.5 ppm) is similar to this ratio in the disseminated ores: 5000–15,000.

4.4. Statistical Treatment of the Geochemical Data

The compositions of 39 elements in the samples from the studied gabbro–dolerite intrusions and associated mineralized zones (Table S1) were investigated by PLS-DA (Figure 10a–c). Three major fields are distinguishable: (1) the intrusions (in green), (2) the disseminated ores (in pink), and (3) the massive ore (in red). The massive ore from the intrusions forms a distinct cluster in the $t_1$–$t_2$ score scatter plot space (Figure 10b), while the disseminated ore data points mostly occupy the intrusions field. Although the ore samples and intrusions can be classified because of their different chemical compositions ($qw^*$, Figure 10b), PLS-DA can differentiate between the Kharaelakh East and West samples (intrusions, disseminated, and massive ores; Figure 11a,b) and between the Norilsk 2, South Pyasinsky and Vologochansky intrusions. The variable importance on the projection (VIP) plot (Figure 11c) indicates that Cu and Ni significantly impact the classification, while Cr, V, Sr, La and Li are not discriminant. A combination of VIP values and score contributions indicates the following three points: (1) massive ore can be distinguished by its relative enrichment in Co, Cu, Ni, Mo and Sb, and depletion in Dy, Er, Eu, Gd, Hf, Ho, Lu, Nd, Sm, Tb, Tm, Y and Yb; (2) disseminated ore is distinguished by higher Cu, Ni and Cs, and lower Be, Nb, Ta, Th, Tl and U than silicate rocks; (3) the gabbro–dolerite intrusions are identified by their depletion in Ni, Cu, Co, Mo and Sb, and their relative enrichment in Be, Cs, rare-earth elements, Ga, Nb and Th (Figure 10a,c). These differences are explained by the varying sulfide contents in the samples.
Figure 10. Partial least-squares discriminant analysis (PLS-DA) of the trace and minor elements data in the samples from the different studied gabbro–dolerite intrusions and their associated disseminated and massive ores. (a) The $qw^*_1$–$qw^*_2$ (first and second loadings) plot shows the correlations among the elemental variables and their relationships with the different sample classes. (b) The $t_1$–$t_2$ (first and second scores) plot shows the distribution of the analyses from different mineralized and nonmineralized samples in the latent variable space defined by $qw^*_1$–$qw^*_2$. The colored polygons delimit the three main fields formed by the intrusion, disseminated ore and massive ore data points. (c) The variable importance on projection (VIP) plot shows the level of importance of the different oxides in the classification of the different intrusions.
Figure 11. Partial least-squares discriminant analysis (PLS-DA) of the major oxide data from the different studied gabbro-dolerite intrusions. (a) The qw"1–qw"2 (first and second loadings) biplot, (b) respective t₁–t₂ plot, (c) variable importance on projection (VIP) plot, and score contribution plots for the (d) Kharaelakh East, (e) Kharaelakh West, (f) Norilsk 2, (g) South Pyasinsky and (h) Vologochansky intrusions.
The results of the PLS-DA for the 10 major oxides in the composition of the studied gabbro–dolerites in Figure 11a–h demonstrate positive correlations among Na$_2$O, K$_2$O, and TiO$_2$; MgO and CaO; MnO and Fe$_2$O$_3$; and Al$_2$O$_3$, SiO$_2$, and P$_2$O$_5$. These elemental correlations cluster the Norilsk 2, Vologanchsky and South Pyasinsky intrusions together, forming the small overlapping fields in the PLS-DA scores scatter plot (Figure 11b), while the Kharaelakh East and Kharaelakh West points, by contrast, are dispersed in the scores scatter plot (Figure 11b). The VIP plot in Figure 11c distinguishes MnO and CaO as the important variables (VIP $\geq$ 1) in the classification of all of the intrusions, whereas Fe$_2$O$_3$ and TiO$_2$ are not important (VIP < 0.8; Figure 11c). The scores contribution plots in Figure 11d–h indicate that, in spite of the overlap seen in Figure 11b, each gabbro–dolerite intrusion is distinguishable because of its distinct average oxide composition, especially Kharaelakh East and Kharaelakh West.

The statistical calculations for the two branches show an overlapping cluster in the $t_1$–$t_2$ plot (Figure 11b), suggesting that the Vologanchsky and South Pyasinsky branches are characterized by similar chemistry, which can be translated to the genetic relationship between the two intrusions. Nevertheless, the VIP plot indicates that different sets of elements are discriminant for each of these intrusions. For instance, higher Sc, V and Tl, and lower Be, Mo, Sb, Zn, Ga, Ta, Nb, Th and W contents significantly contribute to the classification of the Vologanchsky rocks in Figure 11b, whereas higher rare-earth element contents and lower Mo, Pb, Tl and Zn are discriminant for the South Pyasinsky samples, mostly due to rocks from the OV-37 drillhole. The Norilsk 2 contents form a distinct cluster because of higher Pb and Zn, and lower contents of rare-earth elements, Ga and Mo (Figure 12a,b) compared to the other intrusions. Kharaelakh East and Kharaelakh West form distinct clusters in the $t_1$–$t_2$ space (Figure 12b). The Kharaelakh West intrusion particularly overlaps with Pyasinsky-Vologanchsky (rocks from OV-37), implying their similar chemistry despite their different PGE–Cu–Ni resources.

Figure 12 displays the results of the first and second PLS-DA components of 39 trace and minor elements in the composition of the studied gabbro–dolerites, demonstrating the differentiation among Kharaelakh East and the South Pyasinsky and Vologanchsky intrusions (Figure 12a,b). The VIP plot identifies Ga, Mo, Tl, Pb and Zn as the most important elements in the classification of all of the studied intrusions.

The combination of VIP values and score contribution plots in this PLS-DA indicates that higher Be, Cu, Ga, Mo, Ta, W and Zn, and lower Dy, Er, Eu, Gd, Ho, Lu, Sc, Sm, Sr, Tb, Ti, Tm, V, Y and Yb relative to the averages of the entire analyzed dataset are discriminant for the Kharaelakh East intrusion. By contrast, Kharaelakh West is characterized by relatively higher Be, Ce, Dy, Er, Ga, Gd, Ho, La, Li, Lu, Mo, Nd, Pr, Sb, Sm, Sr, Tb, Th, Tm, W, Y and Yb, and lower Co, Cs, Pb, Ta, Ti, V and Zn. The Norilsk 2 intrusion is discriminated from the other intrusions mainly because of its higher Pb and Tl and lower Ga contents. In addition, the South Pyasinsky and Vologanchsky intrusions that form widely overlapping clusters in the positive $t_1$–$t_2$ region (Figure 12b) are characterized by almost similar trace element signatures, although they differ slightly in the concentration of some elements, e.g., lower Mo and higher Co contents in the Vologanchsky compared with the South Pyasinsky intrusion.
Figure 12. Partial least-squares discriminant analysis (PLS-DA) of the trace and minor elements data in the samples from the different studied gabbro–dolerite intrusions. (a) The qw*1–qw*2 (first and second loadings) biplot, (b) respective t1–t2 plot, and (c) variable importance on projection (VIP) plot.

5. Discussion and Conclusions
5.1. Problems of the Origin of the Norilsk Deposits

The Norilsk deposits play a leading role in the Ni and PGE global economy (having produced 225,000 tons of Ni and 90 tons of Pd in 2019 [61]). Their origin has been actively discussed, including the magma compositions of the ore-bearing intrusions. Based on the elevated MgO (10–12 wt.%) in the intrusive rocks compared with the typical trap basalts (e.g., the Tuklonsky-Samoedsky formations, 6–7 wt.%), their formation has been considered to be the result of an independent magmatic event within the Siberian traps province [13,26,36,39,41,62,63]. The ore-bearing rocks were assumed to have crystallized within isolated magmatic chambers. In the 1990s, a hypothesis arose for the Cu–Ni deposits’ formation from tholeiitic magmas in an open magmatic system in which the ore-bearing intrusions were connected with lavas [5–8,14,28,64].

In both cases of open or closed magmatic systems, the sulfur amount in mafic–ultramafic magmas (up to 0.2–0.25 wt.%) [7,65] is not sufficient to create extra-large ore deposits directly from the magma volume in the modern chamber. For example, the Oktyabr’sky deposit comprises huge sulfide veins (up to 50 m) related to thin intrusive bodies (average 89 m thick; [29]). In order to explain this phenomenon, it was suggested that sulfides were transported by magma from an intermediate chamber to the modern one (closed system), or that they crystallized in situ after involving an external sulfur source, such as sulfate-bearing host rocks [19,66,67] or gases [9,68–71] (open magmatic system). Thus, the most important points in the Norilsk ore origin are as follows: (1) the composition of the primary magmas for the ore-bearing intrusions, (2) the type of magmatic system...
(closed or open), and (3) the scope and significance of assimilation. All of these points are interrelated. We disregard the type of magmatic system here because this problem was solved earlier, and geological data evidenced the ore formation within a closed magmatic system [33,36,58]. Here, we concentrate on points 1 and 3.

According to the model of an open magmatic system, only 1% external material is needed for the formation of large sulfide bodies [30]. However, no connection between intrusions and lavas was established in the Norilsk deposits. In the case of a closed magmatic system, 10–12% S-rich host rocks must be assimilated, assuming that all of the sulfur is extracted from them. This expected large-scale assimilation must affect the whole-rock compositions of ore-bearing intrusions, but we did not identify it.

5.2. Geochemical Comparison of Intrusions with Varying Mineralization

The parental magmas of intrusions must reflect their primary compositions and their later changes, including assimilation. In this way, the estimation of their compositions helps in understanding whether assimilation occurred during the intrusion’s formation.

5.2.1. Distribution of the Major Components in the Rocks

In order to consider the magma compositions of mineralized intrusions in the Norilsk area, three massifs have been studied: Kharaelakh (West and East), Pyasinsky-Vologochansky and Norilsk 2 (Figures 4–6). A review of the entire set of analyses (Table S1) demonstrates their principal division into three natural groups: nonmineralized silicate rocks, disseminated ores and massive sulfide ores (Figure 10b). As seen in Figure 10b, the field for disseminated ores overlaps with that of the intrusive rocks. This is consistent with the speculation that there is a genetic link between the disseminated ores and intrusive rocks, as these ores represent gabbro–dolerites with sulfide inclusions, while massive ores most likely crystallized from pure sulfide melt. The compositions of the silicate rocks in the studied intrusions are of the greatest interest because they reflect the composition of the parental magma.

Despite close chemical compositions, the intrusions are characterized according to specific features. The binary plots in Figure 8 show that the Vologochansky samples are divided into the MgO > 15 wt.% and MgO < 10 wt.% groups, while the PLS-DA of the major element oxides in Figure 10 clusters the Vologochansky, South Pyasinsky and Norilsk 2 analyses in the middle of the t1–t2 plot because of their relative depletion in Al2O3, P2O5, K2O and SiO2 (Figure 11a,b,f–h). By contrast, the heterogeneous compositions of the oxides in the samples from the Kharaelakh East and West intrusions caused the dispersion of the corresponding data points in the t1–t2 plot (Figure 11b). Although some analyses from both Kharaelakh East and West plot in the fields for the other studied intrusions, some Kharaelakh East and West analyses also plot in the negative t1 and negative t2 regions indicating P2O5, Al2O3 and K2O enrichments (Figure 11a,b,d). The Kharaelakh West analyses form another discrete subgroup in which the samples are mainly rich in MgO and CaO, and poor in Na2O. These differences are a result of the internal heterogeneity of the intrusions, which reflects the different thicknesses of their main horizons (Figure 7).

The thicknesses of the separate horizons must be taken into account in order to compare the intrusion compositions accurately. It is particularly important for intrusions with complex internal structures, such as Norilsk 2 and Kharaelakh, where the thicknesses of the horizons change significantly. For the calculation of the average mean compositions of the intrusions (Table 2), we used analytical data that included data of barren silicate rocks and rocks containing disseminated ores. We only need the compositions of the silicate constituents for the estimation of the parental magma; accordingly, we subtracted the sulfides from the whole-rock compositions. In order to simplify the calculations, it was assumed that Cu is concentrated in chalcopyrite (Cu 34.57; Fe 30.54, S 34.9, wt.%) and 2/3 of the Ni content is in pentlandite (one-third Ni in olivine), which has the average composition (Fe 33, Ni 34, S 33, wt.%). After the recalculation of the sulfur content in these minerals, it was assumed that the residual sulfur was associated with pyrrhotite (Fe 60%,
S 40%, wt.%). The Fe content summarized in chalcopyrite, pentlandite and pyrrhotite was subtracted from the total iron in the rocks. After this procedure, all of the rock composition (including trace elements) were recalculated at 100 wt.%.

The calculation results indicate the main oxide variations—in particular MgO—which reflect the predominance of picritic and taxitic gabbro–dolerites, as well as troctolites, in the sections of the NV-12, ZF-12 and OV-36 drillholes, in comparison with those of other sections (Table 2). The most representative for the estimation of primary magmas, of course, are the data obtained from numerous drillholes and calculated for the Norilsk 1 and Talnakh intrusions by Godlevsky [39] and Dneprovskaya and coauthors [34], respectively. These authors demonstrated very similar average compositions for the ore-bearing intrusions (Table 2, Nos. 9, 10), while the other sections differ because the thicknesses of their horizons vary significantly.

It is necessary to focus on the Cr content, which is an important characteristic of ore-bearing massifs. However, its high contents (2000–4000 ppm) are typical only for picritic horizons; the other varieties of rocks have low contents. In general, intrusions containing large and unique deposits are characterized by high Cr contents (Talnakh, Kharaelakh, Norilsk 1), but the same contents are typical of massifs with small deposits (Chernogorsky) and with noneconomic mineralization (Manturovsky massif, Imangda area, shown in Figure 2 as “4”), up to 6500 ppm Cr [72]. Meanwhile, large deposits associated with the Pyasinsky-Vologochansky and South Maslovsky (a part of the Maslovsky deposit) intrusions are characterized by low Cr (300–400 ppm).

Table 2. Average mean compositions of the ore-bearing intrusions in the Norilsk area.

| Intrusion       | Kharaelakh East | Kharaelakh West | South-Pyasinsky | Vologochansky | Norilsk 2 | Chernogorsky | Talnakh | Norilsk 1 |
|-----------------|-----------------|-----------------|-----------------|--------------|-----------|--------------|---------|-----------|
| Drilling point  | TG-21           | ZF-12           | NV-12           | OV-37        | OV-36     | OV-29        | MP-18   | Ch-55     | 29 d.h. | 54 d.h. |
| No              | 1               | 2               | 3               | 4            | 5         | 6            | 7       | 8         | 9       | 10      |
| SiO₂            | 50.26           | 50.57           | 47.19           | 51.18        | 48.35     | 49.18        | 49.58   | 47.2      | 48.3    | 46.1    |
| TiO₂            | 0.91            | 1.02            | 0.68            | 1.13         | 1.05      | 0.90         | 0.98    | 0.86      | 0.85    | 0.74    |
| Al₂O₃           | 17.32           | 15.83           | 15.63           | 17.26        | 13.13     | 14.95        | 15.76   | 16.7      | 15.33   | 15.5    |
| FeO             | 10.89           | 7.35            | 10.47           | 9.53         | 9.57      | 10.92        | 10.49   | 9.91      | 12.3    | 13.4    |
| MnO             | 0.18            | 0.19            | 0.18            | 0.18         | 0.20      | 0.21         | 0.29    | 0.16      | 0.19    | 0.15    |
| MgO             | 7.93            | 9.47            | 12.72           | 6.87         | 15.13     | 11.66        | 8.65    | 11.64     | 10      | 11.3    |
| CaO             | 9.49            | 12.13           | 10.50           | 10.98        | 8.93      | 9.64         | 11.66   | 11.4      | 10.4    | 10.3    |
| Na₂O            | 2.01            | 2.41            | 2.01            | 2.26         | 2.07      | 1.91         | 2.10    | 1.85      | 1.86    | 1.32    |
| K₂O             | 0.84            | 0.91            | 0.73            | 0.51         | 1.43      | 0.50         | 0.39    | 0.46      | 0.57    | 0.69    |
| P₂O₅            | 0.18            | 0.12            | 0.09            | 0.10         | 0.15      | 0.12         | 0.11    | 0.07      | 0.2     | 0.25    |
| Cr              | 1058            | 1841            | 277             | 305          | 686       | 578          | 336     | 1800      | 1000    | 1900    |

Note. Numbers 1–7 are according to Table S1, 8 is after [73], 9 is after [34], and 10 is after [39]; d.h. indicates the number of drillholes in the calculations; oxides are given in wt.%; Cr is given in ppm.

5.2.2. Behavior of the Trace Elements in the Rocks

The behavior of the trace elements in the rocks is more representative for each intrusion because it depends less on in-situ differentiation. Therefore, the spider diagrams for the average mean compositions of these intrusions (Figure 13) are similar, and are characterized by almost identical La/Sm, Th/Nb and Gd/Yb ratios.
However, there are large differences in the contents of trace elements in some parts of the Pyasinsky-Vologochansky intrusion (Figure 13). Usually, these differences are due to the accumulation of olivine in the individual horizons of the section, and if they have a substantial thickness, a gross depletion of the trace elements in the rocks occurs. However, in this case, the studied sections do not have such significant differences in the thickness of high-magnesium rocks, except the rocks from the NV-12 drillhole. Despite this, the main parts of the Pyasinsky-Vologochansky intrusion were rich in rare earths, including the section of the NV-12 drillhole. Only the eastern part of the South-Pyasinsky branch (OV-37 drillhole) has values close to those of the Kharaelakh and Norilsk 2 intrusions.

The most striking feature is the enrichment of the Pyasinsky-Vologochansky intrusion (excepting its eastern part) in trace elements compared with the Kharaelakh and Norilsk 2 intrusions. The Vologochansky deposit has a more complex structure than previously suggested. It comprises at least three intrusive bodies (maybe more; we did not study the western part of the Vologochansky branch). Two of them—the western South Pyasinsky and the eastern Vologochansky intrusive bodies—are similar in their chemical compositions, and were formed from the same magma, which was rich in trace elements, whereas the third intrusion, in the eastern part of the South Pyasinsky branch, was depleted in trace elements. The compositions of the parental magmas for the Kharaelakh and Norilsk 2 intrusions are similar to that of the third intrusion in terms of major and trace elements, although both individual branches of the Kharaelakh intrusion (Kharaelakh East and Kharaelakh West) and the Norilsk 2 intrusion have their own geochemical features (Pb, Zn, Mo, Tl, etc.).

Despite their similar compositions, the intrusions differ in their sulfide contents. The Kharaelakh and Pyasinsky-Vologochansky intrusions are characterized by similar morphology, size, geological setting and metamorphic aureole [39]. However, they are dramatically different in their mineralization: the Kharaelakh intrusion comprises $\Sigma$ Cu + Ni = 113 million tons [29], while the Pyasinsky-Vologochansky intrusion contains less than 1 million tons (according to our calculations), i.e., 100 times less. The Norilsk 2 intrusion, despite its different morphology and position in the stratigraphic sequence, has a similar rock composition to the Pyasinsky-Vologochansky intrusion, and comprises only subeconomic mineralization.

5.3. Problem of Host-Rock Assimilation by Magma

In order to explain a huge sulfur volume in the Norilsk deposits, many models suggest the important role of anhydrite, coal and gas assimilation by magma. We provide...
some arguments that demonstrate the fundamental impossibility of this mechanism for deposit formation.

5.3.1. Intrusion Compositions and Contact Zones: The Rapid Crystallization of Magmas

Despite the existing differences in their compositions, the Kharaelakh and Pyasinsky-Vologochansky intrusions do not demonstrate differences in elements that could be explained by the assimilation of limestones and anhydrites, i.e., increased contents of Ca, Ba and Sr, etc., compared with the Norilsk 2 intrusion in basalts. The ore-bearing intrusions located in the different host rocks are similar in composition (Table 2, Figure 13).

It has been proven that assimilation occurred only in the narrow contact zones (1–5 m, Figure 9a,b) and did not influence the composition of the whole rock within the magma chamber. Assimilation is often absent [74] because the parental magmas of ore-bearing intrusions quickly crystallize under near-surface conditions. The textures of the rocks, zoned rock-forming minerals and glass inclusions in the minerals evidence the rapid appearance of a quenched zone, which prevented interaction between magma and host rocks (Figure 14a–d).

Figure 14. Rocks and minerals from the contact zones of the Norilsk intrusions evidence the rapid crystallization of the parental magma. (a,b) contact gabbro-dolerites; (c) zoned olivine, and (d) glass inclusion in olivine. Pl: plagioclase; Cpx: clinopyroxene; Mag: magnetite; Fo: mol.% forsterite in olivine.

5.3.2. Anhydrite Assimilation
S Isotopic Data

In the 1950s, Godlevsky formulated the idea of an external source of sulfur for the Norilsk deposits based on a large volume of anhydrite-containing rocks in the Norilsk area. In order to verify the possibility of sulfur borrowing from anhydrite, Godlevsky and Grinenko [67] studied the isotopic composition of the sulfur in the ores of the Norilsk
deposits. It was demonstrated that the Norilsk ores are enriched in heavy sulfur ($\delta^{34}$S; 12‰ on average) compared with the ores of other Cu–Ni deposits around the world. It was also shown by Grinenko [69] that sulfur is heavier in large deposits than in small ones, which seems to be consistent with the volume of the assimilated matter. It seemed that the idea was brilliantly confirmed. But this correlation is violated when considering a larger volume of intrusions from the northwestern Siberian Platform. For example, Ryabov and coauthors [70] found the heaviest sulfur in masses with poor mineralization (up to 18.6 ppm in the Dzhaltul massif, up to 18.3 ppm in the Vologochan massif, and 21.5 ppm in the Kureika massif). Grinenko [69] rejected the idea of anhydrite assimilation by magmas based on Ca mass-balance calculations.

Ca Balance

As the melting temperature of anhydrite is higher than the temperature of the parental magmas of ore-bearing intrusions (1450 °C versus 1250 °C), it was suggested that anhydrite decomposes at $T = 1100$ °C into CaO and SO$_3$, enriching the magmas in sulfur and forming sulfide ore. If this process occurs, many Ca-bearing minerals must crystallize in intrusive and host rocks. Rad’ko [29] calculated that the Kharaelakh intrusion contains 330 million tons of sulfur. If sulfur were extracted from anhydrite, then 210 million tons of Ca would have to appear around the contact zone; however, there is no enrichment in Ca in the gabbro–dolerites and the surrounding rocks.

Deep-Zone Assimilation

It has been suggested that assimilation occurred in the deep zones of the Norilsk area below the Devonian sediments hosting the ore-bearing intrusions, not in situ [19]. Anhydrite-bearing rocks occur in the Cambrian–Silurian rocks as well, not only in Devonian rocks, as shown in [75]. Anhydrite-bearing rocks are widespread to the south of Norilsk. One example of Silurian evaporites is given in Figure S5; all of the maps are available in [76,77]. These rocks and their contacts with gabbro–dolerite sills (close in composition to the ore-bearing intrusions) are exposed within the Tunguska syncline. The Cambrian-Silurian rocks comprise gypsum, celestine and barite deposits in the south Siberian traps province (Ozernoe, Pesirsky, Uvaktysk and Bolshe-Dovogninsky, etc., in the Lower Tunguska, Podkamennaya Tunguska and Angara river valleys [75]). The contacts of the gabbro–dolerite sills with evaporites outcrop here, but sulfide deposits are absent (Figure 15a,b).

Anhydrite Origin in Igneous Rocks

Li and coauthors [30] described anhydrite grains in the picritic gabbro–dolerites as magmatic minerals based on their dihedral angles of 120°, with olivine and pyroxene that evidence their simultaneous crystallization. This is a typical angle for augite grains in gabbro–dolerites; thus, anhydrite performs interstitials (Figure 2c in [30]). Anhydrite occurs very often as a metasomatic mineral in gabbro–dolerites, and forms similar grains (Figure S6). Stronger arguments should be given to prove a magmatic origin of anhydrite. Magmatic anhydrite crystallizes from melt under oxidation conditions (FMQ+2) [78]. We estimated $f_{O_2}$ during the crystallization of the Taldakh magma [79] using the COMAGMAT model ($f_{O_2}$ = from $−7.2$ to $−8.2$), and based on olivine–spinel equilibrium ($f_{O_2} = −8$) at 1200 °C. According to these data, anhydrite could not crystallize in the picritic gabbro–dolerites, where it was described as a magmatic phase [30].

Moreover, if assimilation occurred and was important for the ore’s origin, the highest $^{87}$Sr/$^{86}$Sr ratio would be typical of the Kharaelakh and Talnakh intrusions, but they are lower than those in the barren Lower Talnakh intrusion (0.705–0.708 in the first intrusions, compared with 0.711 in in the last one). The Pb isotope data do not support the idea of assimilation, either: anhydrite has very radiogenic Pb ($^{206}$Pb/$^{204}$Pb = 20.817–24.528), while the ore-bearing and barren intrusions are characterized by ($^{206}$Pb/$^{204}$Pb = 17.983–18.254) [33,80].
5.3.3. Gas Assimilation

Grinenko [69,81] formulated another idea for the supply of heavy sulfur by parental magma from the oil deposits of eastern Siberia. Among the ancient (pre-Jurassic) deposits of Siberia, the Leno–Tunguska oil and gas province is well known, including the Baikit and Katanga oil and gas regions [82–84]. The Baikit anticline comprises seven deposits, including the largest unique oil and gas deposit, Yurubcheno–Tokhomsky, which is the oldest in the world, localized in Proterozoic (Riphean) rocks. However, it is assumed that the formation of the oil occurred in the middle–late Paleozoic [82,85], while its gas cap was probably formed in the Triassic. Therefore, from the point of view of possible assimilation, only the oil deposits of this area are of interest. According to the estimates of several researchers [83,85], oils are low in sulfur (0.12–0.18 wt.% S), and the gas dissolved in the oil comprises (wt.%) methane (66.17–76.58), ethane (13.58–14.41) propane (5.08–8.11), butane (0.58–1.56) isobutane (0.19–3.88), helium (average 0.014), carbon dioxide (average 0.053) and nitrogen (1.95–2.46). With reserves of 1 million tons of oil in the Yurubcheno–Tokhomsky deposit, a maximum of 1800 tons of sulfur can be extracted from it, whereas 330 million tons of sulfur is concentrated in the Oktyabr’sky deposit alone (related to the Kharraelakh intrusion). Thus, mass-balance calculations do not confirm the idea of sulfur assimilation from oil.

Similar ancient deposits have not yet been discovered in the northern part of eastern Siberia, although Vankoroil Ltd. (Krasnoyarsk, Russia) conducted exploratory work in the Norilsk region (Kystykhtakh River, Samoyedsky Swell) during 2010–2017, and revealed Riphean rocks (the maximum depth of boreholes is 4.5 km). Furthermore, Polyansky and Reverdatto [86] demonstrated that intruding trap sills forced the hydrocarbons from the crystallization chambers. Thus, magma does not assimilate gases emplaced in carbonaceous rocks; it drives them away from their localities.

Ryabov and coauthors [69,71] developed the idea of sulfur borrowing from gas. They proposed sulfur production due to sulfate sulfur reduction, described by two reactions: (1) \( \text{CaSO}_4 + \text{CH}_4 \rightarrow \text{CaS} + 2\text{H}_2\text{O} + \text{CO}_2 \) and (2) \( \text{CaS} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{H}_2\text{S} \). The authors did not analyze the geological conditions of this process, nor the depth (P) and temperature (T) at which it occurred, or how much \( \text{H}_2\text{S} \) magma could dissolve. Taking into account...
account the low H$_2$S content in basaltic magmas (less than the H$_2$O content in within-plate magmas, i.e., <1.2 wt.% [87]), it is clear that it is impossible to obtain 10 wt.% S in the melt to form a unique deposit. A mechanism for the gas flow into magma was not described either: How does gas move in a thermogradient field from a cold zone to a hot one? The model of anhydrite borrowing also suggests that Ca from this mineral formed plagioclase in leucogabbro in ore-bearing intrusions [69]. In this case, ore-bearing intrusions must contain more CaO than barren intrusions. Nevertheless, the ore-bearing intrusions in Norilsk are typical gabbro (Table 2), which can have 10–18 wt.% CaO [88].

5.3.4. Coal Assimilation

Iacono-Marziano and coauthors [89] suggested a two-step formation of the sulfide deposits: anhydrite assimilation at depth and then magma interaction with carbonate rocks (with organic material), which was reproduced in experiments. Sulfides were crystallized in the laboratory, firstly, because the sample was selected from the horizon of disseminated ores in the picritic gabbro-dolerite horizon (drillhole OM-1/1005, [27]), i.e., it already contained sulfides, and secondly, due to the addition of sulfur (0.5–5 wt.% S) to the mixture of coal and basalt. The geological data reveal that magma interaction with coal is restricted to a narrow zone. Figure 15 shows the rocks of the upper contact zone of the Talnakh intrusion (drillhole SF-10) where gabbro-dolerite comprises many small (<1 cm) and large (5 cm) coal pieces. Coal keeps its structure and does not react with basaltic melt (Figure 15b); sulfides are not formed under such conditions.

5.4. Genetic Interpretation of the Results

Regarding the results of this study and the data obtained earlier [58,63], it is concluded that major and trace elements in rocks do not provide information about the potential mineralization of their intrusions. All of the intrusions of the Norilsk intrusive complex have similar average compositions, which do not depend on the composition of the host rocks. This similarity excludes a process of the assimilation of the surrounding rocks by parental magmas in situ, and evidences the independence of the sulfide occurrence from the silicate rock composition. The isotope geochemistry of the Norilsk intrusions indicates the uniformity of their sources ($E_{Nd}$ = from −1 to +1, $^{34}$S/$^{36}$Sr = 0.705–0.710) [17,90], which were located within the crust. The sources were rich in sulfur, with irregular distributions (Figure 16). Source melting produced magmas that carried sulfides from deep zones to the surface. Thus, the magmas served mostly as transporting agents for sulfides concentrated in the lower crust during several geological processes.

In terms of the sulfur and osmium isotope compositions, the sulfides in this zone of the crust have the same isotopic composition as the sulfides of the mantle magmas intruded in the Taimyr Peninsula that formed the ore-bearing Dyumtaleyisky massif [91]. The mantle origin of the heavy sulfur isotopes in the Norilsk ores was suggested by Likhachev [13,92]. However, it was not proved by geochemical data because intrusions with mantle signatures and heavy sulfur isotopes were not discovered. Ripley and coauthors [93] rejected this assumption based on the sulfur isotope data in the basalts of the Norilsk area. In that work, the authors assumed that volcanic and intrusive rocks were comagmatic bodies formed from a single magma. However, this assumption does not match with the geological data, as was stated above [74]. Thus, the data on mantle sulfides was not obtained at the end of the 20th century [13]; these sulfides were analyzed only in 2000s [91].

The most important factor in the origin of the Norilsk deposits is the specific position of the magma sources in the structure of the Siberian traps province, as was demonstrated earlier [35,63]. The origin of the magma sources and the mechanism of sulfide transport are important problems for future research.
Figure 16. Formation schema for the intrusions of the Norilsk intrusive complex. The black points and lenses are sulfide ores in the intrusions of the Norilsk complex (light green). Sedimentary deposits: c-D—Cambrian-Devonian carbonate-terrigenous rocks, C2-P1—terrigenous rocks with coal; volcanic rocks, formations: iv-sv—Ivakinskaya-Syverminskaya, gd—Gudchikhinskaya, nd—Nadezhdinskaya, tk—Tuklonskaya, mr-sm—Morongovskaya-Samoedska. Light green fields—ore-bearing intrusions, dark green—barren intrusions; black marks—sulfides, blue arrows—magma directions.

6. Conclusions

1. The geochemical characteristics of the rocks and related ores for three intrusions of the Norilsk region were studied using XRF, ICP-MS, ICP-AES, FAAS methods. They are the Kharayelakh intrusion with a unique PGE–Cu–Ni Oktyabr’sky deposit, the Pyasino-Vologochansky intrusion with a large Vologochansky deposit, and the Norilsk 2 intrusion with subeconomic mineralization. The similarity of the rock compositions from these intrusions, independent of their mineralization, was established.

2. The rock compositions and volume mineralization of the studied intrusions do not depend on their setting in the cross section. The Kharaelakh and Pyasinsky-Vologochansky intrusions are located in the same Devonian carbonate–terrigenous rocks on the boundary of the Kurejsky and Razvedochninsky formations, but their metal resources differ by two orders of magnitude. The assimilation of the host rocks by parental magmas occurs in the narrow contact zones (with a thickness of the first meters) of the intrusive bodies, and does not affect the weighted average composition of the intrusions or the volume of mineralization.

3. The lack of correlation between the silicate rock compositions and their mineralization indicates that the magmas were mostly transported agents for sulfides from the deep zones of the Earth to the surface.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11080819/s1: Table S1: Chemical rocks compositions of the ore-bearing intrusions in the Norilsk area, Figure S1: Distribution of MgO in the studied drillholes: (a) TG-21, (b) ZF-12, (c) OV-36, (d) NV-12, (e) OV-37, (f) OV-39, and (g) MP-18. H—depth, m, Figure S2: Diagrams Gd/Yb vs. La/Sm (a) and Th/Nb vs. La/Yb (b) for rocks of the Norilsk intrusions, Figure S3: Diagrams S vs. Cu (a), S vs. Ni (b) for rocks of the Norilsk intrusions, Figure S4: Diagrams of (a) Sb-Sa, (b) S-Co, (c) S-Sn, (d, detail) S-Sn, (e) S-Bi, (f, detail) S-Bi, (g) S-Pb, (h) S-Te, (i) S-Cu for rocks of the Norilsk intrusions, Figure S5: Biogeocenotic map of Silurian basin (Early Postnich time—ps1 and Early Ludford Idg) after Tesakov, 2014 [1], Figure S6: Veinlet and metasomatic anhydrite (Anh) in gabbro–dolerites (G) in the Pyasinsky-Vologochansky intrusion (sample OV-42/635.7).
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References
1. Zavaritsky, A.N. Classification of magmatic ore deposits. Econ. Geol. 1927, 22, 678–686. [CrossRef]
2. Godlevsky, M.N. Cooper-Nickel World Deposits and Problems of Their Genesis; TSNIGRI: Moscow, Russia, 1963; 22p.
3. Godlevsky, M.N. Magmatic Deposits: Genesis of Endogenic ore Deposits; Nedra: Moscow, Russia, 1968; pp. 7–83.
4. Naldrett, A.J. Nickel sulfide deposits: Classification, composition, genesis. Econ. Geol. 1981, 75, 628–685.
5. Naldrett, A.J. A model for the Ni–Cu–PGE ores of the Norilsk region and its application to other areas of flood basalts. Econ. Geol. 1992, 87, 1945–1962. [CrossRef]
6. Naldrett, A.J. Magmatic sulfide deposits: Key factors in their genesis. Miner. Depos. 1999, 34, 227–240. [CrossRef]
7. Naldrett, A.J. Magmatic Sulfide Deposits: Geology, Geochemistry and Exploration; Springer: Heidelberg, Germany, 2004; 727p.
8. Naldrett, A.J. Fundamentals of Magmatic Sulfide Deposits. Rev. Econ. Geol. 2011, 17, 1–50.
9. Zotov, I.A. Transmagmatic Fluids in Magmatism and Ore-Forming Processes; Nauka: Moscow, Russia, 1989.
10. Zolotukhin, V.V. Sulfide Cu–Ni formation, its position among other ore formations and genesis. Russ. Geol. Gephys. 1991, 27–36.
11. Arndt, N.T.; Lesher, C.M.; Czamanske, G. K. Mantle-derived magmas and magmatic Ni-Cu-(PGE) deposits. Econ. Geol. 2005, 100, 5–24.
12. Barnes, S.-J.; Lightfoot, P.C. Formation of magmatic nickel-sulfide ore deposits and processes affecting their copper and platinum-group element contents. Econ. Geol. 2005, 100, 179–213.
13. Likhachev, A.P. Platinum–Copper–Nickel and Platinum Deposits; Eslan: Moscow, Russia, 2006; 496p.
14. Li, C.; Ripley, E.M.; Naldrett, A.J. A new genetic model for the giant Ni–Cu–PGE sulfide deposits associated with the Siberian flood basalts. Econ. Geol. 2009, 104, 291–301. [CrossRef]
15. Li, C.; Ripley, E.M. Magmatic Ni-Cu and PGE Deposits: Geology, Geochemistry, and Genesis. Rev. Econ. Geol. 2011, 17. Available online: https://www.segweb.org/store_info/REV/REV-17-Additional-Product-Info.pdf (accessed on 27 July 2021).
16. Lightfoot, P.C. Advances in Cu–Ni–PGE sulfide deposit models and implications for exploration technologies. Ore Depos. Explor. Technol. 2014, 44, 629–646.
17. Malitch, K.N.; Belousova, E.A.; Griffin, W.L.; Badanina, I.V.; Latypov, R.M.; Sluzhenikin, S.F. Chapter 7. New insights on the origin of ultramafic-mafic intrusions and associated Ni–Cu–PGE sulfide deposits of the Norilsk and Taimyr provinces, Russia: Evidence from radiogenic and stable isotope data. In Processes and Ore Deposits of Ultramafic-Mafic Magmas through Space and Time; Elsevier: Chennai, India, 2018; pp. 197–238.
18. Barnes, S.-J.; Le Vaillant, M.; Godel, B.; Lesher, M. Droplets and bubbles: Solidification of sulfide-rich vapor-saturated orthocumulates in the Norilsk-Talnakh Ni–Cu–PGE intrusions. J. Petrol. 2019, 60, 269–300. [CrossRef]
19. Yao, Z.; Mungall, J. Linking the Siberian flood basalts and giant PGE-Cu-Ni sulfide deposits at Norilsk. JGR Solid Earth 2020, 126. [CrossRef]
20. Niggli, P. Ore Deposits of Magmatic Origin: Their Genesis and Natural Classification; Thomas Murby & Co.: London, UK, 1929.
21. Schulz, K.J.; Chandler, W.W.; Nicholson, S.W.; Piatak, N.; Seall, R.R.; Woodruff, L.G.; Zientek, M.L. Magmatic Sulfide-Rich Nickel-Copper Deposits Related to Picrite and (or) Tholeitic Basalt Dike-Sill Complexes—A Preliminary Deposit Model. U.S. Geological Survey Open-File Report 2010–1179; USGS: Reston, VA, USA, 2010; 25p. Available online: http://pubs.usgs.gov/of/2010/1179/ (accessed on 27 July 2021).
22. Mungall, J.E.; Ames, D.E.; Hanley, J.J. Geochemical evidence from the Sudbury structure for crustal redistribution by large bolide impacts. Nature 2004, 429, 546–548. [CrossRef][PubMed]
23. Chai, G.; Naldrett, A.J. Petrology and geochemistry of the Jinchuan ultramafic intrusion: Cumulate of high-Mg basaltic magma. J. Petrol. 1992, 33, 1–27. [CrossRef]
24. Lightfoot, P.C.; Keays, R.R.; Evans-Lamstock, D.; Wheeler, R. S saturation history of Nain Plutonic Suite mafic intrusions: Origin of the Voisey’s Bay Ni–Cu–Co sulfide deposit, Labrador, Canada. Miner. Depos. 2012, 47, 23–50. [CrossRef]
25. Kamo, S.L.; Czamanske, G.K.; Amelin, Y. Rapid eruption of Siberian flood-volcanic rocks and evidence for coincidence with the Permian-Triassic boundary and mass extinction at 251 Ma. Earth Planet. Sci. Lett. 2003, 214, 75–91. [CrossRef]
26. Zolotukhin, V.V.; Vasil’ev, Y.R.; Dyuzhikov, O.A. Diversity of Traps and Initial Magmas: A Case of the Siberian Platform; Nauka: Novosibirsk, Russian, 1978; 289p.
83. Russian Encyclopedia. Available online: http://my.krskstate.ru/docs/minerals/yurubcheno-tokhomskoe/ (accessed on 27 July 2021).
84. BStudy. Available online: https://bstudy.net/952070/estestvoznanie/neftegazonosnye_oblasti_zapada_leno_tungusskoy_neftegazonosnoy_provintsii (accessed on 23 July 2021).
85. Kontorovich, A.E.; Izosimova, A.N.; Kontorovich, A.A.; Khabarov, E.M.; Timoshina, I.D. Geological structure and conditions of formation of giant Yurubcheno-Tokhoma zone of oil in Upper Proterozoic in Siberian Platform. Russ. Geol. Geophys. 1996, 37, 166–195.
86. Polyansky, O.P.; Reverdatto, V.V. Role of fluid in heat and mass transfer during evolution of sedimentary basins with trap magmatism. In Fluids and Geodynamics; Nauka: Moscow, Russia, 2006; pp. 219–243. (In Russian)
87. Naumov, V.B.; Dorofeeva, V.A.; Girnis, A.V.; Yarmolyuk, V.V. Mean Contents of Volatile Components, Major and Trace Elements in Magmatic Melts in Major Geodynamic Environments on Earth. I. Mafic Melts. Geochem. Int. 2017, 55, 629–653. [CrossRef]
88. Le Maitre, R.W. (Ed.) Igneous Rocks. A Classification and Glossary of Terms. In Recommendations of the International Union of Geological Sciences Subcommission on the Systematics of Igneous Rocks, 2nd ed.; Cambridge University Press: Cambridge, UK, 2002; 236p.
89. Iacono-Marziano, G.; Ferraina, C.; Gaillard, F.; Di Carlo, I.; Arndt, N.T. Assimilation of sulfate and carbonaceous rocks: Experimental study, thermodynamic modelling and application to the Talnakh-Norilsk region. Ore Geol. Rev. 2017, 90, 399–413. [CrossRef]
90. Petrov, O.V. (Ed.) Isotope Geology of the Norilsk Deposits; Springer: Berlin/Heidelberg, Germany, 2019; 306p.
91. Krivolutskaya, N.A. Mantle origin of heavy isotopes of sulfur in ores of the Norilsk deposits. Dokl. Earth Sci. 2014, 454, 76–78. [CrossRef]
92. Likhachev, A.P. Possibility of self-enrichment in heavy sulfur isotope and ore metals of mantle magmas and perspective areas of ore localization in the Norilsk district. Otechestvennaya Geol. 2019, 1, 1–18.
93. Ripley, E.M.; Lightfoot, P.C.; Li, C.; Elswick, E.R. Sulfur isotopic studies of continental flood basalts in the Norilsk region: Implications to the association between lavas and ore-bearing intrusions. Geochim. Cosmochim. Acta 2003, 67, 2805–2817. [CrossRef]