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Sulfur isotope signatures of sulfides from the Khibina and Lovozerо massifs (Kola Alkaline Province, Fennoscandian Shield)

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Abstract

The sulfur isotope geochemistry of the Khibina and Lovozerо aigaitic massifs provides an opportunity to understand the role of plume-lithosphere interaction processes responsible for the Paleozoic alkaline igneous activity in the north-eastern part of the Fennoscandian Shield. The stable sulfur isotope $\delta^{34}\text{S}$ analysis using triple collector isotope ratio mass spectrometer (IRMS) has been carried out on the pentlandite, chalcopyrite and pyrite from nepheline syenites. The $\delta^{34}\text{S}$ values for pentlandite from Khibina rocks range from +0.69 to +2.06 ‰ relative to the Vienna Canyon Diablo Troilite standard (VCDT), and the pyrite has significantly higher $\delta^{34}\text{S}$ values up to +4.92 ‰ VCDT. The pentlandite from the Lovozerо samples has value +1.48 ‰ VCDT, $\delta^{34}\text{S}$ values of chalcopyrite is +2.85 ‰ VCDT. The maximum positive $\delta^{34}\text{S}$ values are obtained for Lovozerо pyrite, which vary from +5.41 to +6.30 ‰ VCDT. Comparison of sulfur-geochemical features of Khibina and Lovozerо nepheline syenite with $\delta^{34}\text{S}$ data for the carbonatites from the Khibina, Sallanlatvi, Seblyavr, Vuoriyarvi, Salmagora and Kovdor massifs show later carbonatite formation relatively to associated alkaline rocks. Geochemical sulfur isotope $\delta^{34}\text{S}$ investigations emphasizes that parental magmas of the Khibina and Lovozerо alkaline massifs were derived from a metasomatized subcontinental lithospheric mantle (SCLM). We suggest that high- $\delta^{34}\text{S}$ signature on the SCLM ($\delta^{34}\text{S}$ of +1 to +6 ‰ VCDT) can be explained by subduction of the high- $\delta^{34}\text{S}$ Archaean crust.

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Изотопные характеристики серы сульфидов Хибинского и Ловозерского массивов (Кольская щелочная провинция, Фенноскандинавский щит)

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Реферат

Геохимия изотопов серы Хибинского и Ловозерского агапитовых массивов дает возможность понять роль плум-литосферных процессов, ответственных за палеозойскую щелочную магматическую активность в северо-восточной части Фенноскандинавского щита. Изотопный состав серы ($\delta^{34}\text{S}$) получен для пентландита, халькопирита и пирита из нефелиновых сиенитов с использованием масс-спектрометра с тройным коллектором (IRMS). Значения $\delta^{34}\text{S}$ пентландита из пород Хибинского массива варьируют от +0,69 до +2,06 ‰ относительно стандарта Вена-Каньон-Дьябло-Троилит (VCDT); значительно выше значения для пирита (+ 4,92 ‰ VCDT). Ловозерский пентландит имеет значение $\delta^{34}\text{S}$, равное +1,48 ‰ VCDT; $\delta^{34}\text{S}$ для халькопирита составляет +2,85 ‰ VCDT. Максимально положительные значения $\delta^{34}\text{S}$ для сульфидов Ловозерского массива получены для пирита (от +5,41 до +6,30 ‰ VCDT). Сравнение полученных данных с данными по изотопии серы для карбонатитов Хибин, Салланлатви, Себльявра, Вуориярви, Салмагоры и Ковдора указывает на более позднее образование карбонатитов относительно связанных с ними щелочных пород. Геохимические исследования изотопов серы показывают, что первичным магматическим источником Хибинского и Ловозерского щелочных массивов является метасоматизированная субконтинентальная литосферная мантия (SCLM). Сделано предположение, что высокие значения $\delta^{34}\text{S}$ для SCLM (от +1 до +6 ‰ VCDT) обусловлены субдукцией архейской коры, обогащенной тяжелым ^{34}S изотопом серы.

Для цитирования

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Introduction

The Kola Alkaline Province (KAP) is one of the largest alkaline-carbonatite associations with more than 30 massifs occupying the Kola region, northern Karelia and Finland (Fig. 1). The main stage of alkaline igneous activity in the north-eastern part of the Fennoscandian Shield was marked by the biggest agpaitic complexes of Khibina and Lovozero with numerous carbonatite intrusions of Kovdor, Sokli, Afrikanda, Turiy Mys which were formed in Late Devonian, at 365–370 Ma. The Khibina apatite-nepheline deposits with Lovozero REE commercial mineralization make a great contribution to the mineral resource base of the Arctic zone of the Russian Federation. Geophysical and geological data based on a prospecting drilling program give evidence for significant differences in the internal structure of two giant polyphase magmatic bodies, and commercial mineralization enclosed in these intrusions (*Kramm et al., 1993; Kogarko et al., 2019*).

The Khibina massif is a dome-shaped mountain massif, situated in the central part of the Kola Peninsula. It's located within Archaean gneisses and Proterozoic Pechenga-Imandra-Varzuga palaeoriftogenic volcanic-sedimentary complexes (Fig. 1). In the Khibina massif, peralkaline K-Na and K nepheline syenites are intercalated with the members of the typical ultrabasic-alkaline and carbonatite series. The Khibina massif is a concentrically zoned multiphase intrusion composed of agpaitic nepheline syenites and in a minor amount of ultrabasic alkaline rocks. The zone of fenitized rocks extends for 50–200 m. Numerous nepheline syenite veins and alkaline pegmatites penetrated the country rocks at a distance of more than 100 m from the contact (*Arzamastsev et al., 2008*).

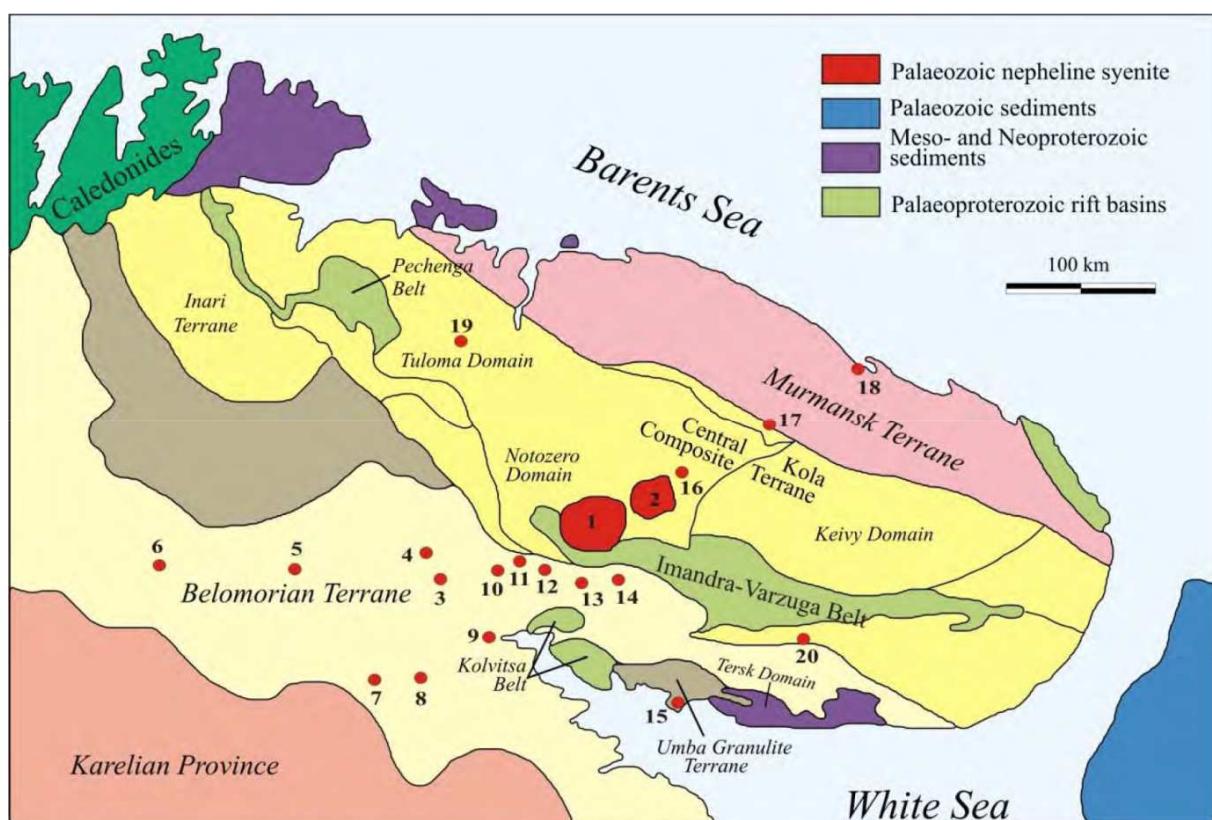


Fig. 1. Scheme of the locations of Kola Alkaline Province intrusions (*Arzamastsev et al., 2008*):
 1 – Khibina; 2 – Lovozero; 3 – Niva; 4 – Mavraguba; 5 – Kovdor; 6 – Sokli; 7 – Sallanlatva;
 8 – Vuoriyarvi; 9 – Kandaguba; 10 – Afrikanda; 11 – Ozernaya varaka; 12 – Lesnaya varaka;
 13 – Salmagora; 14 – Ingозero; 15 – Turiy Mys; 16 – Kurga; 17 – Контозеро; 18 – Ивановка;
 19 – Себльяvr; 20 – Pesochny

Рис. 1. Схема расположения интрузий Колыской щелочной провинции (*Arzamastsev et al., 2008*):
 1 – Хибины; 2 – Ловоzero; 3 – Нива; 4 – Маврагуба; 5 – Ковдор; 6 – Сокли; 7 – Салланлатва;
 8 – Вуориярви; 9 – Кандагуба; 10 – Африканда; 11 – Озерная варака; 12 – Лесная варака;
 13 – Салмагора; 14 – Ингозеро; 15 – Турый Мыс; 16 – Курга; 17 – Контозеро; 18 – Ивановка;
 19 – Себльявр; 20 – Песочный

The Lovozero intrusive complex has the form of a laccolith with a broad base. The drilling program combined with three-dimensional modeling of gravity data made it possible to decipher the internal structure of the massif down to the depth of 10 km. According to these data, the Lovozero massif consists of two zones principally different in density. In the Lovozero massif, agpaitic lujavrites (type locality) form a rhythmic layered complex similar to that in Ilmaussaq, Greenland. A south-western zone, composed of agpaitic syenite to a depth of at least 10 km, is the most probable locus of the magma conduit. In the central part of the massif, at the Seidjavr Lake, a local negative gravity anomaly was detected, which corresponds to a body of alkaline and analcime syenite. A north-eastern zone is suggested to be composed of ultrabasic alkaline rocks similar to that of the adjacent Kurga alkaline-ultramafic massif. The south-eastern, southern, and western contacts of the massif are almost vertical to a depth of 4 km within the nepheline syenite zone but become sloping more gently at depths below 8–10 km. The northern and north-western contacts dip at smaller angles, which vary from 50–60° at the surface to 30–40° at depths of 4–5 km but become nearly vertical from this level to depths of 9–10 km. The alkaline rocks forming the Lovozero massif are represented by plutonic, subvolcanic, and volcanic magma products (*Arzamastsev et al., 2008*).

Alkaline rocks are a powerful data set for understanding connections between surface and mantle sulfur reservoirs over geological timescales. Alkaline magmas (silicate rocks and carbonatites) are associated with mantle plumes (*Sasada et al., 1997; Marty et al., 1998; Ernst et al., 2010*) and/or sub-continental lithospheric mantle (*Goodenough et al., 2002; Downes et al., 2005*) that has been metasomatised by fluids and melts derived from previously subducted slabs. Evolved alkaline rocks are also rich in sulfur-bearing minerals, which reflect the high solubility of sulfur in carbonatic and alkaline silicate melts (*Babielska et al., 2018*). There have been a large number of sulfur isotope investigations of alkaline complexes, few have thoroughly investigated how crustal contamination, degassing and fluid evolution (i. e. changes in temperature-pH-fO₂) altered the primary mantle signature. Understanding these processes is critical to unlocking the alkaline record of magma sources. Global data compilation reveals that δ³⁴S of alkaline magma sources fall between –5 and +5 ‰ VCDT. The igneous δ³⁴S time-series shows a temporal trend with Proterozoic alkaline magmas largely restricted to positive δ³⁴S values (0 – +5 ‰ VCDT) and Phanerozoic suites showing greater δ³⁴S diversity from –5 to +4 ‰ VCDT (*Hutchison et al., 2019*). Here, we present a study of sulfur isotope signatures of the Khibina and Lovozero massifs and demonstrate that an enriched subduction-influenced source (δ³⁴S of +1 to +6 ‰ VCDT) can be reconstructed for the Kola alkaline province of the Fennoscandian Shield.

Materials and methods

The Khibina rock samples (01CH, 04CH and 10CH) were taken from massive nepheline syenite from Mt. Rasvumchorr outcrops. The Lovozero eudialyte-bearing nepheline syenites (01LV, 03LV, 04LV and 05 LV) were collected from the classical outcrops of lujavrite-foyaite-urtite rhythms, exposed at the foot of the western slope of Mt. Alluaiv (Fig. 2). These samples were described by petrography investigation in transmitted and reflected light with the polarized optical microscope Leica DM2500P (Fig. 3) and examined on the scanning electron microscope Hitachi SU6600 with the energy dispersion spectroscope (EDS) mode. The sulfide minerals have been chemically characterized by electron microprobe analysis. For the sulfur isotopes analysis the sulfide grains were hand-picked using a binocular magnifying glass, so the contamination of the accompanying sulfide phases was not excluded. These studies were implemented at the Department of Geology and Soil Science at the Faculty of Earth Sciences and Spatial Management of the Maria Curie-Skłodowska University (UMCS, Lublin, Poland).

The stable sulfur isotopes δ³⁴S study was carried out on the pentlandite ((Fe, Ni)₉S₈, samples 01CH, 10CH) and pyrite (FeS₂, sample 04CH) from Khibina nepheline syenite and on the pentlandite ((Fe, Ni)₉S₈, sample 04LV), chalcopyrite (CuFeS₂, sample 03LV) and pyrite (FeS₂, samples 01LV, 05LV) from Lovozero eudialyte-bearing nepheline syenite. Sulfur isotope analysis was undertaken at the Mass Spectrometry Laboratory of the Institute of Physics of the Maria Curie-Skłodowska University (UMCS, Lublin, Poland) by triple collector isotope ratio mass spectrometer (IRMS), using SO₂ as the analyzed gas. The sulfide mineral specimens were quantitatively converted to SO₂ in a vacuum line by their oxidation with analytical grade CuO reagent at temperatures between 800 and 900 °C. Along with the analyzed specimens, an aliquot of 20 mg of the IAEA-S1 standard (Ag₂S) was converted to SO₂ and analyzed using the mass spectrometer. All results are reported here in standard delta notation as per mil deviations from the Vienna-defined Canyon Diablo Troilite (VCDT). The precision of δ³⁴S values was 0.05 ‰.

Results and discussion

The Khibina massive nepheline syenites have coarse-grained structure and poikilitic texture (Fig. 3, *a*, *b*). The main minerals are automorphic orthoclase, plagioclases, and apatite, among which can be found crystals of aegirine-acmite and xenomorphic crystals of eudialyte. There are also present ilmenite, titanite, magnetite, arfvedsonite, riebeckite, astrophyllite, aenigmatite and lorenzenite. Among the ore minerals it can be found the vast majority of ilmenite, titanite and magnetite. In addition there are relatively often encountered sulfide phases such as pyrite (about 4 %) and in an amount of less than 1 % – chalcopyrite, pentlandite, and arsenopyrite. Chalcozinc and sphalerite are also noticed in some samples. The sulfide phases from Khibina samples – pentlandite ((Fe, Ni)₉S₈, samples 01CH, 10CH) and pyrite (FeS₂, sample 04CH) – show a large spread in $\delta^{34}\text{S}$ values from +0.69 to +4.92 ‰ VCDT. The $\delta^{34}\text{S}$ values for two analysis of pentlandite range from +0.69 to +2.06 ‰, and the pyrite has significantly higher $\delta^{34}\text{S}$ values up to +4.92 ‰ VCDT (Table).

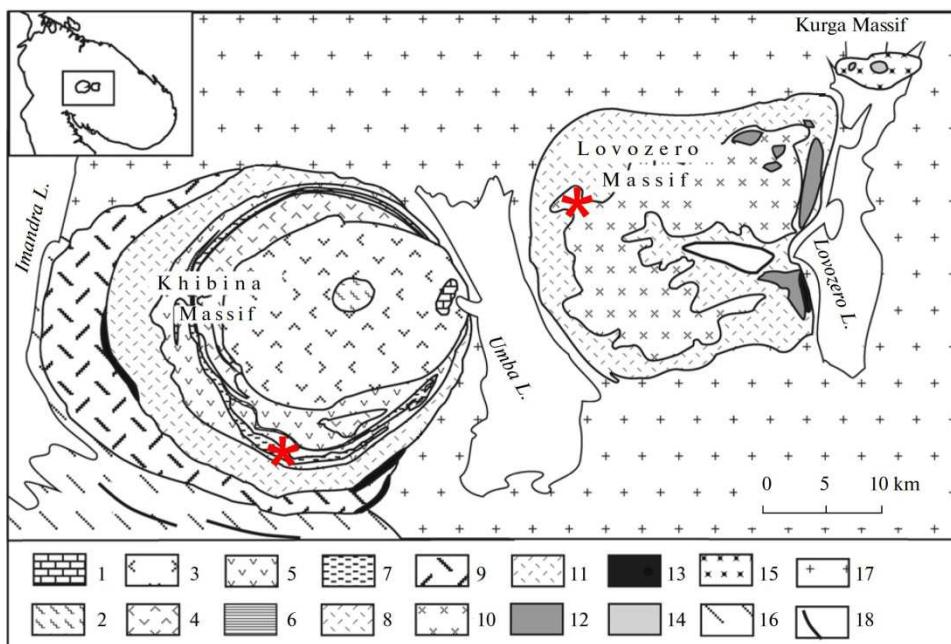


Fig. 2. Schematic geological map of the Khibina and Lovozerо massifs (Arzamastsev et al., 2011).

Khibina massif: 1 – carbonatite; 2 – pulaskite; 3 – foyaite; 4 – nepheline syenite; 5 – massive rischorrhit, jovite and urtite; 6 – apatite-nepheline rock; 7 – ijolite and melteigite; 8 – coarse-grained trachyoid nepheline syenite; 9 – coarse-grained massive nepheline syenite (khibinite). Lovozerо massif: 10 – eudialyte lujavrite; 11 – lujavrite, foyaite and urtite of the differentiated complex; 12 – volcanic rocks of the Lovozerо Formation; 13 – alkaline-ultramafic rocks. Kurga massif: 14 – nepheline syenite; 15 – peridotite. Host rocks: 16 – basaltic porphyry and dolerite (Late Proterozoic); 17 – granodiorite, tonalite, and trondhjemite (Archean); 18 – dikes of alkaline rocks. The stars indicate the sampling locations

Рис. 2. Схематическая геологическая карта Хибинского и Ловозерского массивов (Arzamastsev et al., 2011).

Хибинский массив: 1 – карбонатит; 2 – пуласкит; 3 – фойяит; 4 – нефелиновый сиенит; 5 – массивные рисчоррит, ювит и уртит; 6 – апатит-нефелиновая порода; 7 – ийолит и мельтейгит; 8 – крупнозернистый трахитоидный нефелиновый сиенит; 9 – крупнозернистый массивный нефелиновый сиенит (хибинит). Ловозерский массив: 10 – эвдиалитовый луяврит; 11 – луяврит, фойяит и уртит дифференцированного комплекса; 12 – вулканические породы ловозерской свиты; 13 – щелочно-ультраосновные породы. Кургинский массив: 14 – нефелиновый сиенит; 15 – перидотит.

Вмещающие породы: 16 – базальтовые порфиры и долериты (поздний протерозой);

17 – гранодиорит, тоналит и трондjemит (архей); 18 – дайки щелочных пород.

Звездами показаны места отбора образцов

The Lovozerо eudialyte-bearing nepheline syenites are gray-green color rocks with visible red-blood crystals of eudialyte and fine-crystalline feldspars and aegirine (Fig. 3, *c*, *d*). These rocks have a coarse-grained structure and a porphyritic, linear texture. The orthoclase crystals, twinned according to the Carlsbad law, often have a very elongated form giving the rocks a linear and pseudo-ophitic structure. Between these crystals there are also albite tablets. When an interaction between the minerals occurs, one meets the needles of aegirine in the company of ilmenite and titanomagnetite, as well as individual rutile and titanite grains. The stable sulfur isotopes analyses have been carried out on the three sulfide phases from the Lovozerо samples: pentlandite ((Fe,

Ni_9S_8 , sample 04LV), chalcopyrite (CuFeS_2 , sample 03LV), and pyrite (FeS_2 , samples 01LV, 05LV). The results of the sulfur isotopes study $\delta^{34}\text{S}$ vary widely from +1.48 to +6.30 ‰ VCDT (Table). The pentlandite in the Lovozerovo samples has value +1.48 ‰ VCDT, $\delta^{34}\text{S}$ values of chalcopyrite is +2.85 ‰ VCDT. The maximum positive $\delta^{34}\text{S}$ values are obtained for pyrite, which vary from +5.41 to +6.30 ‰ VCDT (Table).

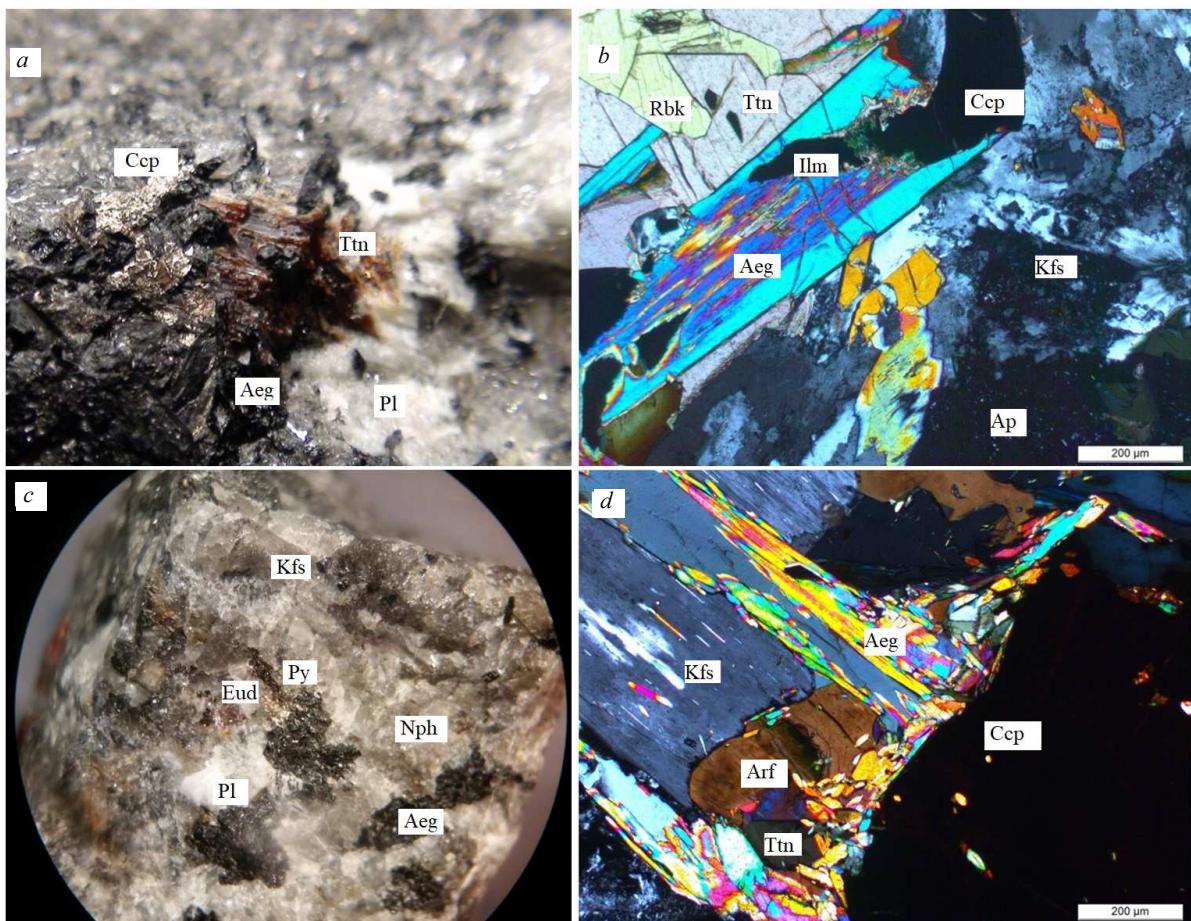


Fig. 3. Photos of the Khibina (a, b – sample 01CH) and Lovozerovo (c, d – sample 04LV) samples of sulfide-bearing nepheline syenite. b, d – photo of the polished thin section in transmitted light. Mineral symbols: Py – pyrite; Ccp – chalcopyrite; Kfs – orthoclase; Pl – plagioclase; Rbk – riebeckite; Aeg – aegirine; Nph – nepheline; Ap – apatite; Arf – arfvedsonite; Eud – eudialyte; Ttn – titanite; Ilm – ilmenite

Рис. 3. Фотографии образцов сульфидсодержащих нефелиновых сиенитов Хибинского (a, b) и Ловозерского массивов (c, d). b, d – фотография полированного шлифа в проходящем свете. Символы минералов: Ру – пирит; Сср – халькопирит; Кfs – ортоклаз; Pl – плагиоклаз; Rbk – рибекит; Aeg – эгирин; Ne – нефелин; Ap – апатит; Arf – арфведсонит; Eud – эвдиалит; Ttn – титанит; Ilm – ильменит

Table. $\delta^{34}\text{S}$ isotope data for sulfides from nepheline syenite of the Khibina and Lovozerovo massifs

Таблица. Изотопные $\delta^{34}\text{S}$ данные для сульфидов из нефелиновых сиенитов

Хибинского и Ловозерского массивов

Massif	Khibina			Lovozero			
Sample	01CH	10CH	04CH	04LV	03LV	01LV	05LV
Mineral	Pn	Pn	Py	Pn	Ccp	Py	Py
$\delta^{34}\text{S}_{\text{VCDT}} (\text{\textperthousand})$	0.69	1.90–2.06	4.80–4.92	1.48	2.85	5.41	5.45–6.30

Variation in the $\delta^{34}\text{S}$ signature can be explained by changes in the redox conditions, fluid sources, and/or the temperature of the hydrothermal fluid. The ranges in $\delta^{34}\text{S}$ values are generally large but vary according to the isotopic fractionation between the sulfide phase and the melt or fluid. This is evidenced by mineral associations, including numerous sulfide minerals such as pentlandite, chalcopyrite and pyrite, which are accompanied by

arsenopyrite, sphalerite and barite. The admixture of these minerals among the analyzed sulfides contributed to the isotopic contamination of sulfur and changes in $\delta^{34}\text{S}$. Almost invariably, there is a decrease in $\delta^{34}\text{S}$ between early and later formed sulfides within a given system (Hutchison et al., 2019). For example, the sulfur isotopic composition ($\delta^{34}\text{S}$) of galena (PbS) from the carbonatites (Khibina, Sallanlatvi, Seblyavr, Vuoriyarvi and Kovdor), as well as from hydrothermal veins of the Khibina massif is significantly lighter than the mantle value of 0 ‰ VCDT (Bell et al., 2015; Hutchison et al., 2019). Conversely, the nepheline syenites which belong to the early magmatic rocks of Khibina and Lovozerо massifs contain sulphides with positive $\delta^{34}\text{S}$ values (Table, Fig. 4).

Geochemical sulfur isotope $\delta^{34}\text{S}$ investigations emphasize that parental magmas of the Khibina and Lovozerо alkaline massifs were derived from a metasomatized sub-continental lithospheric mantle (Fig. 4). These results correlate with the previous studies, which have shown that the isotopic composition of the carbonatites, alkaline rocks, and rare-metal ores estimated indicates that many of them have mantle sources. It was recently confirmed by the work on the Pb-isotopic composition of the alkaline rocks from the KAP (Kogarko et al., 2019). Earlier, the noble gas isotopic data of carbonatites also confirm that the KAP was likely related to a lower mantle plume (Tolstikhin et al., 2002; Marty et al., 1998), and radiogenic isotopes also support ancient (potentially Archaean) sources (Bell et al., 2015). The published isotopic data indicate multistage evolution of the Khibina – Lovozerо volcanic and plutonic system. First of all, at the premagmatic stage 427±6 Ma ago the plume triggered mantle metasomatism that preceded the vigorous Paleozoic magmatism (Arzamastsev et al., 2011). The impact of the plume on the upper mantle metasomatically altered under subduction conditions entailed the interaction of the plume and subduction sulfur-enriched component ($\delta^{34}\text{S}$ of +1 to +6 ‰ VCDT) in the magma source. Since subduction exerts an important control on SCLM composition, this would suggest that high- $\delta^{34}\text{S}$ Archaean crust were subducted and imprinted a high- $\delta^{34}\text{S}$ signature on the SCLM. There is hypothesis argues that a missing Archaean sulphur pool, injected into the mantle at ancient subduction zones and stored in the deep mantle, occasionally recycled back to the near surface in mantle plumes (Farquhar et al., 2016). Thus, our favored hypothesis is that parental magmas of the Khibina and Lovozerо alkaline massifs are associated with subcontinental lithospheric mantle that has been metasomatised by fluids and melts derived from previously subducted slabs.

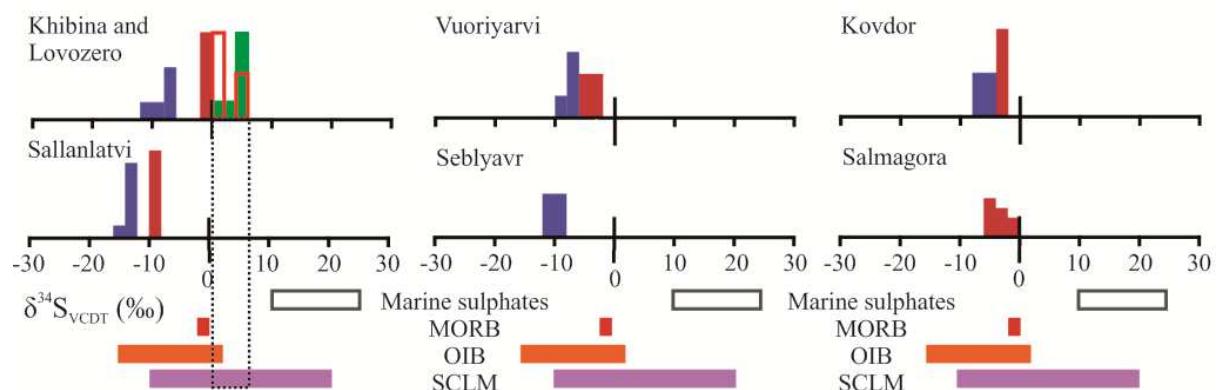


Fig. 4. Compilation of stable sulfur isotopes $\delta^{34}\text{S}$ data for sulfides from the Khibina nepheline syenite (red outlined bars) and Lovozerо nepheline syenite (green filled bars) with $\delta^{34}\text{S}$ data for galena (PbS) from the carbonatites (red and blue filled bars) from the Khibina, Sallanlatvi, Seblyavr, Vuoriyarvi, Salmagora, and Kovdor massifs. Normalized histograms show early- (red) and late-stage (blue) $\delta^{34}\text{S}$ for galena from the carbonatites (Bell et al., 2015; Hutchison et al., 2019). The $\delta^{34}\text{S}$ values of potential sulfur sources are shown by the bars at the base of the plot and include marine sulfates (Farquhar et al., 2010); MORB – mid-ocean ridge basalt (Labidi et al., 2012); OIB – ocean island basalt (Labidi et al., 2015; Cabral et al., 2013; Delavault et al., 2016); SCLM – sub-continental lithospheric mantle (Giuliani et al., 2016)

Рис. 4. Обобщение данных по стабильным изотопам серы $\delta^{34}\text{S}$ для сульфидов из нефелиновых сиенитов

Хибинского (красные, не залитые блоки) и Ловоzerского (зеленые блоки) массивов
 и для галенита (PbS) из карбонатитов (красные и синие блоки) Хибинского, Салланлатви, Себльярв,
 Вуориьярви, Салмагора и Ковдорского массивов. Нормализованные гистограммы показывают раннюю (красный) и позднюю стадии (синий) $\delta^{34}\text{S}$ для галенита из карбонатитов (Bell et al., 2015; Hutchison et al., 2019). Значения $\delta^{34}\text{S}$ потенциальных источников серы показаны интервалами в основании графика и включают: морские сульфаты (Farquhar et al., 2010); MORB – базальты срединно-океанического хребта (Labidi et al., 2012); OIB – базальты океанических островов (Labidi et al., 2015; Cabral et al., 2013; Delavault et al., 2016); SCLM – субконтинентальная литосферная мантия (Giuliani et al., 2016)

Conclusion

The sulfur isotope geochemistry of the two world biggest agpaitic complexes of the Khibina and Lovozero, which are the key magmatic centers of the Paleozoic KAP, provides an opportunity to understand the role of plume-lithosphere interaction processes responsible for the alkaline igneous activity in the north-eastern part of the Fennoscandian Shield. The stable sulfur isotope $\delta^{34}\text{S}$ study has been carried out on the pentlandite ((Fe, Ni)₉S₈) and pyrite (FeS₂) from Khibina nepheline syenite and on the pentlandite ((Fe, Ni)₉S₈), chalcopyrite (CuFeS₂) and pyrite (FeS₂) from Lovozero eudialyte-bearing nepheline syenite. The ranges in $\delta^{34}\text{S}$ values are generally large (from +0.69 to +6.30 ‰ VCDT), but vary according to the isotopic fractionation between the sulfide phase and the melt or fluid. Comparison of sulfur-geochemical features of Khibina and Lovozero nepheline syenite with $\delta^{34}\text{S}$ data for the carbonatites from the Khibina, Sallanlatvi, Seblyavr, Vuoriyarvi, Salmagora and Kovdor massifs show later carbonatite formation relatively to associated alkaline rocks. Geochemical sulfur isotope $\delta^{34}\text{S}$ investigations emphasize that parental magmas of the Khibina and Lovozero alkaline massifs were derived from a metasomatized sulfur-enriched ($\delta^{34}\text{S}$ of +1 to +6 ‰ VCDT) subcontinental lithospheric mantle (SCLM). We suggest that high- $\delta^{34}\text{S}$ signature on the SCLM can be explained by high- $\delta^{34}\text{S}$ Archaean crust subduction.

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Conflict of interest

The authors declare no conflict of interest.

References

- Arzamastsev, A. A., Arzamastseva, L. V., Zaraiskii, G. P. 2011. Contact interaction of agpaitic magmas with basement gneisses: An example of the Khibina and Lovozero massifs. *Petrology*, 19, pp. 109–133. DOI: <https://doi.org/10.1134/S0869591111020032>.
- Arzamastsev, A. A., Yakovenchuk, V. N., Pakhomovsky, Ya. A., Ivanyuk, G. Yu. 2008. The Khibina and Lovozero alkaline massifs: Geology and unique mineralization. Apatity, GI KSC RAS.
- Babiel, R., Marks, M. A. W., Neumann, U., Markl, G. 2018. Sulfides in alkaline and peralkaline rocks: Textural appearance and compositional variations. *Neues Jahrbuch für Mineralogie-Abhandlungen: Journal of Mineralogy and Geochemistry*, 195(2), pp. 155–175. DOI: <https://doi.org/10.1127/njma/2018/0095>.
- Bell, K., Zaitsev, A. N., Spratt, J., Frojdo, S. et al. 2015. Elemental, lead and sulfur isotopic compositions of galena from Kola carbonatites, Russia – implications for melt and mantle evolution. *Mineralogical Magazine*, 79(2), pp. 219–241. DOI: <https://doi.org/10.1180/minmag.2015.079.2.01>.
- Cabral, R. A., Jackson, M. G., Rose-Koga, E. F., Koga, K. T. et al. 2013. Anomalous sulphur isotopes in plume lavas reveal deep mantle storage of Archaean crust. *Nature*, 496, pp. 490–493. DOI: <https://doi.org/10.1038/nature12020>.
- Delavault, H., Chauvel, C., Thomassot, E., Devey, C. W. et al. 2016. Sulfur and lead isotopic evidence of relic Archean sediments in the Pitcairn mantle plume. *Proceedings of the National Academy of Sciences (PNAS)*, 113(46), pp. 12952–12956. DOI: <https://doi.org/10.1073/pnas.1523805113>.
- Downes, H., Balaganskaya, E., Beard, A., Liferovich, R. et al. 2005. Petrogenetic processes in the ultramafic, alkaline and carbonatitic magmatism in the Kola Alkaline Province: A review. *Lithos*, 85(1–4), pp. 48–75. DOI: <https://doi.org/10.1016/j.lithos.2005.03.020>.
- Ernst, R. E., Bell, K. 2010. Large igneous provinces (LIPs) and carbonatites. *Mineralogy and Petrology*, 98(1), pp. 55–76. DOI: <https://doi.org/10.1007/s00710-009-0074-1>.
- Farquhar, J., Jackson, M. 2016. Missing Archean sulfur returned from the mantle. *Proceedings of the National Academy of Sciences (PNAS)*, 113(46), pp. 12893–12895. DOI: <https://doi.org/10.1073/pnas.1616346113>.
- Farquhar, J., Nanping, W. U., Canfield, D. E., Oduro, H. 2010. Connections between sulfur cycle evolution, sulfur isotopes, sediments and base metal sulfide deposits. *Economic Geology*, 105(3), pp. 509–533. DOI: <https://doi.org/10.2113/gsecongeo.105.3.509>.
- Giuliani, A., Fiorentini, M. L., Martin, L. A. J., Farquhar, J. et al. 2016. Sulfur isotope composition of metasomatized mantle xenoliths from the Bultfontein kimberlite (Kimberley, South Africa): Contribution from subducted sediments and the effect of sulfide alteration on S isotope systematics. *Earth and Planetary Science Letters*, 445, pp. 114–124. DOI: <https://doi.org/10.1016/j.epsl.2016.04.005>.
- Goodenough, K. M., Upton, B. G. J., Ellam, R. M. 2002. Long-term memory of subduction processes in the lithospheric mantle: Evidence from the geochemistry of basic dykes in the Gardar Province of South Greenland. *Journal of the Geological Society*, 159(6), pp. 705–714. DOI: <http://dx.doi.org/10.1144/0016-764901-154>.

- Hutchison, W., Babiel, R. J., Finch, A. A., Marks, M. A. W. et al. 2019. Sulphur isotopes of alkaline magmas unlock long-term records of crustal recycling on Earth. *Nature Communications*, 10. DOI: <https://doi.org/10.1038/s41467-019-12218-1>.
- Kogarko, L. N., Veselovskiy, R. V. 2019. Geodynamic origin of carbonatites from the absolute paleotectonic reconstructions. *Journal of Geodynamics*, 125, pp. 13–21. DOI: <https://doi.org/10.1016/j.jog.2019.01.017>.
- Kramm, U., Kogarko, L. N., Kononova, V. A., Vartiainen, H. 1993. The Kola alkaline province of the CIS and Finland: Precise Rb–Sr ages define 380–360 Ma age range for all magmatism. *Lithos*, 30(1), pp. 33–44. DOI: [https://doi.org/10.1016/0024-4937\(93\)90004-V](https://doi.org/10.1016/0024-4937(93)90004-V).
- Labidi, J., Cartigny, P., Birck, J. L., Assayag, N. et al. 2012. Determination of multiple sulfur isotopes in glasses: A reappraisal of the MORB $\delta^{34}\text{S}$. *Chemical Geology*, 334, pp. 189–198. DOI: <http://dx.doi.org/10.1016/j.chemgeo.2012.10.028>.
- Labidi, J., Cartigny, P., Jackson, M. G. 2015. Multiple sulfur isotope composition of oxidized Samoan melts and the implications of a sulfur isotope "mantle array" in chemical geodynamics. *Earth and Planetary Science Letters*, 417, pp. 28–39. DOI: <https://doi.org/10.1016/j.epsl.2015.02.004>.
- Marty, B., Tolstikhin, I. N., Kamensky, I. L., Nivin, V. A. et al. 1998. Plume-derived rare gases in 380 Ma carbonatites from the Kola region (Russia) and the argon isotopic composition in the deep mantle. *Earth and Planetary Science Letters*, 164(1–2), pp. 179–192. DOI: [https://doi.org/10.1016/S0012-821X\(98\)00202-7](https://doi.org/10.1016/S0012-821X(98)00202-7).
- Sasada, T., Hiyagon, H., Bell, K., Ebihara, M. 1997. Mantle-derived noble gases in carbonatites. *Geochimica et Cosmochimica Acta*, 61(19), pp. 4219–4228. DOI: [https://doi.org/10.1016/S0016-7037\(97\)00202-0](https://doi.org/10.1016/S0016-7037(97)00202-0).
- Tolstikhin, I. N., Kamensky, I. L., Marty, B., Nivin, V. A. et al. 2002. Rare gas isotopes and parent trace elements in ultrabasic-alkaline-carbonatite complexes, Kola Peninsula: Identification of lower mantle plume component. *Geochimica et Cosmochimica Acta*, 66(5), pp. 881–901. DOI: [https://doi.org/10.1016/S0016-7037\(01\)00807-9](https://doi.org/10.1016/S0016-7037(01)00807-9).

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