Zircon Xenocrysts from the Shaka Ridge Record Ancient Continental Crust: New U-Pb Geochronological and Oxygen Isotopic Data

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ABSTRACT: Over the past two decades, a significant number of discoveries of ancient zircon xenocrysts in ocean-floor magmatic rocks have been reported. These findings provide compelling evidence for the presence of ancient continental crust within young oceanic lithosphere. Almost all finds of ancient zircon xenocrysts within oceanic crust are from the Mid-Atlantic Ridge. For other localities, however, similar data are very limited. This report presents the first age determinations (U-Pb, SHRIMP-II) and isotope-geochemical data (oxygen, trace and rare earth elements) for zircon xenocrysts from gabbro-diorites of the Shaka Ridge, in the vicinity of the Shaka fracture zone, near the western end of the Southwest Indian Ridge. The work is based on a study of bottom rock material dredged during expeditionary research on the R/V “Akademik Fedorov” (Russia) in 2016. The U-Pb isotope system of the zircon xenocrysts recorded a crystallization age of ~2.8 Ga at an upper discordia intercept and an age of ~600 Ma interpreted as the timing of a superimposed thermal event at a lower discordia intercept. The zircon xenocrysts show geochemical signatures of magmatic origin, i.e., fractionated REE distribution spectra with an increase in chondrite-normalized values from light to heavy REE, positive Ce anomalies and negative Eu anomalies, and high Th/U ratios (0.59–7.77). In discrimination diagrams based on a series of inter-element relationships, zircon compositions fall into the fields of zircons from rocks of continental crust, mostly granitoids. The Li content of the zircons is high (1.8 ppm–50 ppm), adding further evidence to their derivation from rocks of continental crust. During their residence within young oceanic crust, the zircon xenocrysts experienced alterations under the influence of submarine high-temperature hydrothermal fluids, which selectively affected the distribution of trace elements in the zircons and reduced the $\delta^{18}\text{O}$ values to 1.75‰–3.15‰. The presence of obviously older zircons in Shaka gabbro-diorites clearly demonstrates the presence of ancient continental fragments and their recycling into the mantle at the western end of the Southwest Indian Ridge.

KEY WORDS: zircon, U-Pb geochronology, oxygen isotopes, trace elements, rare earth elements, Shaka Ridge, South Atlantic, Southwest Indian Ridge.

0 INTRODUCTION

The finding of ancient zircons (Paleozoic to Proterozoic) in oceanic gabbros from the Mid-Atlantic Ridge near the Kane fracture zone (Pilot et al., 1998) triggered extensive discussion that is still under way. The primary issue is the mechanism of

incorporation of these zircons into young oceanic crust. Initially, attempts were made to explain the presence of obviously older zircons either by contamination during sampling of rocks or separation of minerals. However, a significant number of such discoveries (about twenty publications, links below), and a wide range of laboratories in which sample preparation was performed, suggest that this phenomenon is not uncommon, and zircons should be considered as true xenocrysts (Bea et al., 2020). The results of these studies provide convincing evidence for the presence of ancient continental crust in young oceanic lithosphere (e.g., Bortnikov et al., 2019; Ashwal et al., 2017; Kamenetsky et al., 2001).

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Zircon is a unique indicator and a common representative of ancient continental lithosphere. It retains isotope-geochemical signatures and records information on the reworking of ancient crust during various geodynamic processes (Leontev et al., 2020; Zhao et al., 2019; Xu and Zhang, 2018). Almost all finds of ancient zircons within oceanic crust come from the Mid-Atlantic Ridge (Bea et al., 2020; Bortnikov et al., 2019, 2008; Shulyatin et al., 2019; Kostitsyn et al., 2018, 2015, 2009; Kremenetskiy et al., 2018; Aranovich et al., 2013; Skolotnev et al., 2010; Sharkov et al., 2004; Pilot et al., 1998; Belyatskii et al., 1997). This is probably due to the fact that this area of the world ocean has been systematically studied for several decades. For the Indian Ocean, however, the available data are scarce (Ashwal et al., 2017; Cheng et al., 2016; Torsvik et al., 2013). In this contribution we report the first age determinations and isotope-geochemical data for zircons from the Shaka Ridge, adjacent to the Shaka fracture zone, near the western end of the Southwest Indian Ridge. We provide evidence for the continental derivation of the zircons and discuss possible mechanisms of their transportation into young oceanic crust.

1 GEOLOGICAL BACKGROUND AND SAMPLING

The Southwest Indian Ridge (SWIR) is a Meso-Cenozoic ocean floor uplift. Its formation began as a result of the Gondwana supercontinent breakup in the Mesozoic (Norton and Slater, 1979). The ridge extends ~8 000 km from the Bouvet triple junction in the South Atlantic to the Rodrigues triple junction in the southern Indian Ocean. The SWIR is an ultra-slow spreading ridge with spreading rates of only 14–18 mm/yr. Bouvet Island, a hotspot, is located ~300 km east of the Bouvet triple junction and 55 km south from the nearest SWIR segment (Lin et al., 2003; Georgen et al., 2001). Within the SWIR, there is an intensely dissected topography with elevation differences of up to 4 km or more as well as a significant number of transform faults having their own names. One of such transform faults is the Shaka fault. The namesake Shaka Ridge is located on the northeastern flank of the latter; it is an

underwater upland extending to the east. The Shaka Ridge is thus not a part of the SWIR, but is located in its immediate vicinity (Fig. 1).

Currently, there is a lack of reliable information about the origin and formation of the Shaka Ridge (Rumyantseva et al., 2021). The first detailed geological and geophysical study of the Shaka Ridge area was carried out by the staff of the Woods Hole Oceanographic Institution (WHOI) during December and January, 2001. This research was part of the geophysical mapping and dredging program of the southwestern part of the Indian Ridge between E9° and E16° (Lin et al., 2003, 2001). As a result of these studies, pronounced mantle heterogeneity of the area was established, which is expressed in differing indicators of the gravitational field. The largest negative mantle anomaly (-50 mGal) was recorded in the area of a number of relict volcanic cones at the junction of the Shaka fault and the Shaka Ridge (S52.25°; E10.5°). Dredging of the cones showed that they were composed of alternating layers of ash and lapilli tuff. This evidence confirmed the researchers' assumption that the Bouvet hotspot interacted with this area at ~20 Ma (Lin et al., 2001). The magnetic age of Shaka Ridge rocks is between 35–53 Ma (Sauter and Cannat, 2010; Fisher and Slater, 1983).

Our work is based on a study of bottom rock material dredged during expeditionary research within the Shaka Ridge on the R/V “Akademik Fedorov” (Russia) in the spring of 2016. The research was performed in two stages. At the first stage, a bathymetric survey of seabed topography using a multi-beam echo sounder was carried out. Based on the results, a geomorphological map was prepared, and locations for dredging stations were selected. In geomorphological terms, the study area has a substantial topographic relief with a major northeast-striking fault and individual volcanic edifices. At the second stage, ~696 kg of bottom rock materials were sampled at the selected locations using a bottom dredge sampler. The dredged material represents rock fragments of different composition, from sedimentary siltstones to basalts. All these samples are weakly rounded or angular with some being covered by Fe-Mn

Figure 1. Map of the Shaka Ridge area. Information from open sources (<https://www.ngdc.noaa.gov/gazetteer/>) was used as a topographic basis. “Station 3” denotes sampling location. Inset shows the geographical position of the study area.

crusts. After lifting the dredge aboard the vessel, the bottom rock materials were extracted from the dredge and sorted according to rock types for further geological description, photographing and weighing. Among the bottom rock materials sampled from dredging station FB-2016-3-2 on the northeastern flank of the middle part of the Shaka Ridge (S51.057 8°; E13.164 9°), gabbro, diorite, dolerite, basaltic andesite, trachybasalt and gabbro-diorite are the predominant lithologies. A representative sample of gabbro-diorite from this station (FB-2016-3-2-55) was taken for a further analytical study.

2 ANALYTICAL METHODS

Zircon grains were recovered from the gabbro-diorite (sample FB-2016-3-2-55) by conventional magnetic and heavy liquid techniques. Once separated, the zircon grains were mounted in epoxy together with the TEMORA-2 (Black et al., 2004) and 91500 (Wiedenbeck et al., 1995) zircon standards. Spots for *in-situ* analyses were selected by using both transmitted- and reflected-light images in order to avoid cracks and inclusions. Cathodoluminescence (CL) and back-scattered electron (BSE) images were obtained at the Centre for Isotopic Research of the All-Russian Geological Research Institute (St. Petersburg) using a CamScan MX2500S scanning electron microscope (SEM) coupled with a QLI/QUA2 CL and operated at 12 kV, 5–7 nA and a working distance of 31–33 mm.

The U-Pb dating of zircons was performed on a SHRIMP-II ion microprobe at the Centre of Isotopic Research of the All-Russian Geological Research Institute. The U-Pb measurements were carried out by the technique described in Bröcker et al. (2014), Rodionov et al. (2012) and Williams (1998). The intensity of primary O_2 beam was 4 nA, and the spot (crater) was 20 μm across. The obtained data were processed using the SQUID program (Ludwig, 2001). The U/Pb ratios were normalized to the value of the TEMORA zircon standard, 0.066 8, corresponding to an age of 416.75 Ma (Black et al., 2004). The errors of single analyses (U/Pb ratios and ages) were at the $\pm 1\sigma$ level, and the errors of calculated concordant ages and intercepts with concordia were at the 2σ level. Error in standard calibration was 0.36%. The concordia plots were constructed using the ISOPLOT/EX program (Ludwig, 2003).

Oxygen isotope compositions of zircon were determined at the Institute of Geology and Geophysics of the Chinese Academy of Sciences (Beijing) on a Cameca IMS-1280 ion microprobe. Analytical procedures are similar to those described in Tang et al. (2015) and Li et al. (2010). The Cs^+ primary beam was accelerated at 10 kV with an intensity of ca. 2 nA. The spot size was about 20 μm in diameter (10 μm beam diameter + 10 μm raster). The measured $^{18}O/^{16}O$ ratios were normalized to the standard VSMOW ($^{18}O/^{16}O = 0.002\ 005\ 2$). We performed oxygen isotope measurements at spots located directly adjacent to pits after U-Pb isotope analyses. Before measuring, the sample was re-polished to remove the pits from previous analyses. The instrumental mass fractionation (IMF) was corrected using the TEMORA-2 zircon standard. The second reference zircon 91500 was analyzed as an unknown to ascertain the veracity of the IMF. Four measurements of the 91500 zircon during the course of the present study yielded an average ^{18}O value of $10.07\text{‰} \pm 0.08\text{‰}$ (2SD). It is in agreement with

the value of 9.9‰ for the 91500 zircon standard (Wiedenbeck et al., 2004).

Measurements of zircon trace element composition were performed using a Cameca IMS-4f ion microprobe at the Yaroslavl' Branch of the Institute of Physics and Technology of the Russian Academy of Sciences. We mainly followed the analytical procedure described in Dokukina et al. (2014), Fedotova et al. (2008) and Hinton and Upton (1991). The primary O^{2-} ion beam spot size was $\sim 20\ \mu m$. Each analysis was averaged from 3 measurement cycles. Concentrations of trace elements were calculated from the normalized to $^{30}Si^+$ secondary ion intensities using calibration curves based on a set of reference glasses (Jochum et al., 2006, 2000). NIST-610 reference glass (Rocholl et al., 1997) was used as a daily monitor for trace element analyses. Accuracy of trace element measurements was up to 10% and 20% for concentrations of more than 1 ppm and between 0.1 ppm and 1 ppm, respectively. To construct REE distribution spectra, the composition of zircon was normalized to that of chondrite CI (McDonough and Sun, 1995). The zircon crystallization temperature was determined by the Ti-in-Zrn thermometer (Watson et al., 2006).

3 RESULTS

3.1 Petrogeochemical Features of the Host Rock

On macroscopic examination, sample F-B-2016-3-2-55 is a rounded, slightly angular rock fragment weighing 8.5 kg and $18 \times 17 \times 13\ cm^3$ in size. It is a coarse-grained crystalline rock with a massive structure. Sample petrography is shown in Fig. 2. Rock-forming minerals are plagioclase (An_{45-50} ; 55%; 0.6–4.0 mm in size), hornblende (25%; 0.2–1.5 mm), quartz (10%; 0.4–0.6 mm), K-feldspar (5%; $\sim 0.2\ mm$), and biotite (5%; 0.4–1.0 mm). Accessory minerals are zircon, apatite and titanite with epidote and chlorite occurring as secondary minerals. As is evident from its mineralogy and degree of alteration, the rock appears to have undergone greenschist-facies metamorphism. The structure of groundmass is hypidiomorphic granular with poikilitic domains. Plagioclase is saussuritized and crosscut by thin chlorite veins; it is also densely populated by inclusions of apatite, to a lesser extent biotite and hornblende. Hornblende forms irregularly-distributed elongated crystals with inclusions of biotite. Quartz is mostly xenomorphic and fills interstices between plagioclase crystals and colored minerals, although irregular-shaped individual grains are recognized as well. Biotite is present as individual laths, intergrowths and inclusions in principle rock-forming minerals. Zircon appears as irregular-shaped grains or prismatic crystals showing square cross-sections.

According to the TAS classification diagram (Middlemost, 1994), the studied rock falls into the field of gabbro-diorites of normal alkalinity ($Na_2O + K_2O = 3.62\ wt.\%$) with sodium being predominant over potassium ($Na_2O/K_2O = 2.26$). The bulk sample is characterized by a high Al_2O_3 content (22.65 wt.%), whereas MgO (2.37 wt.%), CaO (10.84 wt.%) and total Fe_2O_3 (5.22 wt.%) abundances are relatively low. The concentrations of MnO , TiO_2 and P_2O_5 are 0.10 wt.%, 0.62 wt.% and 0.13 wt.%, respectively. The bulk rock demonstrates high concentrations of large ion lithophile elements (LILE; $Rb = 49\ ppm$, $Ba = 143\ ppm$, $Pb = 15\ ppm$), yet relatively low levels of high

Figure 2. Microphotograph showing a representative texture of sample F-B-2016-3-2-55. Crossed-polarized light. Bt. Biotite; Hbl. hornblende; Pl. plagioclase; Qz. quartz; Ttn. titanite; Zrn. zircon.

field strength elements (HFSE; Nb = 6.9 ppm, Ta = 0.33 ppm). The distribution of rare earth elements (REE), normalized to chondrite C1, shows a gradual decrease from light to heavy REE with a negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.80$). The bulk-rock geochemistry data is reported in Table S1.

3.2 Zircon Characterization

The zircon grains separated from the gabbro-diorite are elongated (with aspect ratios 1 : 2–1 : 3) or isometric with pitted and corroded surfaces (Fig. 3). The grain size generally does not exceed 150–200 μm . In CL imaging, the zircon population is generally dark with shades from almost black to dark gray. Occasionally, individual domains bright in CL are recognized in both the interior and rim parts of the grains (e.g., grain

6.1, Fig. 3). Some examples show sector-zoned CL responses (e.g., grain 3.1, Fig. 3), where domains with different internal textures randomly alternate with each other. Fine-scale oscillatory zoning is revealed in several zircons (e.g., grain 7.1, Fig. 3), which is commonly considered as being a magmatic signature (e.g., Corfu et al., 2003).

All 15 dated zircon grains plot on a discordia line with an upper intercept with a concordia curve at $2\,810 \pm 4$ Ma and a lower intercept at 590 ± 83 Ma (MSWD = 1.5; Fig. 4). With the exception of three spots (6.1, 14.1 and 11.1 with discordance values of 9%, 15%, and 20% respectively), all other points are clustered in the region of the upper discordia intercept and are considered subconcordant with the values of discordance not greater than 6% (Table 1).

Table 1 U-Pb and oxygen isotope data for zircons from the gabbro-diorite of the Shaka Ridge (sample F-B-2016-3-2-55)

Spot	²⁰⁶ Pb _c (%)	U (ppm)	Th (ppm)	²³² Th/ ²³⁸ U	²⁰⁶ Pb* (ppm)	²⁰⁶ Pb/ ²³⁸ U age (Ma), ±σ	²⁰⁷ Pb/ ²⁰⁶ Pb (Ma), ±σ	D (%)	²⁰⁷ Pb/ ²³⁵ U ±σ (%)	²⁰⁶ Pb/ ²³⁸ U ±σ (%)	ρ	δ ¹⁸ O (‰)	±2SE (‰)		
1.1	0.03	567	556	1.01	263	2 779 ±9	2 813 ±6	1	14.75	0.5	0.539	0.4	0.730	3.04	0.16
2.1	0.00	683	686	1.04	311	2 743 ±9	2 801 ±12	2	14.40	0.8	0.530	0.4	0.470	2.98	0.15
3.1	0.01	480	461	0.99	229	2 845 ±9	2 812 ±6	-1	15.16	0.5	0.555	0.4	0.732	2.11	0.27
4.1	0.00	779	5 857	7.77	381	2 902 ±7	2 819 ±12	-3	15.61	0.8	0.569	0.3	0.377	2.56	0.22
5.1	0.01	2 093	3 321	1.64	920	2 663 ±6	2 783 ±3	5	13.74	0.3	0.511	0.3	0.821	1.75	0.14
6.1	0.02	499	287	0.59	208	2 551 ±9	2 775 ±7	9	12.97	0.6	0.485	0.4	0.718	2.03	0.19
7.1	0.01	1 825	2 424	1.37	805	2 670 ±6	2 794 ±3	5	13.88	0.3	0.513	0.3	0.809	2.69	0.23
8.1	0.01	819	866	1.09	372	2 739 ±7	2 806 ±4	2	14.42	0.4	0.529	0.3	0.740	3.15	0.15
9.1	0.02	1 122	1 216	1.12	535	2 843 ±6	2 813 ±4	-1	15.16	0.3	0.554	0.3	0.759	2.93	0.28
10.1	0.01	947	998	1.09	433	2 747 ±6	2 808 ±4	2	14.49	0.4	0.531	0.3	0.743	2.98	0.15
11.1	0.06	318	277	0.90	117	2 294 ±8	2 743 ±7	20	11.20	0.6	0.427	0.4	0.671	3.04	0.18
12.1	0.01	1 153	1 332	1.19	506	2 660 ±17	2 798 ±8	5	13.85	0.9	0.511	0.8	0.843	3.00	0.18
13.1	0.03	280	170	0.63	121	2 624 ±11	2 794 ±7	6	13.59	0.7	0.503	0.5	0.745	2.90	0.13
14.1	0.04	389	381	1.01	152	2 414 ±8	2 770 ±7	15	12.11	0.5	0.454	0.4	0.685	2.53	0.25
15.1	0.02	943	1 031	1.13	431	2 749 ±7	2 809 ±4	2	14.51	0.4	0.532	0.3	0.785	2.96	0.13

Errors are 1σ ; Pb_c and Pb^* indicate the common and radiogenic portions, respectively; error in standard calibration was 0.36% (not included in above errors but required when comparing data from different mounts); common Pb corrected using measured ^{204}Pb . D (%) discordancy: $D = 100 \times \{[\text{Age}(^{207}\text{Pb}/^{206}\text{Pb})]/[\text{Age}(^{206}\text{Pb}/^{238}\text{U})] - 1\}$.

Figure 3. Cathodoluminescence (CL) photomicrographs of zircons from sample F-B-2016-3-2-55 (ion microprobe crater is about 20 μm).

Figure 4. Wetherill concordia diagram for zircons from sample F-B-2016-3-2-55.

The content of U in the zircon suite ranges from 280 ppm to 2 093 ppm (with an average of 860 ppm). It should be noted that the three most discordant zircons (spots 6.1, 14.1 and 11.1) show U abundances (318 ppm to 499 ppm) not exceeding

those established in the subconcordant zircons. Thorium varies in a wider range than U (170 ppm–5 857 ppm, with an average of 1 324 ppm). The Th contents of the three most discordant grains are also far from the established maximum values and do not exceed the average value, varying from 277 ppm to 381 ppm. The Th/U ratios in the examined zircons are between 0.59 and 7.77, averaging 1.51.

The isotopic composition of oxygen in zircons is characterized by relatively low values of $\delta^{18}\text{O}$ from 1.75‰ to 3.15‰, averaging 2.71‰ (Table 1).

The total abundance of REE in the studied grains varies from 960 ppm to 4 815 ppm, with an average of 2 591 ppm ($\text{Lu}_\text{N}/\text{La}_\text{N}$ ratio averages 4 659; Table 2). In general, the REE distribution patterns are fractionated with a gradual increase in chondrite-normalized values from light to heavy REE (Fig. 5). Note that the REE patterns exhibit a very similar shape in the HREE region, differing only in the overall HREE content. The $\text{Lu}_\text{N}/\text{Gd}_\text{N}$ ratio characterizing the degree of HREE slope is fairly consistent and varies from 14.5 to 28.6 with an average value of 18.8. By contrast, the concentrations of LREE show much more variability. The total LREE content varies from 23 ppm to 252 ppm, with an average of 75 ppm. In zircons with the highest LREE content (spots 4.1 and 7.1), the REE distribution spectra in the LREE region show a flattened (unfractionated)

Table 2 Trace elements concentrations (ppm) in zircons from the gabbro-diorite of the Shaka Ridge (sample F-B-2016-3-2-55)

Spot	1.1	2.1	3.1	4.1	5.1	6.1	7.1	8.1	9.1	10.1	11.1	12.1	13.1	14.1	15.1
La	0.11	0.31	0.64	29.4	0.74	0.64	6.70	2.82	0.32	0.22	0.30	5.54	0.08	1.51	0.19
Ce	35.3	40.1	28.3	143	87.9	31.9	105	43.5	43.7	42.4	19.3	74.9	21.4	24.8	38.4
Pr	0.52	0.87	0.28	12.6	1.83	0.48	5.99	1.98	1.08	0.94	0.63	3.33	0.13	1.13	0.94
Nd	8.47	11.1	4.41	66.4	21.6	4.07	45.0	17.1	14.8	12.3	9.39	20.0	1.50	9.58	12.7
Sm	17.0	18.7	6.98	21.2	29.9	5.52	34.6	15.0	22.7	21.5	13.3	15.5	3.59	10.9	18.3
Eu	0.28	0.29	0.90	3.01	0.38	0.33	1.50	1.12	0.36	0.43	0.42	2.86	0.12	1.19	0.21
Gd	84.3	98.3	37.9	67.3	163	29.5	162	68.9	137	121	63.5	60.5	21.9	48.1	109
Dy	340	402	162	257	692	128	625	280	563	468	259	255	104	186	458
Er	636	795	335	603	1 371	296	1 243	572	1 099	951	517	562	253	402	927
Yb	1 053	1 274	622	1 356	2 131	591	2 062	975	1 715	1 465	837	979	477	707	1 525
Lu	154	188	96	227	317	96	309	144	252	217	130	149	77	110	230
Li	7.47	4.24	11.4	41.5	28.8	17.4	25.6	12.8	13.3	9.52	6.66	35.4	15.2	11.5	11.7
P	449	511	332	259	1 022	321	869	425	744	632	422	649	389	352	629
Ca	74.7	56.5	27.9	185	16.2	24.2	44.3	97.7	12.2	17.7	18.1	177	21.7	59.4	22.6
Ti	24.9	19.1	15.5	53.7	40.6	14.0	27.1	17.1	25.1	25.1	28.8	20.5	14.2	20.1	17.6
Sr	1.17	1.04	3.13	5.50	1.56	0.97	2.49	1.97	1.69	1.62	0.88	2.08	1.36	1.16	1.98
Y	3 904	4 755	2 010	3 011	8 483	1 784	7 108	3 179	6 665	5 439	2 858	3 250	1 418	2 245	5 536
Nb	89.1	78.2	88.9	68.7	108	56.9	62.9	55.3	49.5	43.5	25.9	52.3	27.3	29.2	40.0
Ba	5.09	5.04	286	6.78	2.12	2.66	4.28	5.37	3.62	3.34	1.86	2.43	1.30	3.62	4.16
Hf	10 708	10 166	11 650	9 824	9 970	11 752	11 213	10 892	9 994	9 355	9 531	11 224	10 727	9 762	10 596
Th	595	786	351	4 886	3 175	343	2 331	622	1 284	1 017	298	1 432	176	301	1 065
U	781	1 046	595	2 120	2 677	737	2 370	889	1 569	1 307	488	1 587	425	526	1 374
Th/U	0.76	0.75	0.59	2.31	1.19	0.47	0.98	0.70	0.82	0.78	0.61	0.90	0.41	0.57	0.78
Eu/Eu*	0.02	0.02	0.17	0.24	0.02	0.08	0.06	0.11	0.02	0.03	0.04	0.29	0.04	0.16	0.01
Ce/Ce*	35.2	18.6	16.1	1.80	18.3	13.8	4.00	4.45	18.0	22.8	10.7	4.22	50.2	4.58	22.3
ΣREE	2 329	2 829	1 295	2 786	4 815	1 183	4 599	2 122	3 850	3 300	1 850	2 127	960	1 503	3 319
ΣLREE	44.4	52.4	33.6	252	112	37.1	162	65.4	59.9	55.9	29.7	104	23.1	37.0	52.3
ΣHREE	2 267	2 757	1 254	2 511	4 673	1 140	4 401	2 040	3 767	3 222	1 806	2 005	933	1 454	3 248
Lu _N /La _N	13 024	5 752	1 439	74.4	4 122	1 432	444	491	7 585	9 647	4 137	260	8 798	700	11 973
Lu _N /Gd _N	14.8	15.4	20.6	27.3	15.7	26.3	15.4	16.9	14.9	14.5	16.5	20.0	28.6	18.4	17.1
Sm _N /La _N	238	95.2	17.3	1.15	64.6	13.7	8.26	8.51	113	159	70.3	4.47	67.9	11.6	158
T(Ti) (°C)	831	804	783	917	884	774	839	793	831	831	846	811	775	808	796

Figure 5. REE distribution spectra of zircons from sample F-B-2016-3-2-55 normalized to chondrite CI (McDonough and Sun, 1995).

character, which is reflected in low Sm_N/La_N ratios (1.15 and 8.26, respectively).

The REE patterns of the zircons exhibit positive Ce anomalies and negative Eu anomalies. Note that a negative correlation is observed between the values of a positive Ce anomaly (Ce/Ce^* ratio) and the total LREE abundances ($r = -0.5$). At spot 4.1 having the highest LREE content of 252 ppm, there is virtually no positive Ce anomaly ($\text{Ce}/\text{Ce}^* = 1.15$). By contrast, in zircons showing low LREE levels, the positive Ce anomaly is most pronounced. For instance, spot 13.1 with the total LREE concentration of only 23 ppm shows the most prominent positive Ce anomaly ($\text{Ce}/\text{Ce}^* = 50.2$).

The magnitude of a negative Eu anomaly varies from 0.01 to 0.29 with an average Eu/Eu^* value of 0.09. In zircons with a high content of LREE and flat LREE distribution patterns, small negative Eu anomalies are observed, whereas zircons with a fractionated distribution of both REE (total) and LREE demonstrate well-developed negative Eu anomalies. Hence, a positive correlation is observed between the values of the posi-

tive Ce and negative Eu anomalies ($r = 0.57$); i.e., zircons with a well-developed positive Ce anomaly also demonstrate a prominent negative Eu anomaly.

Hafnium abundances in the analyzed zircons are rather high and vary in a narrow range from 9 355 ppm to 11 751 ppm, with an average of 10 491 ppm. The content of Y ranges from 1 418 ppm to 8 483 ppm (with an average of 4 110 ppm) and shows a strong positive correlation with the total HREE content ($r = 0.99$). The concentration of P, varying from 259 ppm to 1 022 ppm, positively correlates with Y ($r = 0.92$) and HREE ($r = 0.88$) levels, which is consistent with the xenotime-type substitution ($\text{Y, REE}^{3+} + \text{P}^{5+} = \text{Zr}^{4+} + \text{Si}^{4+}$) (Finch and Hanchar, 2003).

Some zircon grains display increased abundances of non-formula elements. Calcium content varies from 12 ppm to 185 ppm, averaging 57 ppm. An increased Ca is characteristic of zircons with small positive Ce and negative Eu anomalies as well as with higher LREE content ($r = 0.64$). Strontium varies from 0.9 ppm to 5.5 ppm, with an average of 1.9 ppm. Ti content is between 14 ppm and 54 ppm, with an average of 24 ppm, which corresponds to a crystallization temperature range of 774–917 °C (average value of 821 °C) using the equation of Watson et al. (2006).

4 DISCUSSION

Grimes et al. (2015, 2009, 2007) demonstrated that the origin of zircons that crystallized from melts in continental and oceanic settings can be revealed based on their Yb, U, Y and Hf abundances. The examined zircon xenocrysts from gabbro-diorites of the Shaka Ridge (sample F-B-2016-3-2-55) have been plotted in the discrimination diagrams with outlined fields for oceanic and continental zircons (Fig. 6). In the Y vs. U/Yb binary plot (Fig. 6a), all the zircon compositions fall within the continental field. About half of the grains are located within the compositional area of zircons from continental granitoids, identified according to Ballard et al. (2002) and Belousova et al. (2006). In the Yb vs. U (Fig. 6b) and Hf vs. U/Yb (Fig. 6c) discrimination diagrams, all the zircon points plot into the area of zircons of continental origin as well. In the discrimination diagrams proposed by Belousova et al. (2002), the zircon population belongs to the compositional field of zircons from granitoids (in Yb/Sm vs. Y plot, Fig. 7a), or to the field of granitoids and partially to the field of zircons from syenites and associated pegmatites (in Ce/Ce* vs. Y plot, Fig. 7b).

Another effective criterion for the discrimination of zircon origin is the concentration of Li (Bouvier et al., 2012; Ushikubo et al., 2008). Zircons from rocks of oceanic crust are characterized by an extremely low Li content (less than 0.01 ppm), while continental crust zircons, as a rule, show much higher Li abundances in the range of 1 ppm–100 ppm (Grimes et al., 2011; Ushikubo et al., 2008). In the studied zircons, Li varies from 1.8 ppm to 50 ppm with an average of 16 ppm (Table 2), which makes it possible to unambiguously assign our samples to zircons of continental crust.

In the La vs. Sm_N/La_N space (Fig. 8) with the outlined compositional fields of unaltered magmatic, hydrothermal, and porous zircons (Bouvier et al., 2012; Fu et al., 2009; Grimes et al., 2009; Hoskin, 2005), the studied zircon xenocrysts com-

Figure 6. The U/Yb-based zircon discrimination diagrams modified after Grimes et al. (2015, 2007). (a) Y vs. U/Yb. The granitoid field comprises zircon analyses from northern Chile and eastern Australia (Belousova et al., 2006; Ballard et al., 2002); (b) Yb vs. U; (c) Hf vs. U/Yb. The compositions of zircons from sample F-B-2016-3-2-55 are shown by red circles.

prise a single trend with a clear negative correlation between these two geochemical parameters. Of these, eight spots (1.1, 2.1, 5.1, 9.1, 10.1, 11.1, 13.1, 15.1) unambiguously plot into the field of unaltered magmatic zircons, while six spots are located either within the overlap between the field of unaltered magmatic zircons and the field of porous zircons (spots 3.1, 6.1, 14.1) or in the area of porous zircons (spots 7.1, 8.1, 12.1). One grain with the highest La content (spot 4.1, Table 2) is located at the border between the Hf of porous and hydrother-

mal zircons. Taking into account that porous zircons are considered by some authors as a variety of hydrothermal zircons (Fu et al., 2009; Kirkland et al., 2009), the proportion of altered zircons among the xenocrysts may be more significant.

Therefore, a series of crucial geochemical signatures of the zircons from gabbro-diorites of the Shaka Ridge region (fractionated REE distribution patterns with a positive slope in chondrite-normalized values from light to heavy REE, positive Ce anomalies and negative Eu anomalies, high Th/U ratios, trace-element geochemistry) indicate the zircons to be of magmatic origin and have been derived from rocks of continental crust, mostly from granitoids (e.g., Balashov and Skublov, 2011; Hoskin and Schaltegger, 2003). These zircons were inherited from much older rocks (~2.8 Ga) with respect to the gabbro-diorite and thus represent genuine xenocrysts. Before being transported into young oceanic crust, the zircons had undergone a thermal influence (probably, metamorphism) with an age of ~600 Ma recorded by a lower discordia intercept (Fig. 4). The increased LREE contents and the flattened normalized LREE distribution spectra in some zircon grains are explained by that metamorphic fluids perhaps exerted some effect on the

geochemical characteristics of the zircons during this thermal event. The fluids also increased the Ca concentration in the zircons; this signature of fluid impact on zircon has been reported previously (e.g., Geisler and Schleicher, 2000).

Alternatively, such a marked increase in Ca and LREE concentrations in some zircon grains could have been caused by high-temperature hydrothermal alterations within young oceanic crust. There are also other indicators of zircon alteration during their residence in the oceanic crust. It is likely hydrothermal fluid influence that affected the La vs. Sm_N/La_N systematics (Fig. 8) and decreased the $\delta^{18}\text{O}$ values down to 1.75‰–3.15‰ (Table 1). Submarine hydrothermal solutions related to volcanic activity have high LREE/HREE and low Sm/La ratios (Bau and Dulski, 1999; Michard and Albarède, 1986) and thus could have contributed to the observed increase of LREE concentrations in some zircon grains. The values of $\delta^{18}\text{O}$ in the examined zircons are lower than typical values for mantle zircons of about 5.3‰ (Valley et al., 1998), which strongly implies the influence of hydrothermal fluid flow (Bindeman, 2008). $\delta^{18}\text{O}$ values in the range of 0–6‰ are typical for minerals from rocks belonging to the lower layer of oceanic crust that is composed of gabbro (Korolev et al., 2018; Valley et al., 2005; Eiler, 2001). Previously, it has been suggested that high-temperature (over 300 °C) hydrothermal alterations may lead to a decrease of $\delta^{18}\text{O}$ in minerals, including zircon, from the rocks of this layer with respect to mantle values (e.g., Korolev et al., 2018; Eiler, 2001; Gregory and Taylor, 1981). By contrast, zircon from oceanic plagiogranites and gabbros in the Mid-Atlantic and SWIR areas that is unaffected by submarine hydrothermal solutions is characterized by a rather narrow $\delta^{18}\text{O}$ interval with an average value of $5.2\text{‰} \pm 0.5\text{‰}$, indicating isotopic-geochemical equilibrium with MORB (Grimes et al., 2011).

It is challenging at this stage of research to give an unambiguous answer to the urgent question—how were the continent-derived zircons delivered into oceanic igneous rocks in the vicinity of the SWIR? Over the past two decades, a number of hypotheses have been put forward to explain the unusual find-

Figure 7. (a) Yb/Sm vs. Y and (b) Ce/Ce* vs. Y discriminant diagrams. The fields of zircon compositions used as discriminants for different rock types are after Belousova et al. (2002). 1. Aplites, leucogranites; 2. granites; 3. granodiorites and tonalities; 4. larvikites; 5. nepheline syenite and syenite pegmatite; 6. syenite pegmatites; 7. carbonatites; 8. syenites; 9. kimberlites; 10. lamproites; 11. mafic rocks. The compositions of zircons from sample F-B-2016-3-2-55 are shown by red circles.

Figure 8. $(\text{Sm}/\text{La})_N$ vs. La (ppm) discriminant diagram. Compositional fields are after Hoskin (2005), Grimes et al. (2009), Fu et al. (2009), Bouvier et al. (2012). The compositions of zircons from sample F-B-2016-3-2-55 are shown by red circles.

ings of continent-derived zircons in oceanic-floor magmatic rocks. A pioneer study of Pilot et al. (1998) proposed two plausible interpretations to explain the occurrence of unusually old zircons (~330 and ~1 600 Ma) near the Kane fracture zone in the Mid-Atlantic Ridge. During the Atlantic opening, fragmented crustal material sank into small circulation cells that developed in the shallow mantle at each side of the ridge axis, and this material was transported through these cells to the ridge axis (Pilot et al., 1998). Alternatively, continental crustal material has been entrapped in the Kane fracture zone since the Atlantic opening as a result of repeated ridge jumping and transform migration (oscillatory spreading), with some of this material subsequently migrating down the ridge axis (Pilot et al., 1998).

The study of Bea et al. (2020), which summarizes a significant number of older-than-host zircon xenocryst samples (190 Ma to 3 Ga) in oceanic rocks of the Atlantic, suggested that the source of ancient xenocrysts are fragments of continental crust preserved in the vicinity of the mid-ocean ridge. Upwelling mafic magma can scavenge continental xenoliths, disintegrating them, and thus releasing zircon xenocrysts. Alternatively, it is assumed that hot mafic magma penetrating zircon-containing oceanic plagiogranites or fragments of continental crust may locally heat these rocks above the solidus. As a result of this process, patches of low-temperature silicate magma enriched with zircon are formed, which then migrate and mix with the rapidly rising magma of mafic composition (Bea et al., 2020 and references therein).

For the Indian Ocean, there are few reports dealing with findings of ancient zircon xenocrysts. The occurrences of Proterozoic (660–840 and >1 971 Ma; Torsvik et al., 2013) and Archaean (2.5–3.0 Ga; Ashwal et al., 2017) zircons on the Island of Mauritius were ascribed to zircon assimilation from ancient fragments of continental lithosphere beneath Mauritius and subsequent transportation to the surface by plume-related lavas (Ashwal et al., 2017; Torsvik et al., 2013). In the work by Cheng et al. (2016), two possibilities for the origin of Jurassic (~180 Ma) zircons in gabbroid rocks of the SWIR are considered: (1) the preservation of an intact Gondwana fragment on the ocean floor; (2) the occurrence of a partially altered continental relic that once resided in shallow regions of the upper mantle, and was entrained and transported to the vicinity beneath the axis.

From these examples, it is obvious that a convincing and unambiguous interpretation of the origin of unusually old zircons in young oceanic rocks has not yet appeared; it is also difficult to verify the explanations (Cheng et al., 2016). Note that the zircons examined in these papers span a very broad range of crystallization age (from 180 Ma to 3 Ga), which indicates their derivation from very different continental sources. In general, there is a series of major factors possibly responsible for the zircon transportation, such as a long-lived subduction zone, generation of mantle plumes, Atlantic opening, Gondwana supercontinent breakup, and further melting of small continental blocks of the sub-Gondwana lithosphere containing an ancient zircon component. However, many authors agree that the preservation of ancient continental fragments in the vicinity of a ridge axis is a necessary requirement for the transportation of zircons to occur. Taking into account the complex geological

history of the study area, geochemical characteristics of the zircon xenocrysts examined here, and petrochemical characteristics of the host gabbro-diorite sample (high LILE, low HFSE), it appears that the zircons were captured as xenocrysts during the formation and migration of parental for the gabbro-diorite melts. Some authors provided strong evidence for the presence of the remains of the sub-Gondwana lithospheric mantle in the form of xenoliths and schlieren within modern oceanic lithosphere (Frey et al., 2002; le Roux et al., 2002; Kamenetsky et al., 2001; Douglass et al., 1999). We suggest that small blocks of continental crust after the Gondwana breakup could have survived in younger oceanic lithosphere and became involved in melting processes. The exact mechanism of crystal recycling into the mantle, however, is yet to be constrained. The continuing discoveries of ancient zircon in the mid-ocean ridges and deep ocean basins will shed additional light on this urgent issue.

5 CONCLUSIONS

(1) For the first time, zircon in gabbro-diorites of the Shaka Ridge was described. The U-Pb isotope system of the zircons records a crystallization age of ~2.8 Ga and an age of a superimposed thermal event (metamorphism?) of ~600 Ma.

(2) Zircon grains show geochemical signatures revealing their magmatic origin, i.e., fractionated REE distribution patterns (HREE-enriched over LREE), positive Ce-anomalies and negative Eu-anomalies, high Th/U ratios (0.59–7.77).

(3) In discrimination diagrams based on the concentrations of several indicator elements (Yb, U, Y, Hf, etc.), the zircons fall into the fields of zircons from rocks of continental crust, mostly granitoids. Our results show the zircons to be derived from ancient continental crust and thus being genuine xenocrysts with respect to the host gabbro-diorite.

(4) During their residence within young oceanic crust, the zircons xenocrysts experienced the influence of a high-temperature hydrothermal fluid, which reduced the $\delta^{18}\text{O}$ values of the zircons to 1.75‰–3.15‰.

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