Geochemistry and Isotopic Age of Zircons from Rocks of Ultramafic Massifs in the Southern Folded Framing of the São Francisco Craton (Southeastern Brazil)

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Abstract—We present the first data on the geochemistry and isotopic age of zircons from rocks of the Roseta (lherzolite and olivine orthopyroxenite) and Córrego da Areia (olivine orthopyroxenite) ultramafic massifs localized among Archean–Proterozoic metamorphic strata in the southern folded framing of the São Francisco Craton. The examined zircons differ in crystal morphology, the intensity and type of cathodoluminescence, oscillatory zoning, the distribution of trace elements, and U–Pb isotopic age. Zircon crystals from the Roseta lherzolite have an age of 800–728 Ma and show negligible cathodoluminescence. Some of them have reaction rims with an age of 663–619 Ma. The crystal cores are enriched in rare earth elements (REE) but are often depleted in U as compared with the reaction rims. The age of zircons from the Roseta olivine orthopyroxenite showing moderate cathodoluminescence and often have a rhythmic oscillatory zoning. They are characterized by an uneven distribution of REE and other trace elements and have high contents of U and Th. Most of these zircons have an ancient isotopic age (2558–2100 Ma). The examined zircons are of several types: relict, xenogenic, syngenetic, and epigenetic. The Roseta and Córrego da Areia massifs are considered to be protrusive outliers of a deep-seated Precambrian mafic–ultramafic complex, which were tectonically transferred along faults into the intensely metamorphosed Archean–Proterozoic strata in the southern folded framing of the São Francisco Craton.

Keywords: ultramafic rocks, zircons, geochemistry, LA-ICP-MS method, isotopic age, U-Pb method, SIMS SHRIMP II, São Francisco Craton, Brazil

INTRODUCTION

Mafic–ultramafic massifs are quite local in Brazil. Some of them, e.g., Barro Alto (Nilson, 1984; Ferreira Filho et al., 2010), Mirabela (Barnes et al., 2011), and Americano do Brasil (Silva et al., 2011), are layered intrusions. Others are part of greenstone belts (Arndt et al., 1989; Schrank and Silva, 1993; van Acken et al., 2016). The rest occur in ophiolite associations (Magalhães, 1985; Strieder and Nilson, 1992; Suita et al., 2004; Queiroga et al., 2007; Pinheiro and Suita, 2012). Among the latter are the Roseta and Córrego da Areia massifs within the Neoproterozoic orogenic belts around the São Francisco Craton. These belts, framing the São Francisco Craton in the south, are composed of Archean–Proterozoic complex metamorphic deposits (Fig. 1).

Corresponding author. *E-mail adress:* felix@igm.nsc.ru (F.P. Lesnov) In recent years, numerous U–Pb isotope dates have been obtained for zircons from various metamorphic rocks (gneisses, granulites, charnockites, amphibolites, etc.) composing the basement of the São Francisco Craton and its southeastern folded framing (Campos et al., 2003; Heilbron et al., 2010; Albert et al., 2016; Coelho et al., 2017; Heilbron et al., 2017). They show a predominance of two groups of zircons of different ages (2890–1656 and 787–550 Ma) in these rocks. There are no data on zircons from mafic–ultramafic rock massifs localized in the southern folded framing of the São Francisco Craton and other regions.

Mafic–ultramafic massifs (mostly small) in the southern folded framing of the São Francisco Craton have been poorly studied in terms of the structural position, geologic structure, chemical composition, and, particularly, time and conditions of formation. The goal of our research was to fill this gap, based on the data obtained in the study of zircons from rocks of the Roseta and Córrego da Areia ultramafic massifs. We have described the geologic structure, mineral and



Fig. 1. Schematic tectonic regionalization of the southern folded framing of the São Francisco Craton, after Trouw et al. (2013) and Coelho et al. (2017), modified (*A*), and of the Brazil area, after Almeida (1977), modified (*B*). *A*: SFC, São Francisco Craton; P, Passos Nappe; G, Guaxupé Nappe; S, Soccoro Nappe; E, Paraiba do Sul Terrane. *1*, Paraná Basin; *2*, alkaline plutons; *3*–5, São Francisco Craton: *3*, basement, *4*, roof, *5*, autochthonous and para-autochthonous metasedimentary rocks; *6*, Andrelândia and Passos Nappes; *7*, Soccoro and Guaxupé Nappes; *8*, Paraiba do Sul Terrane; *10*, External Domain; *11*, Juiz de Fora Domain; *12*, Rio Negro Arc; *13*, Oriental Terrane; *14*, Cabo Frio Terrane. *B*: Cratons: I, Amazon; II, São Luís, III, São Francisco; IV, Paranapanema (the dashed line contours the area overlain by a metasedimentary cover; the rectangle marks the area shown in *A*).

petrographic compositions, and geochemical features of the massif rocks as well as the main properties and U–Pb isotopic age of zircons that were found for the first time in ultramafic rocks of this region. Representative rock samples for a zircon study were taken by M. Pinheiro during the field investigations. Zircons from the Roseta massif were separated from two rocks: lherzolite (80 kg sample, bedrock exposure in the northern part of the massif) and olivine orthopyroxenite (45 kg sample, vein cutting harzburgites, penetrated by a tunnel in the southern part of the massif). Zircons from the Córrego da Areia massif were separated from olivine orthopyroxenite (80 kg sample, bedrock exposure in the central part of the massif).

METHODS

Zircon crystals were investigated by integrated analytical methods. The contents of major components were determined on a JEOL JXA-8100 electron microprobe with an accelerating voltage of 20 kV and a current of 200 nA (Analytical Center for Multielemental and Isotope Research of the Institute of Geology and Mineralogy, Novosibirsk, analyst V.N. Korolyuk). Analysis for rare earth elements (REE) and other trace elements in the bulk rock samples (from which zircons were separated) was performed by ICP-MS (Analytical Center for Multielemental and Isotope Research of the Institute of Geology and Mineralogy, Novosibirsk, analysts I.V. Nikolaeva and S.V. Palesskii). Weighted rock specimens were decomposed in a MARS-5 teflon autoclave, using the mixtures of HNO₂, HF, and HCl precleaned by sub-boiling distillation. After the specimen decomposition, the contents of trace elements in the solutions were determined with an Element mass spectrometer, which was calibrated against standard samples. Indium was added and used as an internal standard. The detection limits of REE were as follows (ppm): La (0.02), Ce (0.03), Pr (0.003), Nd (0.004), Sm (0.001), Eu (0.0006), Gd (0.0005), Tb (0.0005), Dy (0.0006), Ho (0.0005), Er (0.0005), Tm (0.0002), Yb (0.0003), and Lu (0.0002).

Rare-earth elements and some other trace elements in zircons were determined by LA–ICP-MS, using an iCAP Q (Thermo Fisher Scientific, USA) quadrupole inductively coupled plasma mass spectrometer and an NWR-213 (ESI, USA) ($\lambda = 213$ nm) solid-state laser ablation system (Institute of Inorganic Chemistry, Novosibirsk, analyst N.S. Medvedev). The instrument was calibrated against the NIST SRM 610, 612, 614, and 616 standard samples. During the analysis, an epoxy block with implanted zircon crystals was placed in a laser chamber; then, the chamber was evacuated and filled with helium. Laser irradiation of the crystal surface led to the formation of specimen aerosol particles, which were transferred by a helium flow (500 mL/min) to the source of ionization through a fluoroplastic tube, 4 mm inner diameter. The main laser ablation parameters were: laser frequency 20 Hz, spot diameter 60 µm, and energy density 15 J/cm². The signal integration time for each analytical isotope was 0.1 s. Silicon was used as an internal standard in order to take into account the difference in the efficiency of sampling of crystals of different compositions. The measured intensities of analytical isotopes were normalized to the intensity of silicon with regard to its content in the zircon crystal under study, which was predetermined using an electron microprobe. The first stage was test analyses: Several crystals were exposed to laser at a certain point for 1 s. Then, the laser focusing was shifted vertically down by 2 µm, and the measurements were repeated. The results suggest geochemical inhomogeneity (microzoning) in the distribution of trace elements in the analyzed zircon crystals. The second stage was measurement of the contents of trace elements in two representative zircon crystals by horizontal scanning of their surface along certain profiles. The diameter of sampling point was 30 µm. The crystal was scanned at a rate of 10 μ m/s, but the energy frequency and density were not changed, 20 Hz and 15 J/cm², respectively. During one measurement, laser was transferred along the profile for 20–30 µm; scanning was started beyond the crystal, and the beginning of the crystal sampling was determined from the drastically increased signals of Si and Zr. The measurements were made at 25 points along each profile. The contents of trace elements were calculated from the signals of their isotopes normalized to the signal of Si used as an internal standard. The error of determination of the element contents did not exceed 30%. The results of measurements by horizontal laser scanning of zircon crystals confirmed their geochemical inhomogeneity (microzoning). This LA-ICP-MS technique of solid-phase analysis for trace elements was considered elsewhere (Gray, 1985; Moenke-Blankenburg et al., 1992; Fernandez et al., 2007; Chernonozhkin and Saprykin, 2011). The same method and the same equipment were used to study the distribution of trace elements in coexisting minerals from the rocks of the Roseta massif (Pinheiro et al., 2016a).

The U–Pb isotopic age of zircons has been determined on a SHRIMP-II high-resolution secondary-ion mass spectrometer by the technique described by Schuth et al. (2012). The study was carried out at the Center of Isotopic Research at the Russian Geological Research Institute, St. Petersburg. In addition, the morphology and cathodoluminescence (CL) of the zircon crystals have been elucidated, and their U and Th contents have been established.

GEOLOGIC STRUCTURE AND PETROGRAPHY OF THE MASSIFS

The Roseta massif, located 10 km southwest of the Liberdade city (massif center: $21^{\circ}57'36.01''$ S; $44^{\circ}20'17.97''$ W), is structurally confined to a NW striking thrust separating a block of kyanite–microcline gneisses (Carvalhos Klippe) and a block of feldspathic schists (Liberdade Nappe) (Trouw et al., 2000). Schistosity of the rocks of both blocks is of NW strike and SW dip. The massif exposes in an area of ~4 km² and is oval in plan (Fig. 2). It is composed of variably serpentinous lherzolites, harzburgites, clinopyroxenecontaining harzburgites, and vein olivine websterites and olivine orthopyroxenites with amphibole and green spinel impurity.

Olivine in the massif lherzolites amounts to 30–35%. Its grains reach 3 cm in size and show traces of plastic deformations and later recrystallization to mosaic aggregates. The mineral has high contents of NiO (0.71–0.87 wt.%) (Pinheiro and Lesnov, 2016a; Pinheiro et al., 2016b). Orthopyroxene grains in the lherzolite amount to 30–40% and also show traces of plastic deformations and later recrystallization and clinopyroxene lamellae (exsolution structures). Clinopyroxene in the lherzolite is present as xenomorphous



Fig. 2. Schematic geological map of the Roseta massif, after Heilbron et al. (2003) and Paciullo et al. (2003), modified. *1*, kyanite–microcline gneisses (Carvalhos Klippe); *2*, feldspathic schists and gneisses with interbeds of muscovite gneisses (Liberdade Nappe); *3*, ultrabasic rocks; *4*, dips and strikes of rock schistosity; *5*, tectonic contacts of the Roseta massif rocks with the framing rocks; *6*, thrust; *7*, localities of sampling for zircon isotope dating: 1, sample 4758 (lherzolite), 2, sample 4760 (olivine orthopyroxenite).



Fig. 3. Schematic geological map of the Córrego da Areia massif, after Magalhães (1985). *1*, diabase dikes (Mesozoic); *2*, staurolite–garnet schists and quartzites (Carrancas System, Late Neoproterozoic); *3*, quartzites and quartz schists with green mica (São Thomé das Letras Formation, Late Neoproterozoic); *4*, amphibolites and mafic schists (Archean–Paleoproterozoic); *5*, metamorphosed ultramafic rocks (Archean–Paleoproterozoic); *6*, basement rocks, biotite gneisses with amphibolites and metasedimentary rocks (Archean–Paleoproterozoic); *7*, schistosity dips and strikes of rock schistosity; *8*, direction of mineral linearity; *9*, synforms; *10*, antiforms; *11*, *12*, thrusts: *11*, predicted, *12*, observed; *13*, locality where sample 4756M was taken for zircon isotope dating (olivine orthopyroxenite).

grains (20–30%). There is also an accessory phase of fine Cr-spinel segregations (up to 2%) in the interstices of olivine and pyroxene grains.

Olivine orthopyroxenite composes a thin vein (penetrated by a tunnel) cutting serpentinous harzburgites. The rock is characterized by an uneven distribution of olivine grains, subordinate orthopyroxene and amphibole grains, rare clinopyroxene grains, and fine green spinel segregations. Olivine has extremely low contents of NiO (0.01–0.02 wt.%) (Pinheiro et al., 2016b).

The Córrego da Areia massif, located in the Carrancas province, 55 km northwest of the Roseta massif (massif center: 21°30′53.859″ S; 44°34′2.661″ W), is a N–S striking lenticular body ~2 km long and ~40 m wide (Magalhães, 1985). It is structurally confined to a N–S striking thrust of western dip. Staurolite–garnet schists, quartzites, biotite gneisses,

and amphibolites expose in the massif framing (Fig. 3). The massif is composed of coarse-grained olivine orthopyroxenites with amphibole impurity (5-20%) and fine green spinel segregations (1-4%).

The chemical and trace-element compositions of lherzolite and olivine orthopyroxenites from the two massifs are presented in Table 1. Lherzolite has low contents of TiO₂, CaO, P₂O₅, and alkalies, is slightly enriched in NiO, Zr, Hf, U, and Th, and is abnormally rich in LREE (Fig. 4). Olivine orthopyroxenite from the Roseta massif has low contents of NiO and high contents of Sr, Y, Nb, Ba, Zr, Hf, and REE (Fig. 4). The chondrite-normalized REE patterns of websterites from this massif show permanent negative Ce anomalies (Pinheiro and Lesnov, 2016b). Olivine orthopyroxenite from the Córrego da Areia massif has low contents of NiO, TiO₂, Sr, Ba, Y, Nb, Ta, Zr, Hf, U, Th, and REE but is slightly enriched in Cr₂O₃ and has a higher Zr/Hf ratio than olivine orthopyroxenite from the Roseta massif.

MORPHOLOGY AND CATHODOLUMINESCENCE PROPERTIES OF ZIRCON CRYSTALS

Zircon crystals were separated from three samples: lherzolite from the Roseta massif (sample 4758, 20 crystals), olivine orthopyroxenite from the Roseta massif (sample 4760, 60 crystals), and olivine orthopyroxenite from the Córrego da Areia massif (sample 4756M, 60 crystals). Zircons from the Roseta lherzolite are of two types according to their morphology and cathodoluminescence (CL) properties. The first type is mostly irregular-shaped crystals; some of them have preserved segments with a crystallographic faceting. The crystal cores show negligible CL and oscillatory zoning (Fig. 5). The second type is crystals with 20-40 µm wide reaction rims. Zircon crystals from the Roseta olivine orthopyroxenite are of elongate-prismatic habit, often with slightly rounded faces. Most of these zircons are characterized by moderate to intense CL and unrhythmic oscillatory zoning. Some of them contain fine inclusions with more intense CL (Fig. 6). Some of the crystals have narrow rims with intense CL. Most of zircon crystals from the Córrego



Fig. 4. Chondrite-normalized REE patterns of the studied bulk lherzolite and olivine orthopyroxenites from the Roseta and Córrego da Areia massifs (data from Table 1).

Table 1. Contents of major components (wt %) and trace elements (ppm) in lherzolite and olivine orthopyroxenites from the Roseta and Córrego da Areia massifs

Component	Roseta massif	ssif Córrego da A			
	Lherzolite	Olivine orthopyrox	enite		
	(sample 4758)	(sample 4760)	(sample 4756M)		
SiO ₂	53.92	32.95	45.83		
TiO ₂	0.06	2.41	0.23		
Al ₂ O ₃	1.72	17.96	7.48		
Fe ₂ O _{3 tot}	8.04	18.75	13.10		
MnO	0.16	0.17	0.17		
MgO	32.65	23.42	24.52		
CaO	1.50	2.61	5.20		
Na ₂ O	0.05	0.17	0.33		
K ₂ O	0.02	0.02	0.06		
P_2O_5	0.01	0.19	0.02		
BaO	< 0.01	0.01	< 0.01		
V ₂ O ₅	0.01	0.06	0.02		
Cr ₂ O ₃	0.56	0.02	0.28		
NiO	0.43	0.10	0.10		
LOI	0.77	1.64	2.65		
Total	99.91	100.56	100.01		
Zr	168	548	56		
Hf	3.7	13.8	1.28		
Rb	1.07	0.65	1.62		
Sr	7.7	109	45		
Y	11.1	39	3.4		
Nb	0.14	18.8	0.18		
Cs	0.11	0.14	0.14		
Ba	5.6	24	12.2		
Та	< 0.05	0.83	< 0.05		
Th	0.08	1.29	0.03		
U	0.05	0.19	0.03		
La	5.8	30	1.08		
Ce	0.82	45	2.3		
Pr	1.48	6.8	0.32		
Nd	4.9	25	1.45		
Sm	0.87	5.3	0.39		
Eu	0.33	1.85	0.21		
Gd	1.30	5.9	0.51		
Tb	0.22	0.89	0.08		
Dy	1.40	5.5	0.51		
Но	0.32	1.21	0.11		
Er	0.81	3.6	0.35		
Tm	0.095	0.56	0.05		
Yb	0.53	3.7	0.37		
Lu	0.08	0.54	0.05		
ΣREE	18.96	135.9	7,78		
$(La/Yb)_n$	7.53	5.77	7.78		
Zr/Hf	45.4	39.7	43.8		

Note. Analyses were carried out by XRF (major components, analyst N.G. Karmanova) and ICP-MS (trace elements, analysts I.V. Nikolaeva and S.V. Palesskii) at the Analytical Center of the Institute of Geology and Mineralogy, Novosibirsk.

da Areia olivine orthopyroxenite are of elongate-prismatic habit, with a moderate to low CL intensity, and seldom show an oscillatory zoning. Some of them have $5-30 \mu m$ wide rims with intense CL (Fig. 7).

CHEMICAL COMPOSITION AND GEOCHEMISTRY OF ZIRCONS

The contents of ZrO_2 , HfO_2 , and SiO_2 in the analyzed zircon crystals from samples 4758 and 4756M vary over narrow and nearly the same intervals of values (Tables 2 and 3). These zircons are similar in the range of ZrO_2/HfO_2 values: 27.5–44.9 and 27.9–45.9, respectively. The rims of several crystals from lherzolite (Roseta massif) and olivine orthopyroxenite (Córrego da Areia massif) are more or less enriched in Zr and Hf than the cores.

In recent literature, the contents of REE and other trace elements in zircons are usually determined by LA-ICP-MS at arbitrary single points of crystals. These analyses show that trace elements are usually unevenly distributed throughout the crystals; therefore, such single determinations are insufficiently correct (Lesnov, 2015). Our aim was not to determine the contents of trace elements at single points of all zircon crystals from the collection under study but to analyze the distribution of impurities within two representative crystals by LA-ICP-MS, through their vertical and horizontal scanning with a laser beam. At the initial stage of our study, the contents of trace elements were determined by vertical scanning at ten microlevels at arbitrary points of several crystals. These measurements showed that the contents of trace elements in the crystals varied significantly with the depth of laser beam penetration, which suggests geochemical inhomogeneity (microzoning) of these zircons. At the second stage of the study, the contents of trace elements were determined during horizontal scanning of two representative zircon crystals at intervals between points 1 and 25 located along linear profiles (Fig. 8). These measurements showed that the reaction rim on crystal 4758 13 (intervals between points 1-3 and 23-25) is depleted in Ce, Eu, Gd, Dy, Ho, Er, Yb, Y, Nb, and, partly, Hf relative to the crystal core (the interval between points 6-12) (Table 4). The constructed curves of variation in REE contents along the above profile are convex upward, which indicates enrichment of the crystal core with these elements as compared with the crystal rim (Fig. 9). The shape of the curves of variation in REE contents along the profile through crystal 4756M 11 also indicates that its rim is slightly depleted in REE relative to its core (Table 5, Fig. 9). The geochemical inhomogeneity of zircon crystals is also seen from different shapes of the chondrite-normalized REE patterns of the scanned crystals and from the different arrangements of REE composition points in them (Fig. 10). For example, the core of crystal 4758 13 (points 9-15) shows REE patterns with strong positive Ce anomalies specific to magmatic zircons.



Fig. 5. Morphology of zircon crystals from lherzolite (sample 4758, Roseta massif). White circles show the position of SIMS SHRIMP spots (25 μm in diameter). Here and in Fig. 7, a dotted square marks the crystal in which the content of trace elements was determined by LA–ICP-MS (see Fig. 8). Here and in Figs. 6–8, CL photomicrographs.

The REE patterns of the crystal rim (points 20–23) show no positive Ce anomaly and thus are atypical of magmatic zircons. The chondrite-normalized REE patterns of crystal 4756M at all scanned points also have a shape characteristic for magmatic zircons but differ in the arrangement of REE composition points, which testifies to geochemical inhomogeneity of the crystal (Fig. 10).

The determined contents of U and Th at different points of the studied zircon crystals showed their geochemical inhomogeneity (Table 6, Fig. 11). For example, the cores of crystals with a reaction rim from the Roseta lherzolite, showing negligible CL, are characterized by low contents of U (4–33 ppm) and Th (4–12 ppm) and high Th/U ratios (0.18–0.50). The reaction rims of these crystals have higher contents of U (134–318 ppm), lower contents of Th (4–12 ppm), and extremely low Th/U ratios (0.02–0.04) as compared with the cores. The cores of crystals without a reaction rim from the same lherzolite are enriched in U (247–1675 ppm) and Th (35–187 ppm) and have low Th/U ratios (0.01–0.14). Zircons from the Roseta olivine orthopyroxenite have varying contents of U (59–308 ppm), low con-

tents of Th (2–5 ppm), and extremely low Th/U ratios (<0.03). Zircons from the Córrego da Areia olivine orthopyroxenite have varying but high contents of U (65–929 ppm) and Th (15–401 ppm); most of them are characterized by high Th/U ratios (0.09–1.60).

Thus, the REE and trace-element patterns of zircons from the Roseta and Córrego da Areia rocks show their geochemical inhomogeneity related both to the variation in the contents of impurities accumulated during the crystal growth and to their epigenetic redistribution. Therefore, it is necessary to take into account the geochemical inhomogeneity of individual zircon crystals during a LA–ICP-MS study of the distribution of trace elements in them.

ISOTOPIC AGE OF ZIRCONS

We determined the isotopic age of zircons from lherzolite (sample 4758) (Table 7) and olivine orthopyroxenite (sample 4760) (Table 8) from the Roseta massif. The age of zircons from the lherzolite varies in two intervals of values. The age of the cores of crystals having reaction rims and showing negligible CL (analyses 1.1, 2.1, 8.1, 9.1, and 12.1) is within 800–728 Ma (Middle Neoproterozoic). The age of the cores of crystals lacking reaction rims and also showing negligible CL (analyses 3.1, 4.1, 5.1, 6.1, 7.1, 10.1, and 11.1) is within 663–619 Ma (Middle–Late Neoproterozoic).

The same range of age values has been established for the reaction rims of the first group of crystals (analyses 1.2, 8.2, 11.2, 12.2, and 13.2). The centers of the confidence interval ellipses for the second-group ages correspond to the concordant age of 638.2 ± 5.4 Ma (Fig. 12). The age of zircons from olivine orthopyroxenite from the Roseta massif (sam-



Fig. 6. Morphology of zircon crystals from olivine orthopyroxenite (sample 4760, Roseta massif).

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Analysis SiO ₂	ZrO ₂	HfO_2	Ce ₂ O ₃	Yb_2O_3	ThO ₂	UO ₂	Total	ZrO_2/HfO_2
1.1c 32.29	65.85	1.61	0.003	0.030	B.d.l.	0.006	99.79	40.9
1.1r 32.72	65.20	2.37	0.007	B.d.l.	0.002	0.069	100.37	27.5
2.1c 32.59	65.04	2.08	0.011	0.050	0.029	0.001	99.81	31.3
2.1r 32.84	65.46	2.07	0.008	0.008	B.d.1.	0.032	100.43	31.4
5.1r 32.66	65.06	2.32	B.d.l.	0.009	B.d.1.	0.014	100.07	28.0
6.1c 32.56	65.70	1.70	B.d.l.	B.d.l.	0.021	0.087	100.07	38.6
6.1r 32.52	66.18	1.65	B.d.l.	B.d.l.	0.002	0.218	100.57	40.1
8.1c 32.47	65.55	1.46	0.021	0.041	B.d.l.	B.d.1.	99.57	44.9
8.1r 32.53	65.48	2.26	B.d.l.	B.d.l.	0.001	0.015	100.29	29.0
9.1c 32.59	65.28	1.57	B.d.l.	0.031	0.010	0.016	99.50	41.6
10.1c 32.51	65.20	1.46	0.017	B.d.l.	0.082	0.684	99.96	44.7
10.1r 32.76	65.57	1.18	0.021	B.d.l.	0.008	0.202	99.74	55.6
11.1c 32.43	65.42	2.02	0.001	0.030	0.011	0.067	99.98	40.8
11.1r 32.70	65.36	2.25	B.d.l.	0.011	0.004	0.053	100.57	29.0
12.1c (a) 32.44	65.42	1.53	0.014	0.057	B.d.l.	B.d.1.	99.47	43.4
12.1c (b) 32.64	66.03	1.52	B.d.l.	0.028	B.d.1.	0.007	100.22	43.4
12.1r 32.59	65.62	2.26	B.d.l.	B.d.l.	B.d.1.	B.d.1.	100.48	29.0
13.1c 32.43	65.47	1.59	0.008	0.035	0.004	B.d.1.	99.55	41.2

Note. Here and in Table 3, B.d.l., below detection limit; measurement points within the crystal: c, core; r, rim.

Table 3. Chemical composition of zircons from olivine orthopyroxenite (sample 4756M, Córrego da Areia massif), wt.%

Analysis	SiO ₂	ZrO ₂	HfO ₂	Ce ₂ O ₃	Yb ₂ O ₃	ThO ₂	UO ₂	Total	ZrO_2/HfO_2
1.1c	32.41	65.22	1.50	0.015	B.d.1.	0.015	0.008	99.18	43.5
1.1r	32.33	65.54	1.67	0.016	0.008	B.d.l.	B.d.l.	99.57	39.2
2.1c	32.39	64.70	1.62	0.010	0.017	0.055	0.032	98.81	39.9
2.1r	32.68	65.25	1.69	0.030	0.002	0.030	0.033	99.75	38.6
3.1c	32.51	65.44	1.56	0.018	B.d.l.	0.017	0.005	99.55	41.9
3.1r	32.38	64.74	2.29	0.024	0.036	0.005	B.d.1.	99.50	28.3
4.1c	32.54	64.99	1.80	0.002	B.d.l.	0.027	0.172	99.54	36.1
4.1r	32.24	65.13	2.07	0.028	0.017	0.016	0.094	99.63	31.5
5.1c	32.43	65.05	1.59	0.028	0.002	0.056	0.096	99.72	40.9
13.1c	32.47	65.30	2.25	B.d.l.	0.045	0.003	0.034	100.11	29.0
14.1c	32.08	64.19	1.80	0.008	0.102	0.019	0.063	98.85	35.7
14.1r	32.62	65.34	1.44	B.d.l.	0.044	0.044	0.036	99.48	45.4
20.1c	32.72	65.72	1.78	B.d.l.	B.d.l.	0.008	0.040	100.26	36.9
20.1r	32.39	64.99	2.33	0.032	0.051	B.d.1.	B.d.l.	99.89	27.9
21.1c	32.59	65.07	1.54	0.022	0.018	0.017	B.d.1.	99.28	42.3
21.1r	32.52	65.40	1.53	0.098	B.d.l.	0.140	0.201	100.16	42.7
22.1c	32.44	66.01	1.54	B.d.l.	B.d.l.	0.016	0.002	100.06	42.9
22.1r	32.49	65.71	1.57	0.009	B.d.l.	0.013	0.004	99.82	41.9

ple 4760), which are similar in morphology and CL properties, is in the range 622.6–596.9 Ma (Late Neoproterozoic) (Table 8).

Most of zircon crystals from olivine orthopyroxenite from the Córrego da Areia massif (sample 4756M) have a much older isotopic age than zircons from the Roseta massif. Their age values show three intervals: 2558–2504 Ma (Late Neoarchean), 2198–2074 Ma (Early–Middle Paleoproterozoic), and 589–576 Ma (Late Neoproterozoic). Measurements in crystals 20.1 (analyses 20.1c and 20.2r) and 21.1 (analyses 21.1r and 21.2c) showed that their cores are much older than their rims (Table 9). The centers of the confidence interval ellipses for the ages of zircons from the Córrego da Areia orthopyroxenite are approximated by two discordiae (Fig. 13).



Fig. 7. Morphology of zircon crystals from olivine orthopyroxenite (sample 4756M, Córrego da Areia massif).



Fig. 8. Photomicrographs of zircon crystals 4758_13 (lherzolite, Roseta massif) and 4756M_11 (olivine orthopyroxenite, Córrego da Areia massif) (see Figs. 5 and 7). Arrows show the profiles along which an LA–ICP-MS analysis for trace elements was carried out.

Table 4. Contents of trace elements in zircon crystal 4758_13 (lherzolite, Roseta massif), ppm

Element	nt Measurement point													
	1	2	3	4	5	6	7	8	3	9	10	11	12	13
La	0.23	0.018	B.d.l.	0.029	0.013	0.022	B.d.1.	. ().049	0.029	0.019	B.d.l.	0.023	0.042
Ce	2.1	1.7	4.6	5.9	4.9	6.8	7.2	6	5.7	4.5	8.2	9.4	8.2	4.8
Nd	0.53	0.80	3.5	3.9	3.3	3.4	3.7	2	4.8	4.3	4.0	5.0	4.7	2.0
Sm	1.0	2.4	10.0	10.0	10.0	12.0	18.0	1	14.0	14.0	14.0	17.0	18.0	8.7
Eu	0.39	0.97	3.4	5.0	4.0	4.6	5.2	4	5.3	4.0	7.5	5.1	6.8	3.0
Gd	7.9	17.0	69	76	82	89	100	1	100	86	120	100	110	52
Tb	3.1	5.3	24	26	19	30	34	2	28	27	32	34	32	21
Dy	53	72	310	290	300	430	450	3	360	360	420	410	430	260
Но	28	24	120	120	100	160	170	1	170	140	130	160	170	86
Er	170	170	530	610	530	630	840	7	700	500	690	740	700	470
Tm	52	37	130	110	97	140	150	1	160	120	140	160	180	88
Yb	490	440	1100	1200	1000	1200	1700	1	1600	1300	1600	1900	2000	950
Lu	110	61	180	170	130	190	200	2	240	160	210	250	290	130
Y	280	770	1600	3300	2900	4400	4700	3	3700	3100	3900	5100	4300	2700
Nb	6	3.2	5.5	5.7	4.4	7.5	7.7	8	8.2	6.2	6.3	9.5	8.6	5.8
Element	Measure	ement poir	nt										Det	ection limit
	14	15	16	17	18	19	20	21	22	23	24	25		
La	0.017	0.017	0.048	0.086	0.12	1.7	2.0	1.9	1.8	1.3	1.1	0.87	0.01	l
Ce	5.4	5.4	5.0	5.8	3.8	2.6	2.1	2.1	1.7	0.73	0.3	B.d.l.	0.01	l
Nd	2.2	2.0	1.5	0.71	0.67	1.4	2.2	2.6	1.1	0.61	1.8	B.d.l.	0.01	l
Sm	8.3	6.9	6.4	4.0	1.6	1.0	0.92	0.28	0.37	0.52	5.6	6.2	0.00)4
Eu	3.5	2.8	2.1	1.8	0.71	0.62	0.53	0.49	0.22	0.52	0.28	B.d.l.	0.01	l
Gd	54	51	34	22	11.0	6.3	5.0	4.9	3.6	1.8	5.7	B.d.l.	0.01	l
Tb	23	19.0	14.0	8.6	3.8	2.6	2.0	1.8	1.2	0.97	1.2	0.61	0.00)6
Dy	270	230	190	140	59	52	38	29	19	11.0	6.4	9.7	0.00)5
Но	110	94	83	61	30	28	20	17	10.0	5.4	5.1	6.5	0.00)5
Er	470	460	370	340	170	150	120	110	60	29	26	22	0.00)7
Tm	120	100	99	86	42	50	33	23	16	4.9	5.3	3.0	0.00)5
Yb	1300	1500	1300	1200	540	500	310	230	160	42	55	43	0.01	l
Lu	180	160	180	170	100	91	87	66	43	9.8	14	5.8	0.0	05
Y	2600	2800	2400	2100	1200	920	650	710	380	560	210	170	0.01	l
Nb	6.3	5.6	6.0	7.6	6.0	5.4	4.4	5.9	5.0	6.3	3.1	2.8	0.0	1

Note. Here and in Table 5, the analyses were carried out by LA-ICP-MS (horizontal scanning along the crystal profile shown in Fig. 8) at the Institute of Inorganic Chemistry, Novosibirsk. B.d.l., below detection limit.

DISCUSSION

In recent decades, significant progress has been made in the study of various properties of accessory zircons from igneous felsic and mafic rocks and from metamorphic rocks, especially in their isotopic dating and in the determination of their formation conditions (Hancher and Hoskin, 2003). Hoskin and Schaltegger (2003) published a detailed review of the results of study of the main properties of zircons from igneous, metamorphic, and sedimentary rocks, including the data on their U-Pb isotopic age. These authors noted that the solution of the problems of petrogenesis and reconstruction of the mantle, lithosphere, and crust evolution processes

must be based on study of not only the isotopic age of zircons from different rocks but also their crystal morphology and CL and geochemical properties. This review lacked data on zircons from ultramafic rocks (Savelieva et al., 2007; Malitch et al., 2009; Skolotnev et al., 2010; Lesnov, 2015). The information in these publications made it possible to expand the range of application of the U-Pb method for dating and elucidating the formation conditions of mafic-ultramafic massifs. Our first data on the isotopic age and other properties of zircons from ultramafic rocks of the Roseta and Córrego da Areia massifs supplement the available information on this problem.

Table 5. Contents of trace elements in zircon crystal 4756M_11 (olivine orthopyroxenite, Córrego da Areia massif), ppm

Element	Measu	Measurement point																
	1	2	3	4	Ļ	5		6	7		8		9		10	11	12	13
La	2.3	7.7	3.6	3	3.1	0.8		1.3	1.6		2.1		4.8		8.4	17	110	290
Ce	31	350	180	1	50	51		160	160		220		190		210	400	720	1100
Nd	8.1	51	27	9	9.9	5.8		19	23		28		35		42	110	320	600
Sm	3.1	27	13	6	5.5	5.0		16	19		27		29		34	55	120	170
Eu	1.3	10.0	3.0	2	2.4	0.8	7	4.6	4.4		6.4		6.0		8.6	13	27	31
Gd	18	59	24	2	20	12		47	45		69		65		86	120	170	190
Tb	3.8	19	8.1	8	3.9	4.3		13	13		19		16		19	26	36	36
Dy	58	270	130	1	70	55		150	150)	230		170		230	270	320	320
Но	22	160	72	8	38	26		63	52		79		59		88	88	96	95
Er	170	1100	640	5	530	150)	310	240)	380		260		360	390	400	360
Tm	47	290	200	1	50	43		75	53		87		59		100	87	92	80
Yb	520	3500	2600	2	2100	530		860	570		1000		730		1100	1000	920	700
Lu	150	840	580	3	30	78		110	73		110		79		140	120	110	100
Y	160	1400	2200	2	2000	910)	1200	140	00	2200		1700		1900	2800	2500	3000
Nb	1.9	15	15	1	4	8.2		13	13		17		13		13	16	12	14
Element	Meas	urement p	oint															
	14	15		16		17	18	19)	20		21		22		23	24	25
La	91	72		24		11	18	43	3	35		34		21		9.2	5.6	3.3
Ce	1100	14	00	490		310	430	98	30	850		930		520		290	140	83
Nd	560	45	0	170		93	170	34	40	260		280		130		72	32	23
Sm	200	20	0	84		53	77	13	30	100		120		54		44	16	11
Eu	35	38		15		9.7	15	2	l	17		21		7.5		5.1	2.5	1.3
Gd	230	21	0	110		74	100	13	30	120		130		49		43	27	12
Tb	36	36		22		18	19	23	3	22		19		9.9		6.5	3.2	2.0
Dy	320	33	0	200		190	180	18	30	160		150		67		42	33	24
Но	87	97		62		61	60	52	2	49		46		21		16	14	7.6
Er	330	38	0	260		240	250	23	30	220		210		87		72	43	22
Tm	65	84		62		56	60	52	2	45		49		21		21	10.0	9.1
Yb	610	86	0	630		640	590	49) 0	480		450		220		180	100	70
Lu	110	12	0	81		77	99	9′	7	110		110		46		42	26	15
Y	2800	26	00	1900)	1800	140	0 1'	700	180	0	160	0	130	0	780	400	300
Nb	12	14		13		12	12	19)	16		15		12		7	3.8	3.4

The Roseta and Córrego da Areia massifs are small ultramafic bodies located among Archean–Neoproterozoic metamorphic deposits in the southern folded framing of the São Francisco Craton. Both massifs are structurally confined to gentle faults and seem to be weakly eroded protrusions, outliers of deep-seated large ultramafic bodies, belonging to a Precambrian ophiolite association. The massifs are composed of variably serpentinous restitic harzburgites and lherzolites, with olivine orthopyroxenites and websterites developed after them, which formed under the impact of later mafic melts. Zircons from the massif rocks differ little in chemical composition but are significantly different in crystal morphology, CL, geochemical properties, and isotopic age. Zircons from the Roseta lherzolite are of two types. Crystals of the first type are of irregular shape and sometimes have signs of crystallographic faceting. Their cores show negligible CL and oscillatory zoning. Crystals of the second type have reaction rims. Zircon crystals from the Roseta olivine orthopyroxenite are of elongate-prismatic habit; many of them show moderate to intense CL and irregular oscillatory zoning. Most of zircon crystals from the Córrego da Areia olivine orthopyroxenite are also of elongate-prismatic habit and show moderate to low CL and, sometimes, oscillatory zoning.

Vertical and horizontal LA-ICP-MS scanning of two representative zircon crystals has revealed geochemical in-

Analysis	Roseta r	nassif		Analysis	Roseta r	nassif	Analysis	Córrego da Areia massif			
	Lherzoli	te, sample 4	758		Olivine	orthopyroxen	ite, sample 4760	-	Olivine 4756M	orthopyro	xenite, sample
	U	Th	Th/U		U	Th	Th/U	-	U	Th	Th/U
1.1c	12	6	0.50	1.1c	308	3	0.01	1.1c	85	35	0.41
1.2r	134	4	0.03	2.1c	106	3	0.03	2.1c	315	251	0.80
2.1c	29	12	0.41	3.1c	136	B.d.l.	< 0.01	3.1c	149	64	0.43
3.1c	1675	81	0.05	4.1c	256	2	0.01	3.2r	65	15	0.23
4.1c	1591	187	0.12	5.1c	346	B.d.l.	< 0.01	4.1c	929	79	0.09
5.1c	247	1	0.004	6.1c	164	5	0.03	5.1c	285	140	0.49
6.1c	793	104	0.13	7.1c	169	3	0.02	6.1c	446	311	0.70
7.1c	380	35	0.09	8.1c	132	3	0.02	7.1c	666	401	0.60
8.1c	13	4	0.31	9.1c	106	3	0.03	8.1c	123	197	1.60
8.2r	318	12	0.04	10.1c	113	3	0.03	9.1c	475	360	0.76
9.1c	8	4	0.50	11.1c	67	2	0.03	9.1ac	342	176	0.51
10.1c	707	70	0.10	12.1c	236	4	0.02	10.1c	258	76	0.29
11.1c	364	7	0.02	13.1c	106	2	0.02	11.1c	275	212	0.77
11.2r	361	13	0.04	14.1c	59	2	0.03	12.1c	375	218	0.59
12.1c	8	4	0.05	15.1c	63	B.d.l.	< 0.01	13.1c	194	60	0.31
12.2r	203	5	0.02	16.1c	120	3	0.03	14.1c	215	45	0.21
13.1c	33	6	0.18	_	_	5	0.03	15.1c	420	220	0.52
13.2r	198	6	0.03	-	_	B.d.l.	< 0.01	16.1	446	59	0.13
_	_	_	_	-	_	_	_	17.1c	398	371	0.93
_	_	-	_	_	_	_	_	17.2r	244	176	0.72
_	_	_	_	_	_	_	_	18.1c	266	162	0.61
_	_	_	_	_	_	_	_	19.1c	161	219	1.36
_	_	_	_	_	_	_	_	20.1c	387	79	0.20
_	_	-	_	_	_	_	_	20.2r	125	198	1.58
_	_	_	_	_	_	_	_	21.1r	113	77	0.68
_	_	_	_	_	_	_	_	21.2c	210	149	0.71
_	_	_	_	_	_	_	_	22.1c	348	171	0.49

Table 6. Contents of U and Th in zircon crystals from rocks of the Roseta and Córrego da Areia massifs, ppm

Note. Analyses were carried out along with U–Pb isotope dating of zircons on a SIMS SHRIMP II mass spectrometer at the Center of Isotopic Research of the Russian Geological Research Institute, St. Petersburg. Measurement points within the crystal: c, core; r, rim.

homogeneity. The crystal cores have low contents of U and Th. The reaction rims are depleted in REE, Hf, and Y but are enriched in U relative to the cores. During the rim formation, which was obviously related to the infiltration of epigenetic fluids, the crystals lost REE and trapped U. Zircons from the Roseta olivine orthopyroxenite have medium contents of U and extremely low contents of Th. Most of zircons from the Córrego da Areia olivine orthopyroxenite have medium contents of U and are enriched in Th. Geochemical inhomogeneity of the zircons is also manifested as Th/U variations. For example, the cores of crystals with reaction rims from lherzolite often show high Th/U ratios (0.18-0.50), whereas the reaction rims show low ones (0.02-0.04). The cores of crystals lacking reaction rims are also characterized by low Th/U ratios (0.01-0.14). Zircons from the Roseta olivine orthopyroxenite have extremely low Th/U ratios (<0.03). In zircons from the Córrego da Areia olivine orthopyroxenite, Th/U is within 0.09-1.60. Thus,

magmatic zircons have mostly high Th/U ratios (>0.5) in contrast to metamorphic zircons (Th/U \sim 0.01), but the cause of this difference is still unclear (Hoskin and Schaltegger, 2003).

The age of zircons from the Roseta lherzolite falls in two intervals of values. The first interval (800–728 Ma, Middle Neoproterozoic) is the age values of the cores of crystals having reaction rims. The second interval (663–619 Ma, Middle Neoproterozoic) includes the age values of the crystals lacking reaction rims and of the reaction rims of the former crystals. Probably, zircons from lherzolite (regarded as an ultramafic restite) are relict; they formed in the uppermantle protolith and have an older isotopic age. During the later transformations, their U–Pb isotope systems were, most likely, disturbed and nonuniformly recrystallized.

The age values of zircons from the Roseta olivine orthopyroxenite are within 622.6–596.9 Ma (Late Neoproterozoic). These zircons seem to be syngenetic, formed during



Fig. 9. Curves of variation in trace-element contents along the scanned profiles of zircon crystals 4758_13 (lherzolite, Roseta massif) and 4756M_11 (olivine orthopyroxenite, Córrego da Areia massif) (see Fig. 8). Numerals on the abscissa axis are the numbers of measurement points (following Tables 4 and 5).

Table 7	. Results	of U-Pb	isotope	dating of	zircon o	crystals fr	om lhe	erzolite	(samr	ble 4758,	Roseta	massif)
				0		<i>.</i>			1			

Analysis	²⁰⁶ Pb _c , %	²³² Th/ ²³⁸ U	²⁰⁶ Pb*, ppm	Age, Ma (²⁰⁶ Pb*/ ²³⁸ U)	Age, Ma (²⁰⁷ Pb/ ²⁰⁶ Pb)	Discordance, %	²⁰⁷ Pb*/ ²³⁵ U (± %)	²⁰⁶ Pb*/ ²³⁸ U (± %)	R _r
1.1c	B.d.l.	0.47	1.3	777 ± 18	807 ± 120	4	1.166 (6.1)	0.1282 (2.4)	0.395
1.2r	B.d.l.	0.03	12.0	638.5 ± 7.6	610 ± 42	-4	0.864 (2.3)	0.1041 (1.2)	0.544
2.1c	B.d.l.	0.42	3.3	800 ± 12	732 ± 140	-8	1.160 (6.8)	0.1321 (1.7)	0.241
3.1c	B.d.l.	0.05	152.0	646.4 ± 6.3	664 ± 13	3	0.898 (1.2)	0.1055 (1.0)	0.864
4.1c	0.02	0.12	146.0	654.8 ± 6.4	628 ± 14	-4	0.894 (1.2)	0.1069 (1.0)	0.852
5.1c	B.d.l.	< 0.01	22.2	642 ± 7	623 ± 34	-3	0.874 (2.0)	0.1047 (1.2)	0.589
6.1c	0.07	0.14	69.1	621.7 ± 6.4	622 ± 28	0	0.845 (1.7)	0.1012 (1.1)	0.646
7.1c	0.09	0.09	34.0	637.8 ± 6.8	648 ± 32	2	0.878 (1.9)	0.1040 (1.1)	0.599
8.1c	2.69	0.35	1.4	728 ± 19	374 ± 480	-49	0.890 (22.0)	0.1196 (2.8)	0.131
8.2r	0.09	0.04	28.2	632.9 ± 6.9	650 ± 36	3	0.872 (2.0)	0.1032 (1.1)	0.562
9.1c	1.81	0.51	0.9	789 ± 25	916 ± 380	16	1.250 (19.0)	0.1302 (3.3)	0.177
10.1c	0.03	0.10	64.5	650.3 ± 6.8	669 ± 21	3	0.905 (1.5)	0.1061 (1.1)	0.738
11.1c	0.13	0.02	32.3	632.2 ± 6.9	591 ± 43	-7	0.847 (2.3)	0.1030 (1.1)	0.505
11.2r	0.12	0.04	31.5	624.2 ± 7.2	641 ± 46	3	0.856 (2.4)	0.1017 (1.2)	0.496
12.1c	1.12	0.53	0.9	787 ± 22	803 ± 240	2	1.180 (12.0)	0.1299 (3.0)	0.251
12.2r	0.16	0.02	18.4	644.1 ± 7.3	648 ± 43	3	0.887 (2.3)	0.1051 (1.2)	0.509
13.1c	B.d.l.	0.19	3.1	663 ± 11	684 ± 87	-7	0.930 (4.4)	0.1083 (1.7)	0.396
13.2c	0.06	0.03	17.2	618.9 ± 6.7	578 ± 46	1	0.824 (2.4)	0.1008 (1.2)	0.482

Note. Here and in Tables 8 and 9, the analysis numbers follow the crystal numbers. B.d.l., below detection limit. The errors of age determination are at the 1σ level. The error of calibration of the standard is 0.33 %. $^{206}Pb_e$, common lead; Pb*, radiogenic lead. Isotope ratios and contents of common Pb are corrected based on measured ^{204}Pb . R_e , coefficient of correlation between the errors of determination of $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$. Measurement points within the crystal: c, core; r, rim.



Fig. 10. Chondrite-normalized REE patterns of zircon crystals 4758_13 (lherzolite, Roseta massif) (*A*) and 4756M_11 (olivine orthopyroxenite, Córrego da Areia massif) (*B*). Analyses were performed by LA–ICP-MS scanning of the crystals between points 1 and 25 (marked in the patters) along the profiles shown in Fig. 8 (data from Tables 4 and 5).

Table 8. Results of U-Pb isotope dating of zircon crystals from olivine orthopyroxenite (sample 4760, Roseta massif)

Analysis	²⁰⁶ Pb _c , %	232Th/238U	²⁰⁶ Pb*, ppm	Age, Ma (²⁰⁶ Pb/ ²³⁸ U)	Age, Ma (²⁰⁷ Pb/ ²⁰⁶ Pb)	Discordance, %	²⁰⁷ Pb*/ ²³⁵ U (±%)	²⁰⁶ Pb*/ ²³⁸ U (±%)	R _r
1.1c	0.10	0.01	26.6	616.1 ± 5.9	624 ± 32	2	0.838(1.8)	0.1003 (1.0)	0.557
2.1c	0.62	0.03	9.0	601.8 ± 7.3	599 ± 88	0	0.808(4.3)	0.0978 (1.3)	0.296
3.1c	0.26	B.d.l.	11.5	603.2 ± 7.4	643 ± 61	7	0.827(3.1)	0.0981 (1.3)	0.413
4.1c	0.16	0.01	21.7	606.3 ± 6	546 ± 66	-10	0.794(3.2)	0.0986 (1.0)	0.325
5.1c	0.07	B.d.l.	29.9	617.2 ± 5.9	$585 \pm$	-5	0.824(1.7)	0.1005 (1.0)	0.591
6.1c	0.30	0.03	13.9	605.1 ± 6.3	589 ± 61	-3	0.809(3)	0.0984 (1.1)	0.360
7.1c	0.38	0.02	14.2	601.3 ± 6.6	563 ± 63	-6	0.7943.1	0.0978 1.1	0.368
8.1c	0.32	0.02	11.3	609.2 ± 6.6	580 ± 66	-5	0.811(3.3)	0.0991 (1.1)	0.346
9.1c	0.46	0.03	9.0	601.1 ± 6.9	563 ± 80	-6	0.793(3.9)	0.0977 (1.2)	0.308
10.1c	0.39	0.03	9.7	611.2 ± 7.4	579 ± 79	-5	0.813(3.8)	0.0995 (1.3)	0.331
11.1c	0.33	0.02	5.8	622.6 ± 8	619 ± 37	-1	0.845(4.2)	0.1014 (1.4)	0.320
12.1c	0.15	0.02	20.5	620 ± 6	621 ± 41	0	0.842(2.2)	0.1010 (1.0)	0.476
13.1c	0.24	0.02	8.8	596.9 ± 7.4	571 ± 65	_4	0.791(3.3)	0.0970 (1.3)	0.394
14.1c	0.20	0.04	4.9	601.3 ± 8.1	739 ± 86	23	0.862(4.3)	0.0978 (1.4)	0.328
15.1c	0.39	0.01	5.4	606.7 ± 8	670 ± 92	11	0.842(4.5)	0.0987 (1.4)	0.306
16.1c	0.46	0.02	10.2	606.1 ± 7	555 ± 130	-8	0.797(6.0)	0.0986 (1.2)	0.204

Table 9. Results of U-Pb isotope dating of zircon crystals from olivine orthopyroxenite (sample 4756M, Córrego da Areia massif)

Analysis	²⁰⁶ Pb _c , %	²³² Th/ ²³⁸ U	²⁰⁶ Pb*, ppm	Age, Ma (²⁰⁶ Pb/ ²³⁸ U)	Age, Ma (²⁰⁷ Pb/ ²⁰⁶ Pb)	Discordance, %	²⁰⁷ Pb*/ ²³⁵ U (±%)	²⁰⁶ Pb*/ ²³⁸ U (±%)	R _r
1.1c	0.19	0.43	35.6	2558 ± 26	2507 ± 32	-2	11.080(2.3)	0.4871 (1.2)	0.553
2.1c	1.17	0.82	84.3	1725 ± 16	2010 ± 20	17	5.233 (1.6)	0.3068 (1.1)	0.694
3.1c	0.17	0.44	50.1	2125 ± 22	2101 ± 15	-1	7.010 (1.5)	0.3905 (1.2)	0.814
3.2r	0.19	0.24	22.8	2198 ± 25	2054 ± 26	-7	7.110 (2.0)	0.4063 (1.4)	0.683
4.1c	13.93	0.09	124.0	786.7 ± 8.3	1574 ± 59	100	1.742 (3.3)	0.1298 (1.1)	0.336
5.1c	0.35	0.51	88.7	1985 ± 19	2010 ± 13	6	6.508 1.3	0.3606 1.1	0.837
6.1c	1.20	0.72	123.0	1775 ± 16	2402 ± 17	35	6.772 (1.5)	0.3169 (1.1)	0.726
7.1c	9.98	0.62	101.0	928.8 ± 9.7	1798 ± 54	93	2.340 (3.2)	0.1550 (1.1)	0.352
8.1c	0.30	1.65	9.9	575.7 ± 7.6	588 ± 84	2	0.767 (4.1)	0.0934 (1.4)	0.337
9.1c	5.17	0.78	99.1	1321 ± 13	1974 ± 83	49	3.800 (4.8)	0.2275 (1.1)	0.233
9.1ac	0.83	0.53	101.0	1883 ± 18	2069 ± 26	10	5.980 (1.8)	0.3393 (1.1)	0.591
10.1c	0.13	0.30	78.1	1941 ± 18	2024 ± 13	4	6.039(10.1)	0.3513 (1.1)	0.840
11.1c	0.20	0.80	81.0	1899 ± 18	2051 ± 13	8	5.981 (1.3)	0.3426 (1.1)	0.830
12.1c	0.17	0.60	105.0	1814 ± 17	2053 ± 11	13	5.678 (1.2)	0.3250 (1.1)	0.871
13.1c	0.03	0.32	63.7	2088 ± 21	2076 ± 13	-1	6.771 (1.4)	0.3824 (1.2)	0.846
14.1c	0.47	0.21	17.7	588.6 ± 6.9	514 ± 60	-13	0.759 (3.0)	0.0956 (1.2)	0.409
15.1c	1.15	0.54	96.3	1506 ± 14	1938 ± 20	29	4.311 (1.6)	0.2633 (1.1)	0.692
16.1c	0.85	0.14	92.4	1381 ± 13	1862 ± 17	35	3.752 (1.4)	0.2389 (1.1)	0.758
17.1c	4.01	0.96	99.8	1578 ± 16	2002 ± 33	27	4.710 (2.2)	0.2774 (1.1)	0.520
17.2r	0.94	0.75	74.4	1940 ± 20	2042 ± 19	5	6.095 (1.6)	0.3510 (1.2)	0.734
18.1c	0.65	0.63	79.5	1909 ± 18	2075 ± 21	9	6.099 (1.6)	0.3446 (1.1)	0.679
19.1c	0.01	1.41	54.2	2135 ± 21	2095 ± 14	-2	7.028 (1.4)	0.3927 (1.2)	0.825
20.1c	0.07	0.21	158.0	2504 ± 22	2498 ± 18	0	10.740(1.5)	0.4747 (1.1)	0.714
20.2r	11.90	1.64	37.3	1656 ± 23	2445 ± 78	48	6.420 (4.9)	0.2929 (1.6)	0.326
21.2c	0.22	0.73	68.6	2074 ± 21	2128 ± 14	3	6.917 (1.4)	0.3794 (1.2)	0.815
21.1r	1.95	0.70	30.2	1706 ± 19	2023 ± 15	19	5.200 (2.3)	0.3029 (1.3)	0.538
22.1c	0.51	0.51	108.0	1978 ± 18	2084 ± 12	5	6.383 (1.3)	0.3591 (1.1)	0.835



Fig. 11. Correlation between the U and Th contents in zircon crystals from: *A*, lherzolite (sample 4758), *B*, olivine orthopyroxenite (sample 4760) from the Roseta massif; *C*, olivine orthopyroxenite (sample 4756M) from the Córrego da Areia massif.

the crystallization of mafic melts produced later than lherzolites and contaminated with their material. The syngenetic nature of these zircons is indirectly evidenced by the prismatic habit of their crystals, the high contents of Zr (548 ppm) and Hf (13.8 ppm) in the olivine orthopyroxenite, and the localization of its vein among harzburgites. Most of zircon crystals from the Córrego da Areia olivine orthopyroxenite (sample 4756M) are much older than zircons from the Roseta olivine orthopyroxenite. Their age falls in three intervals of values: 2558-2504 Ma (Late Neoarchean), 2198-2074 Ma (Middle Paleoproterozoic), and 589-576 Ma (Late Neoproterozoic). There are two hypotheses of the genesis of two ancient zircon populations from these massifs: (1) These ancient zircons might be xenogenous, i.e., they were trapped by their parental melt from the host ancient metamorphic rocks. (2) The zircons crystallized during the formation of orthopyroxenites, i.e., are syngenetic; in this case, their age might indicate the time of ancient mafic magmatism that gave rise to these orthopyroxenites. The occasional younger zircon crystals (589-576 Ma) are probably epigenetic, i.e., formed during the infiltration of later fluids into orthopyroxenites. In general, zircons from rocks of the Roseta and Córrego da Areia massifs resulted from magmatic processes; therefore, their separation into relict, xenogenous, syngenetic, and epigenetic does not contradict

but extends the term "magmatic zircons" used along with the terms "metamorphic zircons" and "hydrothermal-metasomatic zircons" in geology.

Finally, we should emphasize that the estimated isotopic ages of zircons from the Roseta and Córrego da Areia ultramafic massifs are in the same intervals of values (2558–2074 and 800–576 Ma) as the ages of zircons from various metamorphic rocks composing the southern folded framing of the São Francisco Craton (2890–1656 and 787–550 Ma). This fact suggests two major stages of zircon generation in the regional lithosphere: Neoarchean–Paleoproterozoic and Neoproterozoic.

CONCLUSIONS

(1) Zircon crystals in lherzolite and olivine orthopyroxenites from the Roseta and Córrego da Areia ultramafic massifs (fragments of a Precambrian ophiolite association in the southern folded framing of the São Francisco Craton in southeastern Brazil) have been first studied by X-ray spectroscopy and LA–ICP-MS, and their U–Pb isotopic age has been determined.

(2) Most of zircon crystals from the Roseta lherzolite lack crystallographic faceting and show no CL and oscillatory zoning; some of them have a reaction rim. These zircons are characterized by an uneven distribution of REE, U, and Th and have low Th/U ratios. Their cores are slightly enriched in REE relative to their reaction rims. The isotopic age of the cores is 800–619 Ma, and the reaction rims are somewhat younger. Lherzolite is an upper-mantle restite; it contains relict zircons, whose U–Pb isotope systems were disturbed during epigenetic processes and were nonuniformly recrystallized.

(3) Zircons from the Roseta olivine orthopyroxenite composing a vein cutting harzburgites are short-prismatic crystals with moderate to intense CL and rhythmical oscillatory zoning. They have medium to high contents of U, low contents of Th, and extremely low Th/U ratios. Their isotopic age is within 597–623 Ma. Olivine orthopyroxenite is considered to be a hybrid rock developed after harzburgites under the impact of later mafic melts. It contains syngenetic zircons, whose isotopic age probably marks the time of formation of the orthopyroxenite vein.

(4) Zircons from the Córrego da Areia massif are shortprismatic crystals with moderate to intense CL and rhythmical oscillatory zoning. They have medium to high contents of U; many of them are characterized by high Th/U ratios. Most of these crystals are ancient (2558–2074 Ma), and single crystals are much younger (589–576 Ma). Genesis of these crystals is still debatable. We suggest that the ancient crystals are xenogenous or syngenetic and the younger ones are epigenetic.

(5) The Roseta and Córrego da Areia massifs are regarded as protrusive outliers of a deep-seated Precambrian maf-



Fig. 12. U–Pb concordia diagram based on the isotopic age of the cores of zircon crystals from the Roseta lherzolite (sample 4758) (data from Table 7).

ic–ultramafic complex, which were tectonically transferred along faults into highly metamorphosed Archean–Proterozoic deposits in the southern folded framing of the São Francisco Craton.

(6) The established two strongly different intervals of the isotopic ages of zircons from rocks of the studied ultramatic massifs are close to the age intervals of zircons from metamorphic complexes in the southern folded framing of the



Fig. 13. U–Pb concordia diagram based on the isotopic age of the cores of zircon crystals from the Córrego da Areia olivine orthopyroxenite (sample 4756M) (data from Table 9).

São Francisco Craton. This suggests two major stages of zircon generation in the regional lithosphere: Neoarchean–Paleoproterozoic and Neoproterozoic.

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