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Petrochemical features of tholeiites from the Shaka ridge (South Atlantic)

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Abstract. The article presents original data of chemical composition of tholeiitic basaltoids and andesites, dredged from the Shaka Ridge (South Atlantic) in the course of field research in spring 2016 on the scientific expedition vessel "Akademik Fedorov". The analytical part of the work on estimating the contents of petrogenic, trace and rare-earth elements was carried out using the classical method ("wet chemistry"), X-ray fluorescence analysis (XRF) and inductively coupled plasma mass spectrometry (ICP-MS). The studied samples demonstrate elevated concentrations of large-ion lithophile elements, or LILE, (Ba, Rb, Pb) and light rare earth elements, or LREE, (La, Ce, Nd, Sm) relative to high field strength elements, or HFSE, (Nb, Ta) and heavy rare earth elements, or HREE, (Dy, Yb, Lu). The specifics of trace element geochemistry suggest a significant contribution of crustal or subduction components to the magmas of the Shaka Ridge. Discrimination diagrams of basaltoids and allied rocks with fields of different geodynamic settings indicate that they were formed in the setting of the mid-ocean ridge basalt (MORB). The reason behind the appearance of subduction and crustal marks in the rocks is possibly associated with assimilation of crustal matter by magmas or lies in their inheritance from the mantle source.

***Key words*:** Shaka Ridge; South Atlantic; geochemistry; tholeiitic basalts; contamination

Introduction. In recent decades, studies of oceanic rocks have shown that they demonstrate wide variations of chemical composition both on a regional scale of the ocean basin and on a local one – within the segment of the mid-ocean ridge [10, 14, 15, 17, 20].

The area of the Shaka Ridge in the South Atlantic is still poorly explored. The studied area is a unique object, as the interaction between the mantle plume and the mid-ocean ridge (MOR) takes place there, which makes it possible to reconstruct geological processes to understand chemical composition and heterogeneity of the Earth's mantle.

The study of the settings of oceanic rock formation is complicated by possible contamination, which leads to "blurring" of typical geochemical characteristics. Earlier, "contaminated" basaltoids with geochemical characteristics uncommon for MOR have already been found within the Mid-Atlantic [15] and Southwest Indian ridges in the South Atlantic [10]. Currently there is no single theory that could explain their origin.

Characteristics of the area. The studied area is located within the Shaka Ridge, the western end of the Southwest Indian Ridge (SWIR) (Fig.1). Currently there is no reliable information about the origin and formation of the Shaka Ridge. SWIR is a modern ultraslow mid-ocean ridge, the spreading rate along which amounts to 14-18 mm/year. Its formation began as a result of breakup of the supercontinent Gondwana in the Mesozoic era [11]. The ridge stretches for 8,000 km from the Bouvet triple junction (BTJ) in the South Atlantic to the Rodriguez triple junction in the Central Indian Ocean. Bouvet Island, which is a hotspot, is located about 300 km east of TSB and 55 km from the nearest SWIR segment [4, 13]. SWIR is characterized by an intensely dissected topography with a height difference of up to 4 km and more, as well as the presence of multiple transform faults (TFs), many of which have their own names. One of such TFs is the Shaka Fault, on the northeastern flank of which the homonymous Shaka Ridge is located in the form of an underwater elevation, stretching to the northeast.

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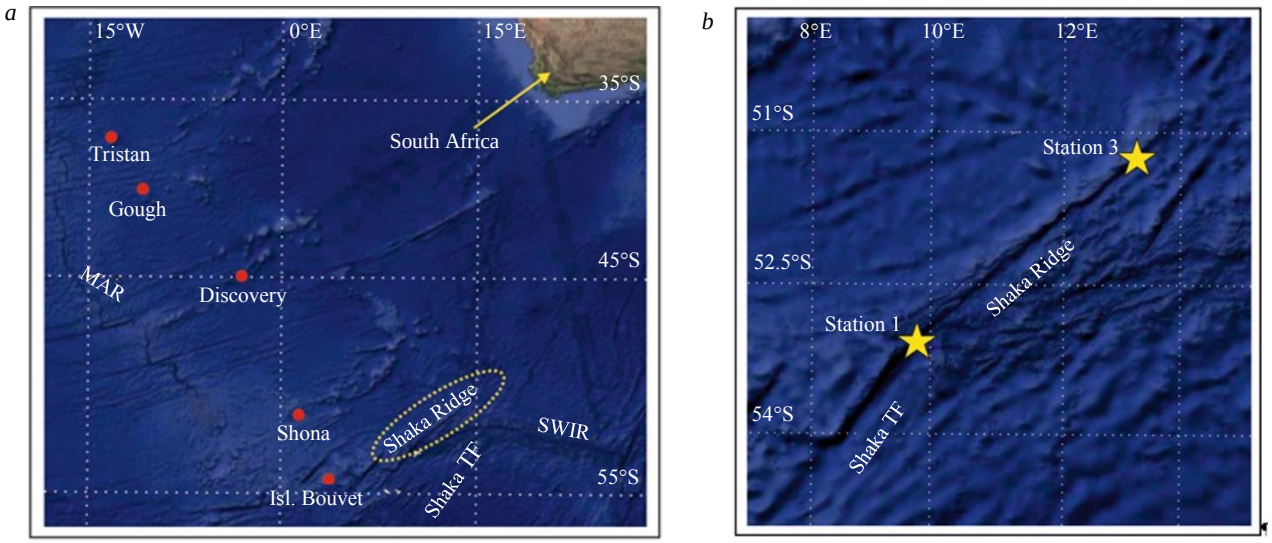


Fig.1. Map of the Shaka Ridge area (*a*) and the dredging stations along the Shaka Ridge (*b*)
As a topographic basis, authors used information from open sources https://www.google.com/maps

The first detailed geological and geophysical studies of the Shaka Ridge area were carried out by the staff of the Woods Hole Oceanographic Institution (WHOI) as part of geophysical mapping and dredging program of SWIR between 9°E and 16°E in December 2000 – January 2001. As a result of performed research, conclusions were drawn about mantle heterogeneity of the area, expressed in various characteristics of the gravitational field, and the interaction of Bouvet hotspot with the Shaka TF about 20 million years ago [13].

Factual material and analytical methods. Samples of studied rocks were taken from two dredging stations along the Shaka Ridge in the course of field research on the Akademik Fedorov vessel in spring 2016. All samples were taken using a dredge-type sampler from pre-selected dredging stations. In total, about 696 kg of bottom-rock material (BRM) were raised to the surface within the studied water body. The raised BRM represents rocks of various compositions – from sedimentary siltstones to magmatic basaltoids. Rocks of similar composition were selected as an object of study – mainly composed of Pl and Cpx, with minimal signs of secondary changes (sericitization and chloritization were observed exclusively in dolerite samples). The location of dredging stations for the studied samples is shown in Fig.1, *b* and in Table 1.

Table 1

Location and coordinates of dredging stations for the studied samples

Dredging station	Location	Latitude, °	Longitude, °	Depth, m
F-B-2016-3-2	Northeastern flank of the middle part of the Shaka Ridge	–51.0578	13.1649	1,450
F-B-2016-1-1	South foot of a local upland on the South-West extremity of the Shaka Ridge	–52.5717	9.4455	2,300

Analytical work to determine the content of major and trace elements was carried out in several scientific organizations. The content of petrogenic elements was estimated using the method of classical analysis (“wet chemistry”) on the premises of the chemical-spectral laboratory of the Analytical Center at VNIIOkeangeologia. The content of trace elements was determined using inductively coupled plasma mass spectrometry (ICP-MS) at VSEGEI Central Laboratory and X-ray fluorescence analysis (XRF) by means of standard methods at VNIIOkeangeologia.

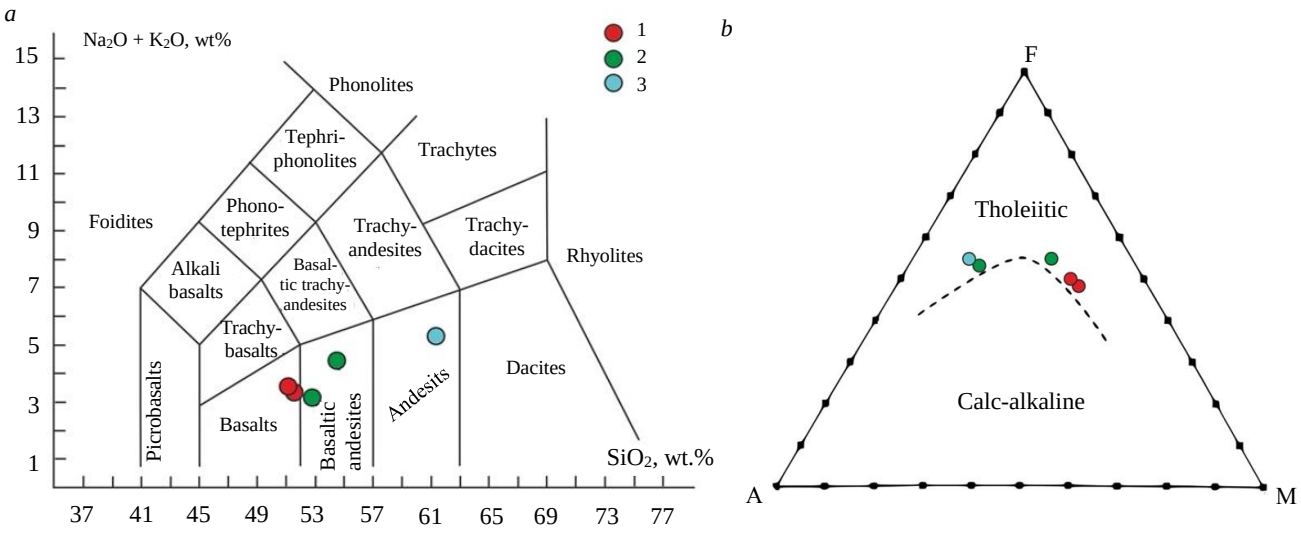


Fig.2. TAS diagram (SiO_2 – Na_2O + K_2O) for Shaka Ridge rocks with fields according to [3] (*a*), ternary AFM diagram (Na_2O + K_2O (A) – FeO + Fe_2O_3 (F) – MgO (M)) according to [9] (*b*)
1 – basalt suit; 2 – basaltic andesite suit; 3 – andesite suit

Petrochemical characteristics. According to TAS classification diagram (Fig.2, *a*), studied rock samples fall into the range from basalts to andesites of normal alkalinity. On the AFM diagram (Fig.2, *b*), all the figurative points in the tholeiite field.

The basalt suit (samples 1-1-2, 3-2-45 in Table 2, Fig.3, *a*, *b*) is represented by hypabyssal analogues of basalts – dolerites. Their phenocrysts include: An_{40-55} – 53-55 %, Cpx – 40-42 %, Ol – 0-5 %, Opx – 0-5 %, Bt – 0-5 %. The SiO_2 content in the rocks of the basalt suit is consistent and varies in the range from 51.5 до 51.6 wt.%. The sum of alkalis Na_2O + K_2O equals 3.34-3.66 wt.%. At the same time, there is a slight predominance of sodium over potassium, Na_2O/K_2O = 1.77-2.34. The magnesia coefficient Mg# varies in a narrow range from 0.43 to 0.45. The rocks are also characterized by a relatively high Al_2O_3 content – an average of 14.3 wt.% – and a relatively low content of total iron: Fe_2O_3 – an average of 10.2 wt.%, MgO – 7.86 wt.% and CaO – 9.99 wt.%. Average MnO content equals 0.19 wt.%, TiO_2 – 0.89 wt.%, P_2O_5 – 0.15 wt.%.

Table 2

Content of tholeiites from the Shaka Ridge

Component	Sample				
	1-1-2	1-1-3	1-1-9	3-2-45	3-2-49
SiO_2	51.6	52.9	61.2	51.5	55.1
TiO_2	0.62	0.93	0.84	1.16	1.12
Al_2O_3	13.7	17.7	14.8	14.9	20.3
Fe_2O_3	2.16	2.78	1.40	2.15	2.51
FeO	8.27	6.54	7.20	7.80	4.46
FeO*	10.4	9.32	8.60	9.95	6.97
MnO	0.19	0.18	0.33	0.19	0.19
MgO	8.47	4.82	1.91	7.26	2.38
CaO	10.6	10.12	5.08	9.41	8.65
Na_2O	2.34	2.37	4.42	2.34	3.40
K_2O	1.00	0.75	1.00	1.32	0.75
P_2O_5	0.11	0.08	0.04	0.19	0.12
LOI	1.12	0.83	1.32	1.37	1.02
Total	100.11	100.00	99.63	99.58	100.02
Ba	123	127	343	244	127
Rb	36	27	30	41	24
Th	3.10	0.96	2.08	1.49	0.90
U	0.62	0.27	0.56	0.48	0.25
Nb	3.03	0.69	3.23	4.30	0.72

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End of Table 2

Component	Sample				
	1-1-2	1-1-3	1-1-9	3-2-45	3-2-49
Ta	0.12	0.05	0.14	0.19	0.05
La	6.58	4.68	7.98	11.7	4.50
Ce	14.2	12.3	19.6	25.4	11.9
Pb	10.0	9.00	14.0	9.00	9.00
Nd	8.65	8.85	13.2	14.8	8.20
Hf	1.81	1.88	3.24	2.92	1.82
Zr	61.9	61.9	104	105	56.9
Sm	2.25	2.83	4.05	3.63	2.52
Eu	0.72	0.86	1.09	1.02	0.89
Gd	2.87	3.49	4.39	3.91	3.09
Dy	3.66	3.86	5.25	4.19	3.67
Y	21.4	21.9	30.6	24.2	21.4
Yb	2.19	2.32	3.30	2.54	2.23
Lu	0.35	0.37	0.50	0.39	0.33
Ce/Pb	1.42	1.37	1.40	2.82	1.32
Nb/U	4.89	2.56	5.77	8.96	2.88
Nb/Y	0.14	0.03	0.11	0.18	0.03
Zr/Y	4.34	2.83	3.40	4.34	2.66
Zr/Nb	20.4	89.7	32.2	24.4	79.0
Y/Nb	7.06	31.7	9.47	5.63	29.7
ΔNb	0.01	–0.63	–0.26	–0.23	–0.55
Eu/Eu*	0.87	0.84	0.79	0.82	0.97

Note. $FeO^* = Fe_2O_3 + FeO$.

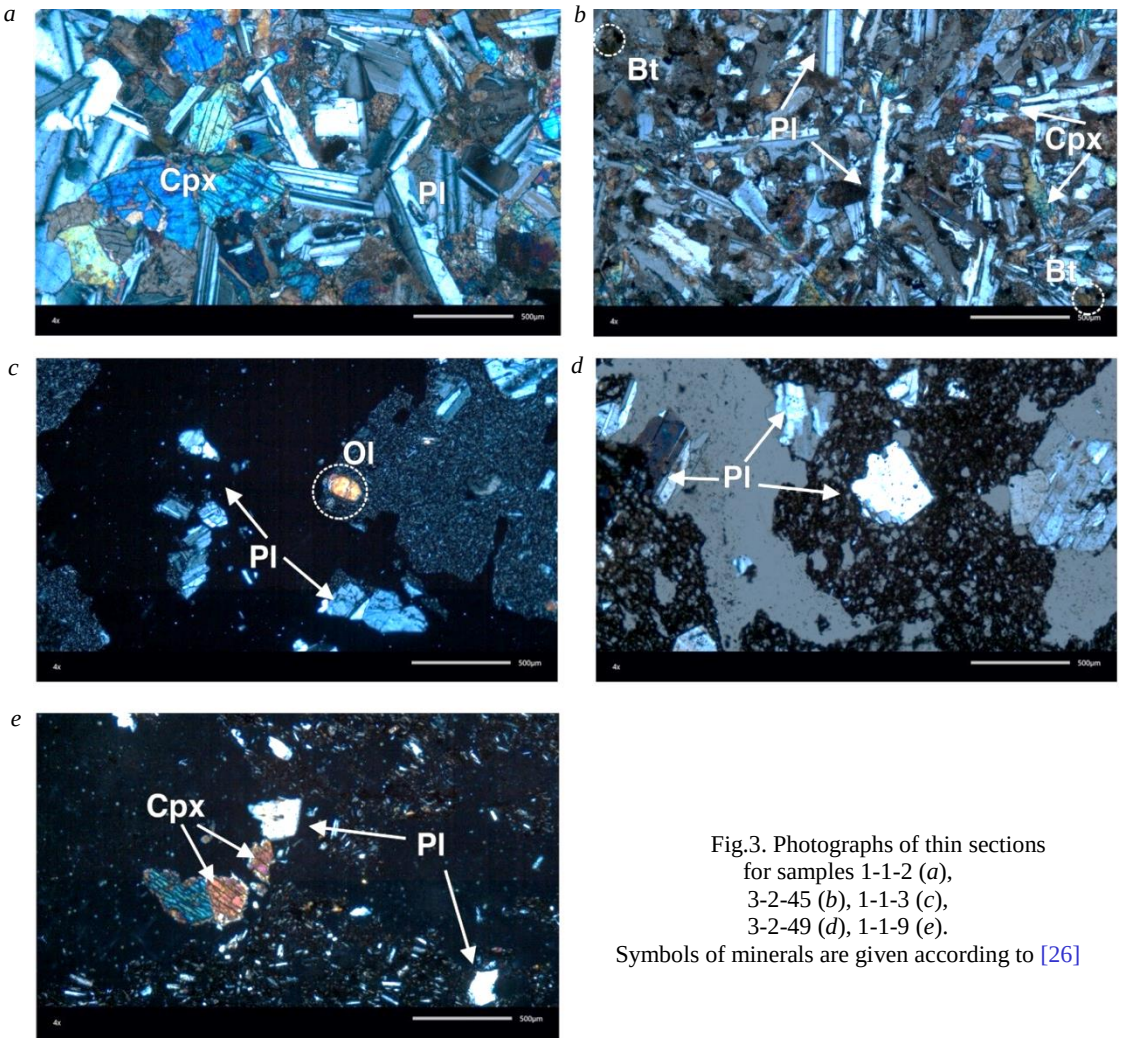


Fig.3. Photographs of thin sections for samples 1-1-2 (*a*), 3-2-45 (*b*), 1-1-3 (*c*), 3-2-49 (*d*), 1-1-9 (*e*). Symbols of minerals are given according to [26]

The basaltic andesite suit (samples 1-1-3, 3-2-49 in Table 2, Fig.3, *c*, *d*). The phenocrysts include: An_{40-50} – 90-94 %, Cpx – 5-10 %, Ol – 0-1 %. The groundmass is composed of Pl – 50-90 % and glass – 42-50 %. The share of phenocrysts in total rock volume amounts to ~30-80 %. The SiO_2 content varies in a narrow range from 52.89 to 55.08 wt.%. The sum of alkalis $Na_2O + K_2O$ ranges from 3.12 to 4.15 wt.%. There is a predominance of sodium over potassium, on average Na_2O/K_2O equals 3.85. The magnesia coefficient Mg# of this rock suit is lower, 0.26-0.34. The rocks are characterized by high Al_2O_3 content – 19.0 wt.% and a relatively low content of total iron: Fe_2O_3 – 8.15 wt.%, MgO – 3.60 wt.% and CaO – 9.39 wt.%. The MnO content equals 0.19 wt.%, TiO_2 – 1.03 wt.%, P_2O_5 – 0.10 wt.%.

The andesite suit (samples 1-1-9 in Table 2, Fig.3, *e*) is represented by an icelandite sample. Its phenocrysts include: An_{40} – 50 %, Cpx – 50 %. The groundmass is composed of glass – 50 %, Pl – 40 %, Cpx – 10 %. The share of phenocrysts in total rock volume is 20 %. The SiO_2 content in the rock amounts to 61.2 wt.%. The sum of alkalis $Na_2O + K_2O$ equals 5.42 wt.%. Sodium predominates over potassium (Na_2O/K_2O = 4.42). The magnesia coefficient Mg# is 0.18. It is observed that the content of Al_2O_3 is relatively high – 14.84 wt.% and the content of total iron is relatively low: Fe_2O_3 – 8.60 wt.%, MgO – 1.91 wt.% and CaO – 5.08 wt.%, all these values are slightly lower than in the suits described above. The average MnO content equals 0.33 wt.%, TiO_2 – 0.84 wt.%, P_2O_5 – 0.04 wt.%.

Studied samples are characterized mainly by sodium and sodium-potassium type of alkalinity. All of them belong to the tholeiite series. The magnesiality of the rocks varies from medium to low. In this case, the magnesia coefficient is associated with the Cpx content of the rocks. All the rocks are characterized by low titanium content.

Geochemical characteristics. The study of oceanic rocks is often complicated by the ambiguity of diagnostic geochemical characteristics. Ratios of incompatible elements are especially meaningful for the analysis, since they are more stable in the process of rock changes, being sensitive indicators of mantle source characteristics.

A remarkable feature of the studied samples on multi-element spider diagrams (Fig.4), normalized to the primitive mantle, is elevated concentrations of large-ion lithophile elements, or LILE, (Ba, Rb, Pb) and light rare earth elements, or LREE, (La, Ce, Nd, Sm) relative to high field strength elements, or HSFE, (Nb, Ta) and heavy rare earth elements, or HREE, (Dy, Yb, Lu). The general nature of spectra, attributed to different rock suits, is universal. In principle, the multi-element spectra are close to those of the continental crust and the global subducted sediment (GLOSS). N.Green [7] noted that enrichment in LILE and LREE relative to Nb and Ta in basaltic magmas may reflect the presence of a subduction or a continental crust component in the melting center. In her studies, M.Wilson [27] compared N-MORB compositions to contaminated basalts by constructing spider diagrams. If the

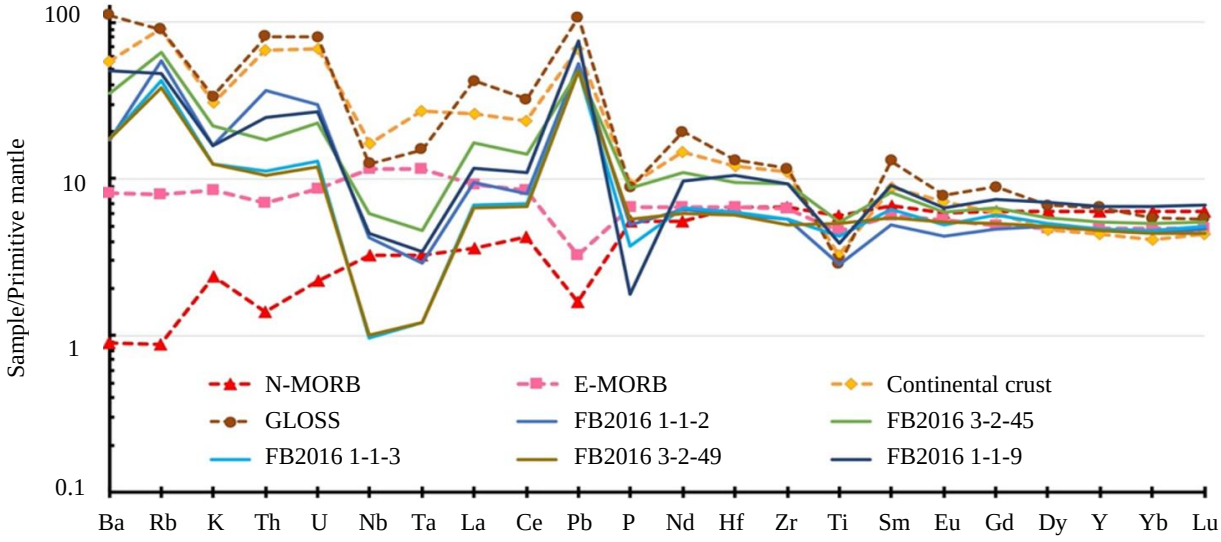


Fig.4. Trace element distribution in the Shaka Ridge rocks, normalized to the primitive mantle [24]

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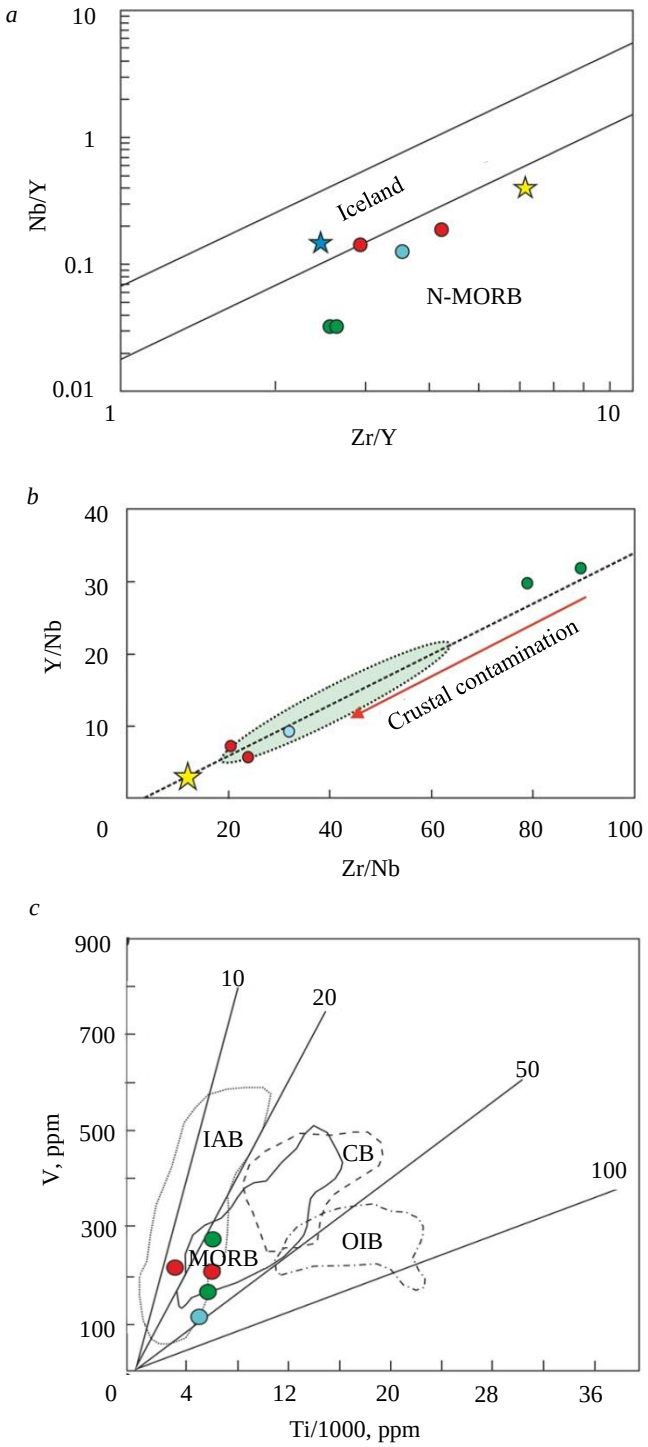


Fig.5. The Nb/Y – Zr/Y discrimination diagram for Shaka Ridge rocks [25] (*a*), a blue star corresponds to the value of primitive mantle composition [24], a yellow star – to the average composition of the continental crust [19]; the Zr/Nb – Y/Nb ratio for Shaka Ridge rocks (*b*), a dotted line corresponds to the calculated mixing curve between the enriched component and the depleted parent [27], an arrow follows an increase in the level of rock contamination by crusal material, a star stands for average composition of the continental crust [21], a field, encircled with a dotted line – for N-MORB composition along the Southwest Indian Ridge [5]; the Ti/1000 – V discrimination diagram for Shaka Ridge rocks [22] (*c*), MORB stands for MOR basalts, IAB – for island arc basalts, OIB – for ocean island basalts, CB – for continental rift basalts

melt contains at least 5 % of the Earth's crust substance, the multi-element spectrum demonstrates an increase in total content of trace elements and Nb-Ta anomaly begins to show up. When the content of crustal material is 15 %, these trends in the multi-element spectrum become even more distinct, and it begins to resemble spectra for magmas, associated with the subduction zone.

Tholeiites of the Shaka Ridge have low content of Ce/Pb (1.32-2.82) and Nb/U (2.56-8.96), which indicates either crustal contamination or contribution of a subducted component [28]. Oceanic basaltoids are often compared to compositional fields of similar rocks in Iceland in terms of their Nb/Y and Zr/Y ratios (Fig.5, *a*). The excess or deficiency of Nb in relation to the lower limit of the Icelandic rock mass can be quantified using the parameter $\Delta Nb = 1.74 + \log(Nb/Y) - 1.92 \log(Zr/Y)$. It is not affected by fractional crystallization of olivine and plagioclase, since Nb, Zr, and Y are extremely incompatible in these phases. In the examined samples, the value of ΔNb parameter varies from +0.01 to –0.63. Tholeiites of the Shaka Ridge are mainly located in the field below the data, corresponding to the Icelandic rock mass, thus falling into the N-MORB field (Fig.5, *a*, Table 2).

The correlation between Zr/Nb and Y/Nb ratios (Fig.5, *b*) in the studied rocks is in good agreement with the calculated mixing curves between the enriched and depleted sources. All figurative points are located along the probable mixing line. Basalt and andesite suits are compactly arranged in the "enriched" area, close to the compositions of continental crust. Points, corresponding to compositions of the basaltic andesite suit, are located at a distance from others in the "depleted" area. This implies that basaltoids and andesites became enriched in the process of contamination. Basaltic andesites, on the other hand, are less enriched and, hence, characterized by a smaller contribution of crustal material to parental magmas.

Geodynamic setting of rock formation was assessed using discrimination diagrams based on the content and ratios of immobile elements, including high field strength elements Nb, Zr, Ti, Y, Yb. On the Ti/V diagram (Fig.5, *c*), the

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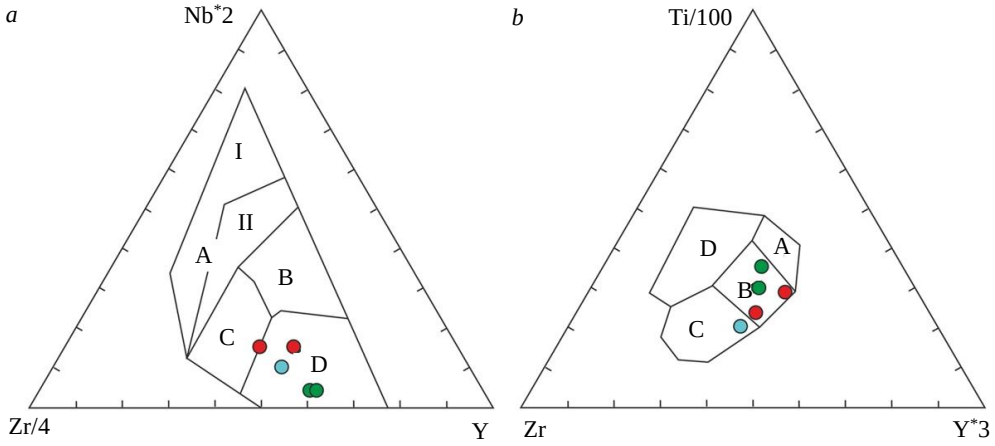


Fig.6. Zr/4 – 2Nb – Y discrimination diagrams [16] (*a*),
A-I – alkali intraplate basalts, A-II – intraplate tholeiitic basalts, B-E – MORB, C – intraplate tholeiitic basalts and ocean arc basalts, D-N – MORB and ocean arc basalts; Zr – Ti/100 – 3Y [18] (*b*); A – island arc tholeiites, B – MORB, island arc tholeiites and calc-alkaline basalts, C – calc-alkaline basalts, D – intraplate basalts

figurative points, corresponding to the composition of the studied rocks, mainly lie in the overlapping field of island arc basalts (IAB) and mid-ocean ridge basalts (MORB). Tectonic setting of the samples was also visualized on several triple diagrams. In Fig 6, *a*, all the points lie in the field, simultaneously corresponding to normal MOR basalts (MORB) and ocean arc basalts. In Fig. 6, *b*, all the figurative points fall into the field, simultaneously corresponding to rock compositions of MORB, island arc basalts and calc-alkaline basalts, except for one. It belongs to the field of calc-alkaline basalts, but close to the border of the field, where the rest of the points lie.

The amount of REE in the studied tholeiites from the Shaka Ridge area varies from 215 to 329 ppm. The studied rock samples demonstrate poorly differentiated REE distribution spectra with an insignificant slope from LREE to HREE, normalized to CI chondrite (Fig.7). The majority of spectra are characterized by a weak negative Eu anomaly. The Eu/Eu^* value ranges from 0.79 to 0.97. This indicates a weakly manifested process of plagioclase fractionation [1]. The spectra of basaltic andesite samples are almost identical. The difference is only in the value of Eu anomaly, it is practically absent in sample 3-2-49 ($Eu/Eu^* = 0.97$), as well as in the Gd content. The highest LREE enrichment is demonstrated by the dolerite sample 3-2-45. In the HREE area, the spectra are generally similar to each other and differ only in total content of these elements. The spectra of the studied samples fall into the field between the spectra of the continental crust and N-MORB, the values of which are presented in paper [26].

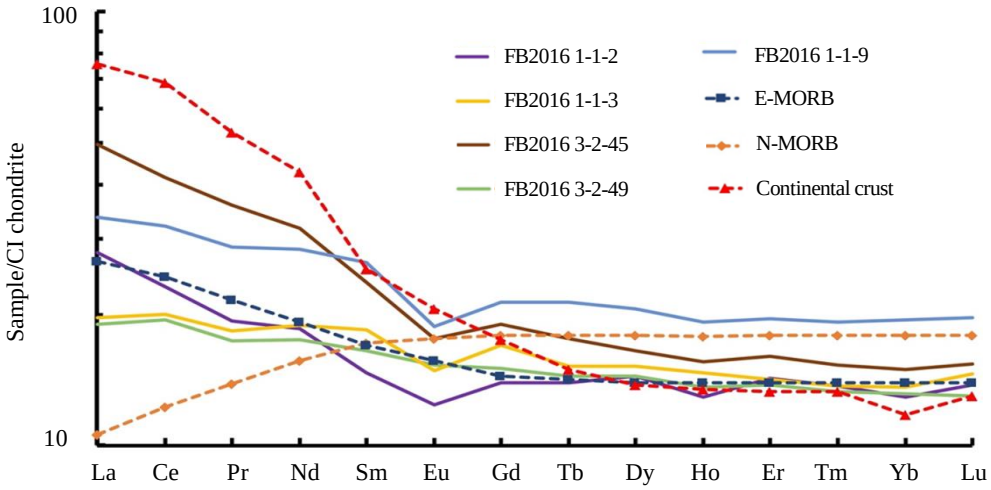


Fig.7. REE distribution within the Shaka Ridge, normalized to CI chondrite [25]

Discussion. Considered samples of tholeiitic dolerites, basaltic andesites and andesites demonstrate distinct negative Nb-Ta anomalies combined with enrichment in large-ion lithophile elements (Rb, Ba, Th, U). Such marks characterize both crustal and subduction material. Similar characteristics were observed earlier for basalts of the Atlantic and Indian oceans [2, 6, 10, 12, 15].

The article [14] provides several probable sources of heterogeneity along the Mid-Atlantic Ridge: dispersion of the depleted plume component, layered Sub-Gondwana lithosphere, recycling of crustal material and pelagic sediments. According to the authors, all these alternative versions are not mutually exclusive.

In the studies by A.A.Peive and S.G.Skolotnev [2], similar discoveries with crustal (subduction) characteristics were made near Bouvet Island. It has been suggested that the marks could be inherited from the continental mantle or the ancient oceanic crust. The study area has a complex prehistory of its formation, namely: a long-lived subduction zone, formation and manifestation of mantle plumes, breakup of the supercontinent Gondwana, opening of the Atlantic Ocean basin. As a result of these multiple processes, blocks of continental crust may have survived amid the younger oceanic lithosphere.

At this stage of research, it is difficult to give an unambiguous answer to the question of how the studied rocks from the Shaka Ridge acquired their marks of island arcs or continental crust.

Conclusions. Based on a petrographic description and petrochemical characteristics, several rock suits have been identified among the tholeiites of the Shaka Ridge area: basalts, basaltic andesites and andesites. The specifics of trace element geochemistry for the studied rocks suggest a significant contribution of subduction and crustal material to the melting center. The reason behind the appearance of subduction and crustal marks in the rocks is possibly associated with assimilation of crustal matter by magmas or lies in their inheritance from the mantle source. A complex prehistory of the area, which includes a long-lived subduction zone, formation and manifestation of mantle plumes, breakup of the supercontinent Gondwana, opening of the Atlantic Ocean basin and subsequent melting of small fragments of the Sub-Gondwana lithosphere within the asthenospheric mantle, most likely led to manifestation of heterogeneities and contamination of magmas in this area.

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