New U-Pb and Sm-Nd Data and REE Distribution in Sulphides of Paleoproterozoic PGE Layered Intrusions in the Arctic Part of the Fennoscandian Shield

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Abstract
The U-Pb (on zircon) and Sm-Nd analysis is a popular isotope-geochronological tool for estimating the age of rocks from PGE mafic-ultramafic intrusions. Sulphides can be used to study the geochronology of ore processes as well, since they should indicate the time of ore mineralization. Gabbronorite has been sampled from the Passivaara reef at the Penikat layered intrusion (Finland) for U-Pb and Sm-Nd isotope single zircon analyses in order to separate sulphide minerals. The Sm-Nd isotope age of gabbronorite has been dated at 2426 ± 36 Ma; eNd(T) = −1.4 ± 0.4. The Sm-Nd isotope age on sulphides and rock-forming minerals reflects the crystallization time of the ore-bearing gabbronorite from the Passivaara reef of the Penikat layered intrusion. The mass-spectrometer analytical environment and modes of operation have been adjusted to detect REE in sulphide minerals on example of pyrite from the PGE Penikat layered intrusion (Finland) and chalcopyrite from the Talnakh deposit (Norilsk area, Russia) has been estimated. The total REE content in pyrite is ca. 3.5 ppm, which is enough to define the Sm-Nd age of pyrite. The study shows how to use the mineral/chondrite spectra to evaluate the accuracy of the REE analytical results on example of State Standard Sample 2463 (Russia).

Keywords
Platinum Group Elements, Layered Intrusion, Rare Earth Elements, Uranium-Lead and Samarium-Neodymium Analyses, Zircon, Sulphide Minerals, Fennoscandian Shield
1. Introduction

The current research pioneers in complex U-Pb (on zircon) and Sm-Nd (on sulphide minerals) dating of basic-ultrabasic rocks from the Penikat intrusion (Finland). The minerals have been sampled in Finland and studied in the framework of the INTERREG-TASIS international project. The paper [1] summarizes the latest U-Pb (on zircon and baddeleyite) and Sm-Nd data (obtained for the first time on rock-forming and sulphide minerals), as well as Nd-Sr and He²/He⁴ data on Paleoproterozoic PGE layered intrusions of the NE Fennoscandian Shield (the Monchegorsk, Fedorovo-Pana and Imandra ore areas, Russia).

Basically, sulphides are ore-forming minerals in PGE deposits that can have commercially valued Pt-Pd mineralization. The study of noble metal deposits at the Kola Peninsula comprises the geochronological research and analytical treatment of its results. Data on the content and distribution of REE in minerals are required to define the age of an ore-forming event and to study the behavior of light lanthanides during the sulphide magma generation.

The REE content in sulphides is often less than 0.1 ppm. The composition of REE is not completely studied; and data on REE analyses are scarce [2] [3] [4] [5]. Palessky [6] reviews methods of REE analysis of geological samples and notes that the atomic absorption and atomic emission spectrometry is nowadays more widely adopted, compared to the X-ray fluorescence and neutron activation analyses. However, these popular methods do not allow to simultaneously reveal the whole range of elements in geological samples because of their low detection limits or constraints on the range of elements to identify. Thus, the content of such monoisotopic elements as Pr, Tb, Ho, and Tm cannot be measured by the isotope dilution method. It is possible to analyze REE by ICP MS method on ELAN-9000 (Perkin Elmer) mass-spectrometers in the amount of up to 1 ppt (instrumental detection limit is 0.1 ppt). Timofeev [7] shows a possibility of analyzing microimpurities of rare and trace elements on ELAN mass-spectrometers with no preliminary concentration. A simultaneous determination of the whole REE range with no preliminary concentration is described in [8].

Rimskaya-Korsakova et al. [4] show the REE content in the chalcopyrite of the Talnakh deposit at a ppb level that is six to thirty times lower than that in chondrite. The authors preliminarily separated REE from the matrix of the unsealed liquid samples, and concentrated REE to analyze on ICP MS, PlasmaQuad PQ2STE.

2. Geological Setting of the Penikat Intrusion

The age of the Penikat intrusion is 2440 Ma, according to [9]. It is ca. 23 km long and 1.5 to 3.5 km wide (Figure 1). Layered country rocks are represented by Archaean and Early Proterozoic granitoids. The overlying rocks are tholeitic volcanic, subvolcanic bodies and polymictic conglomerates.

The intrusion comprises two structural elements: marginal and layered series. The layered series includes 5 megaunits identified by a repeated regular rock
This megacyclicity is associated with injections of new magmas into the chamber of the intrusion during the crystallization. It is confirmed by mineral and cumulate compositional variations [9].

The thickness of the first megaunit varies from 270 to 410 m in different parts of the intrusion. The ultramafic layer of the megaunit is represented by plagioclase- and chromite-bearing bronzitites with granophyres, biotite, ilmenite and chlorine-bearing apatite. The bronzitites are overlain by plagioclase-bronzite mesocumulates and plagioclase-augite-bronzite cumulates. In the middle part of the layer, there are plagioclase-bronzite (chromite) mesocumulates with augite oicocrysts.

The second megaunit is 160 - 230 m thick. It has a layer of ultramafic rocks represented by alternating websterites, lherzolites with interlayers of gabbronorites and pyroxenites. The upper part of the megaunit cross-section is mainly...
composed of gabbro-norites. In some units, gabbro-norites contain chromite and are separated by websterites into two layers.

The third megaunit has a thickness of 75 to 330 m. The ultramafic unit is represented by websterites with dispersed chromite, sometimes websterites and lherzolites. The ultramafic unit is overlain by plagioclase-augite-bronzite cumulates, and the megaunit cross-section is completed by plagioclase-bronzite orthocumulates with poikilitic intercumulative augite and pegmatoid gabbro-norites.

The fourth megaunit is 760 to 1100 m thick. The contact between the rocks of the third and fourth megaunits is uneven due to the igneous erosion [9] [10]. The cross-section of the lower zone is composed of ultramafic rocks (alternating cumulative bronzitites and augite with intercumulative augite and bronzite). The ultramafic rocks are overlain by cumulative gabbro-norites.

The upper part of the cross-section is made up of rhythmically alternating poikilitic bronzite cumulates, plagioclase-bronzite mesocumulates and plagioclase-augite-bronzite adamulates. The uppermost part of the rhythms is composed of poikilitic plagioclase mesocumulates. The second zone includes monotonous plagioclase-augite-bronzite cumulates with separate wedging-out layers of plagioclase cumulates. The third zone comprises poikilitic plagioclase mesocumulates, where augite and bronzite form large poikilitic crystals. This layer is overlain by plagioclase-bronzite mesocumulates, where augite grains occur as poikilitic oikocrysts. These rocks are overlain by a norite layer. The intercumulative augite discontinues to form oikocrysts. Up the cross-section, there is a homogeneous layer of plagioclase-augite-bronzite adamulates with a pair of discontinuous anorthositic interlayers. The cross-section of the zone is composed of plagioclase-bronzite cumulates as thick as 1.5 m. The fourth zone, which is up to 300 m thick, is mainly composed of plagioclase-augite-bronzite adamulates with interlayers of poikilitic plagioclase adamulates and anorthositic.

The visible thickness of the fifth megaunit varies from first meters to 900 m. The bottom bronzititic layer is overlain by a layer (190 - 250 m thick) of plagioclase-bronzite cumulates, where augite forms poikilitic oikocrysts. There are bronzites and plagioclase-augite-bronzite adamulates with a discontinuous layer of anorthozites and cumulative magnetite in the upper part of the layer. Presumably, the cross-section of the megaunit is composed of with poikilitic plagioclase-bronzite cumulates and plagioclase-augite adamulates.

The Penikat intrusion comprises 7 PGE-rich zones. The SJ-, AP- and PV-reefs are the most important, being found in the MCU IV [9] [10], with only the SJ-reef presented in the upper part of the third megaunit. It is suggested that the source of PGEs in all three reefs was represented by the rocks formed from the magmas of the bonitite series [9] [10].

3. Analytical Procedures

**U-Pb (TIMS) dating of single zircon and baddeleyite grains**

The samples of single grain accessory minerals have been prepared for further
U-Pb analyses, using the ion-exchange chromatography. First, handpicked crystals are treated in ultrasonic bath for cleaning in spirit or in acetone and then in 7N nitric acid. Next, the crystals are heated for about 15 minutes on a warm rangette and three times flushed with recurrent purification water. The chemical mineral decomposition has been performed in teflon bombs with 3 to 5 mcl of mixed $^{208}$Pb/$^{235}$U tracer with T. Krogh’s method [11] in concentrated nitric acid during 5 - 7 days at a temperature of 210°C. After complete decomposition, the column effluent is evaporated on a warm rangette, and then 10 drops of 6.2 N chlorohydric acid are added. The sample is placed into the thermostat for 8 - 10 hours at a temperature of 140°C - 150°C for homogenization. Pb and U are separated for isotope investigations using ion-exchange chromatography in columns with Dowex IX8 200 - 400 mesh resin. Pb is eluted with 10 drops of 6.2 N chlorohydric acid. Then, one drop of 0.1 N phosphoric acid is added, and the solution is evaporated on a rangette down to 3 mcl. U is eluted separately from Pb with 20 drops of water and one drop of 0.1 N phosphoric acid added, and evaporated on a rangette down to 3 mcl. All chemical procedures are carried out in an ultraclean block with blank Pb and U contamination of ca. 1 - 3 pg, and ca. 10 - 15 pg, respectively. The isotope composition and concentrations of Pb and U are measured on Re bands at 7-channel mass-spectrometer Finnigan-MAT 262 (RPG), on collectors, with $^{204}$Pb and $^{205}$Pb measured at a temperature of 1350°C - 1450°C in an ion counting mode, using a multiplier or quadrupole RPG accessory. Silicagel is used as an emitter. U concentrations are detected at a temperature of 1450°C - 1550°C, using a collector and a multiplier in a mixed statically dynamic mode. When U concentrations are negligible, the multiplier or quadrupole RPQ accessory is applied in a dynamic mode. All the measured isotope ratios are adjusted for mass-discrimination (0.12% ± 0.04%) obtained during the parallel analyses of SRM-981 and SRM-982 standards. Coordinates of points and isochron parameters are calculated using programs by K. Ludwig [12] [13]. Ages are estimated according to the accepted values of U decay constants [14], with errors indicated on a 2b level. The model by J. Stacey & J. Kramers [15] is used to adjust numbers for the admixture of common Pb.

**REE analyses in sulphides (LA-ICP-MS)**

There are no standard samples for sulphide minerals to study REE concentrations and dissemination. In order to analyze REE in geological sulphide samples, first we have reproduced the certified REE concentrations in GSO 2463 (apatite) and international standard composition samples at the National Centre for Petrographic and Geochemical Research (CNRS), Nancy, France, for granite (AC-E), diorite (DR-N) and anorthosite (AN-G). The analysis has been made with no preliminary separation and concentration on ELAN 9000 DRC-e GMS (Perkin Elmer, USA). Then we have analyzed the chalcopyrite of the Talnakh deposit (Norilsk area, Russia) to compare the data with those obtained by Rimskaya-Korsakova et al. [4]. The results have testified to the accuracy of the analysis. Afterwards, we have measured the REE content in sulphides from the PGE Penikat deposit, Finland.
The analysis on ELAN 9000 DRC-e has been made with the following parameters: plasma power of 1.300 - 1.350 W; sprayer gas flow (high-clean Ar) within 0.75 - 1.0 l/min; ion lens voltage < 11 V; and level of doubly charged and oxide ions < 2.5%. A geological sample weighing up to 100 mg in a polystyrene hermetically sealed test tube mixed with distilled acids (HN0₃, HF, HCl 5 ml each) has been exposed to water bath at a temperature of 50°C - 60°C until fully dissolved. No HCl has been added during opening of sulphide minerals. When opening the sample, we have registered an increased pressure of acid and nitrogen oxide vapour that suppressed the volatility of the components in the sample. The chilled sample has been mixed with 0.1 ml H₂O₂, and the dissolved sample was diluted with 2% HNO₃. The level of total REE content in the blank sample was <0.5 ppb (see the REE spectrum in Figure 1, Curve 7). This blank sample qualifies the level of analytical accuracy and the limit of element detection.

Since the samples have yielded high concentrations of those elements that may cause a matrix effect and ion interference, the calibration curves have been plotted with interfering agent added to the blank calibration solution. The multicomponent standard solutions by Perkin Elmer (“Multi-element ICP-MS Calibration Std”) have been used. The sample itself has been selected as an interfering agent. The amount of the interfering agent has been chosen so that the macrocomponent concentration after mixing exceeded the REE concentration in the calibration solution by a factor of 100. The approximation linearity of the REE correction curves is 99.99%. Spectral superimposition has been detected by ELAN 9000 DRC-e MS software, and adjusted by introduction of correction equations (Table 1) into the analytic program defined with reference to natural abundance of REE isotopes. The blank sample solution free from the interfering agent has been used to analyze the solution of the opened sample.

There are only few available national and international publications on this issue [8] [16] due to the lack of the Sm-Nd system investigations. Meanwhile, the study of REE distribution in sulphides of hydrothermal sources in the mid-ocean ridges shows that REEs can be found in the crystal lattice of sulphides [3] [17] [18]. The influence of crystal-chemical parameters of sulphide minerals on the REE accumulation in monomineral sulphide fractions is studied in [19] [20]. One of the conclusions of this research is that REEs may enter the crystal lattice of sulphide minerals with main cations in the lattice being replaced by lanthanides.

The REE study of reference samples has been continued using ICP-MS (ELAN-9000). REE concentrations in apatite (State Standard Sample (SSS) 2463), sulphide from the Talnakh deposit (sample from [8] has been used as a reference) and international reference samples (National Center of Petrographic and Geochemical Research, Nancy, France) have been studied to validate certified values of the REE distribution, using quadrupole mass-spectrometer ELAN 9000 DRC-e (Perkin Elmer, USA) at I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of the Kola Science
Table 1. Results of REE analysis for sulphide minerals.

| Isotope  | Penikat, Finland, pyrite | Talnakh, Russia, chalcopyrite | Overlapping of oxide masses allowed to by ELAN software | Intensity correction subtracted from definite intensity* |
|----------|---------------------------|-------------------------------|------------------------------------------------------|--------------------------------------------------------|
|          | Concentration, ppm | RSD, %, n = 81  | Concentration, ppm | RSD, %, n = 81  |                                                   |                                                  |
| $^{139}$La | $0.63 ± 0.03$  | 4.8  | $0.020 ± 0.001$  | 5.0  |                                                   |                                                  |
| $^{140}$Ce | $1.557 ± 0.007$  | 4.0  | $0.050 ± 0.003$  | 6.0  |                                                   |                                                  |
| $^{141}$Nd | $0.194 ± 0.004$  | 2.1  | $0.0092 ± 0.0008$  | 8.7  |                                                   |                                                  |
| $^{142}$Sm | $0.82 ± 0.03$  | 3.7  | $0.054 ± 0.003$  | 5.6  |                                                   |                                                  |
| $^{151}$Eu | $0.144 ± 0.007$  | 4.9  | $0.028 ± 0.002$  | 7.1  |                                                   |                                                  |
| $^{152}$Gd | $0.0147 ± 0.0005$  | 3.4  | $0.0066 ± 0.0006$  | 9.1  |                                                   |                                                  |
| $^{157}$Sm | $0.0794 ± 0.0012$  | 1.5  | $0.0460 ± 0.0005$  | 1.1  |                                                   |                                                  |
| $^{159}$Tb | $0.010 ± 0.001$  | 10  | $0.0076 ± 0.0007$  | 9.2  |                                                   |                                                  |
| $^{160}$Yb | $0.044 ± 0.002$  | 4.5  | $0.047 ± 0.003$  | 6.4  |                                                   |                                                  |
| $^{161}$Ho | $0.0068 ± 0.0006$  | 8.8  | $0.0095 ± 0.0006$  | 6.3  |                                                   |                                                  |
| $^{164}$Tm | $0.0165 ± 0.0005$  | 3.0  | $0.025 ± 0.002$  | 8.0  |                                                   |                                                  |
| $^{166}$Yb | $0.0022 ± 0.0002$  | 9.1  | $0.0029 ± 0.0003$  | 10.3 |                                                   |                                                  |
| $^{170}$Lu | $0.0089 ± 0.0005$  | 5.6  | $0.019 ± 0.001$  | 5.3  |                                                   |                                                  |
| $^{174}$Y | $0.0013 ± 0.0001$  | 7.7  | $0.0022 ± 0.0002$  | 9.1  |                                                   |                                                  |
| $^{178}$Yb | $0.150 ± 0.006$  | 4.0  | $0.34 ± 0.03$  | 8.8  |                                                   |                                                  |

*Equation factors are reported by Timofeev [7].

Centre, Russian Academy of Sciences, Apatity. Chemical and analytical conditions of the sample decomposition are described in [8]. The fitted conditions of the sample decomposition and analysis have provided an opportunity to determine REE concentrations in samples of reference rocks. The obtained results validate certified values (Figure 1, Figure 2).

REE analyses of sulphides from the PGE reef of the Passivaara (Finland).

Further, the Sm-Nd isotope and geochronological study has been provided for sulphide minerals and whole-rock samples from the ore-bearing gabbronorite of the Penikat layered intrusion, Finland. The research indicates considerable concentrations of REE, including Sm and Nd, in sulphides and whole rock from these gabbronorites used in the Sm-Nd isotope analysis (Figure 3, Table 1, Table 2).

The REE spectra analysis in sulphide minerals reflects a distribution trend similar to the studied whole rock samples. Thus, it supports the conclusion that the REE distribution style in sulphides is inherited from the parental rock, and sulphides formed at a stage of rock crystallization. This is corroborated by age-related isotope and geochronological Sm-Nd data obtained for the ore-bearing gabbronorites from this intrusion.

In the current research, concentrations of REE have been estimated. Accord-
According to these data, the concentration of Ba is 10.6 ppm (**Table 1**). Meanwhile, concentrations of Ba in the geological standard samples are up to 391, 60 and 37 ppm in diorite, granite, and anorthosite respectively. Such Ba concentrations have not affected the procedure of analysis, because the level of oxide ions concentration in plasma can be adjusted during the analysis. In addition, the sample has yielded high content of Si, Fe, Al, Mg, Ca, Na, K, Ti, and P ions that display

![Figure 2. REE distribution in sulphides from the Talnakh deposit.](image1)

**Figure 2.** REE distribution in sulphides from the Talnakh deposit.

![Figure 3. REE distribution in sulphides and whole rock from ore-bearing gabbronorite in the Penikat layered intrusion (Finland).](image2)

**Figure 3.** REE distribution in sulphides and whole rock from ore-bearing gabbronorite in the Penikat layered intrusion (Finland).
higher affinity with oxygen than Ba. Besides, a Ba-bearing agent in the calibration solution allows considering Ba oxide and hydroxide spectra that are superimposed on Sm and Eu.

The REE spectrum for SSS of apatite shows that the uncertified values for Gd, Er and Tm (Figure 4, Curve 1, a) do not conform with the gentle incline of the curve, unlike those obtained in the current research (Figure 4, Curve 1, 6). The uncertified values for Ho and Lu have been validated by our studies and correspond to the gentle incline of the REE distribution curve (La → Lu). It can be suggested that the uncertified values of Ho and Lu concentrations in SSS 2463 agree with the real values, while the uncertified values for Gd, Er and Tm stated in the certificate of the state standard samples seem to be exaggerated. Estimations of REE concentrations for the world-class geological standard samples conform with the certified values (Figure 4, Curves 2 - 4). Fitted and approved conditions of the sample opening and analysis on the on geological composition standard samples have confirmed the possibility to measure REE concentrations without preliminary mineral matrix separation. This allowed analyzing the sulphides of the Talnakh deposit (Russia) and Penikat layered intrusion (Finland). As opposed to the results of REE analysis in the chalcopyrite of the Talnakh deposit [3], higher concentrations of Ce, La, Nd and P have been obtained. The results are shown in Table 1; the REE mineral/chondrite spectra are plotted (Figure 4, Curves 5 and 6 c, 5).

### Table 2. REE concentrations in sulphides and rock samples from gabbronorite of the Passivaara reef of the Penikat layered intrusion (Finland).

|        | Concentration, ppm |
|--------|---------------------|
|        | Chalcopyrite | Electromagnetic pyrite | Nonelectromagnetic pyrite | Pyrrhotite | WR |
| La     | 1.032 | 1.493 | 2.926 | 0.974 | 8.310 |
| Ce     | 2.077 | 3.582 | 6.371 | 2.240 | 19.192 |
| Pr     | 0.240 | 0.464 | 0.823 | 0.290 | 2.533 |
| Nd     | 0.863 | 1.838 | 3.524 | 1.260 | 10.968 |
| Sm     | 0.180 | 0.295 | 0.620 | 0.290 | 2.018 |
| Eu     | 0.034 | 0.042 | 0.124 | 0.060 | 0.396 |
| Gd     | 0.279 | 0.323 | 0.687 | 0.230 | 2.305 |
| Tb     | 0.033 | 0.036 | 0.078 | 0.030 | 0.320 |
| Dy     | 0.210 | 0.220 | 0.482 | 0.160 | 1.830 |
| Ho     | 0.045 | 0.048 | 0.092 | 0.030 | 0.401 |
| Er     | 0.123 | 0.138 | 0.300 | 0.080 | 1.033 |
| Tm     | 0.020 | 0.022 | 0.040 | 0.010 | 0.131 |
| Yb     | 0.127 | 0.140 | 0.282 | 0.070 | 0.770 |
| Lu     | 0.019 | 0.021 | 0.040 | 0.010 | 0.110 |
Sm-Nd isotope analysis of sulphides

Sulphide minerals (pyrite, pentlandite, chalcopyrite, etc.) have been prepared for further Sm-Nd analysis using a modified [21] classic [22] technique. To decompose sulphides, a weighted portion (20 to 50 mg) is mixed with a $^{148}$Sm/$^{150}$Nd tracer solution, treated with aqua regia ($\text{HCl} + \text{HNO}_3$) until complete decomposition and evaporated dry. Afterwards, it is converted to chlorides through evaporating the sample in 4.5 - 6 N HCl. After the fractional acid decomposition, the dry residue is dissolved in ~1 ml 2.3 N HCl, while total REEs are separated from the solution via cation-exchange chromatography. A stepwise elution method is applied to 2.3 and 4.5 N HCl in a chromatographic column with cation-exchange resin Dowex 50 × 8 (200 - 400 mesh). The separated REE fraction is evaporated dry, dissolved in 0.1 N HCl and loaded to the second column with KEL-F solid ion-exchange resin HDEHP. The resin is used to separate Sm and Nd. The selected Sm and Nd fractions are evaporated to get prepared for further mass-spectrometric analysis. All the measurements of the Nd isotope composition and Sm and Nd concentrations using an isotope dilution technique have been performed at a 7-channel solid-phase mass-spectrometer Finnigan-MAT 262 (RPQ) in a static double-band mode in collectors, using Ta + Re filaments. Re filaments have been used as ionizers; the sample has been applied to the Ta filament with a preliminarily deposited diluted $\text{H}_3\text{PO}_4$ microdrop. The reproducibility error for 11 Nd isotope composition determinations of La Jolla = 0.511833 ± 6 (2$\sigma$, N = 11) has been within 0.0024% (2$\sigma$). The same error has been obtained for 44 parallel analyses of a new Japanese standard, JNd,1 = 0.512072 ± 2 (2$\sigma$, N = 44). The error in $^{147}$Sm/$^{144}$Nd ratios is accepted for the static calculation of the Sm and Nd concentrations in BCR-1 to be 0.2% (2$\sigma$), which is an average of 7 measurements. The blank intralaboratory contamination in Nd and Sm is 0.3 ng and 0.06 ng, respectively. The measured Nd isotope ratios have been
normalized per \(^{148}\text{Nd}/^{144}\text{Nd} = 0.241570\) and afterwards recalculated for \(^{143}\text{Nd}/^{144}\text{Nd}\) in La Jolla = 0.511860. Isochron parameters have been computed using K. Ludwig programs [22]. The decompositions constants are as per [12].

Values of \(\varepsilon_{\text{Nd}}\) have been calculated according to [14] for a one-stage model and according to [23] for a two-stage model.

**U-Pb and Sm-Nd isotope dating of the Sompuyarvi PGE reef of the Penikat intrusion**

Single zircon crystals have been sampled for further U-Pb dating. The crystals are elongated prismatic (up to 180 µm in size), colored dark brown (Figure 5(b)). Coordinates of the two points occur on the U-Pb concordia and reflect the similar age of 2430 ± 2 Ma (Figure 5, Table 3).

The isochron Sm-Nd age on sulphide minerals, plagioclase, clinopyroxene and

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![Figure 5](image-url). Mineral Sm-Nd isochron for PGE-bearing gabbro-norite (a) and U-Pb age on single zircon (b) from the Penikat layered intrusion (Finland).

**Table 3.** Isotope Sm-Nd data on whole rocks, rock-forming and sulphide minerals from PGE-bearing gabbro-norite of the Penikat layered intrusion (Finland).

| Concentration, ppm | Isotope ratios | Model age, Ma | \(\varepsilon_{\text{Nd}}\) |
|--------------------|----------------|---------------|--------------------------|
|                    | Sm  | Nd  | \(^{147}\text{Sm}/^{144}\text{Nd}\) | \(^{143}\text{Nd}/^{144}\text{Nd}\) | Err. | CHUR | DM |                 |
| Whole rock          | 2.004 | 10.066 | 0.14938 | 0.511811 | 28 | 2655 | 3155 | −1.4 |
| Plagioclase         | 0.654 | 3.655 | 0.07654 | 0.510639 | 22 |      |      |     |
| Clinopyroxene       | 1.901 | 6.398 | 0.17956 | 0.512285 | 9  |      |      |     |
| Chalcopyrite        | 0.109 | 0.647 | 0.13085 | 0.511499 | 53 |      |      |     |
| Pyrrhotite          | 0.301 | 2.017 | 0.17299 | 0.512185 | 47 |      |      |     |
| Sulphide mix        | 0.114 | 0.709 | 0.12648 | 0.511431 | 46 |      |      |     |

Average standard values during measurements: N = 7 (La Jolla: = 0.511836 ± 12); N = 21 (JNd1: = 0.512097 ± 15).
whole rocks is 2426 ± 38 Ma (Figure 5(a), Table 3). This age complies within the error with the earlier obtained age of the Penikat intrusion to be 2410 ± 64 Ma [17]. It is especially important that figurative sulphide points lie on the isochron that corroborates the idea of the sulphide genesis and rock crystallization.

U-Pb isotope data on single zircon from the studied gabbronorite show the age of 2430 ± 2 Ma, which is much coeval to the Sm-Nd age. A thin magmatic zonation has been detected in all of the zircon grains, using the cathodoluminescence technique (Figure 5(b), Table 4).

4. Conclusions

The U-Pb isotope dating of zircons from gabbronorites of the PGE reef of the Penikat and Sompuyarvi intrusions (Finland) has been provided. The conducted research implies the following:

- the pattern of the REE distribution in sulphide minerals from gabbronorite of the Penikat layered intrusion is inherited from the parental magma melt, while sulphides formed at the very same time with the rocks of the massif, as confirmed by the Sm-Nd isotope and geochronological data;
- along with rock-forming minerals, sulphide with a high mineral genesis temperature [24] can be used for the Sm-Nd isotope dating of ore-bearing mafic-ultramafic intrusions;
- the study shows a possibility to analyze REE in sulphide minerals (Talnakh deposit, Russia, and PGE Penikat layered intrusion, Finland) on ELAN 9000 DRC-e (Perkin Elmer, USA) with no preliminary separation of the mineral matrix; as a result, the REE distribution spectra have been obtained;
- the concentration of Sm and Nd in sulphide minerals (Penikat, Finland) is high enough to be detected by the Sm-Nd isotope analysis;
- the REE distribution spectra have been obtained for SSS 2463 to estimate concentrations of Gd, Er and Tm.

Isotope Sm-Nd data on rock-forming and sulphide minerals show the age much similar to the U-Pb single zircon age. Thus, we may suggest that minerals had a narrow range of closure temperatures.

Future U-Pb isotope dating will use not only zircon. It is planned to introduce baddeleyite to compare the temperature of the U-Pb and Sm-Nd systematics

| №  | Weight mg | Concentration (ppm) | Isotope composition* | Isotope ratios and age in Ma** |
|----|-----------|---------------------|----------------------|--------------------------------|
|    |           | Pb      | U   | 206Pb/238U | 207Pb/235U | 207Pb/206Pb | 206Pb/238U | 207Pb/235U | 207Pb/206Pb | 206Pb/238U | 207Pb/235U | 207Pb/206Pb | % Dis |
| Gabbronorite of Penikat |
| 1  | 0.136     | 24.87   | 33.26 | 260.12 | 0.458 ± 0.004 | 9.929 ± 0.138 | 0.157 ± 0.002 | 2429 ± 21 | 2428 ± 34 | 2428 ± 24 | −0.04 |
| 2  | 0.184     | 28.14   | 42.74 | 254.48 | 0.457 ± 0.004 | 9.845 ± 0.138 | 0.156 ± 0.002 | 2426 ± 21 | 2420 ± 34 | 2416 ± 24 | −0.41 |

*The ratios are corrected for blanks of 1 pg for Pb and 10 pg for U and for mass discrimination 0.12% ± 0.04%. **Correction for common Pb has been estimated for the age, according to Stacey and Kramers [10].

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closure. These studies are considered valuable, since there are almost no such data in the world practice.

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**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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