**ORIGINAL PAPER**



# **Evidence of mingling between contrasting magmas in the Ribeirão do Óleo Pluton, Coastal Terrane and the tectonic implications on the Ribeira Belt, Brazil**

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#### **Abstract**

Gneiss–migmatitic rocks and granites between the Cubatão and Itariri shear zones characterize the Mongaguá Complex-Coastal Terrane. Three major units are defned: (1) the Itariri Suite (IS) composed of monzogranites, granodiorites, tonalites, and locally gneiss–migmatitic rocks; (2) the Areado pluton composed of monzogranite and locally tonalite; and (3) the Ribeirão do Óleo Pluton mainly composed of monzogranites, which is the subject of this article. Combined feld observations, petrography, Sr–Nd–Hf isotopes, U–Pb zircon data, and preliminary geochemical studies are presented for the Ribeirão do Óleo Pluton (ROP), intrusive in granite-gneisses of the IS. It is a plutonic association of weakly peraluminous, medium-tohigh-K biotite monzogranites that surround microgranular intermediate enclaves, which are products of magma mingling. Diferent from the most examples of magma mingling described in the literature, the ROP mingling did not result from the intrusion of hot mafic magma into colder host felsic magma. Conversely, the emplacement of the monzogranite started most likely during the medium-to-fnal stage of crystallization of the quartz microdiorite. A detailed study of LA-ICP-MS U–Pb zircon ages, including zircon morphology and internal structure, was useful to determine more precisely the emplacement sequence and the relation between the units of the ROP. Intermediate and acid facies have Paleoproterozoic and Neoproterozoic inheritances, moreover a mixture of xenocrysts, antecrysts, and autocrysts, indicative of a complex evolution of the ROP. Several magma crystallization pulses are recorded at 655–624 Ma, 627–601 Ma, and 613–586 Ma. The negative εHf(*t*) ranging from −17.26 to −12.51 in monzogranites,  $\varepsilon Nd(t)$  values of −10.66 to −7.83 at  $t$  =600 Ma in both facies,  ${}^{87}Sr/{}^{86}Sr$ of ca. 0.708 for the monzogranite and 0.706 for the quartz microdiorite indicate a strong crustal contribution in the genesis of intermediate and acid magmas of this pluton.

**Keywords** Ribeira Belt · Coastal Terrane · Magma mingling · LA-ICP-MS · Lu–Hf isotopes

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# **Introduction**

Expressive shear zones limit tectonic compartments with distinct lithologies, geochronology, and isotopic compositions of the Ribeira Belt (RB) in southeastern São Paulo State, which is a part of the Mantiqueira Province (MP) defned by Almeida et al. [\(1981](#page-24-0), [2000](#page-24-1)). The largest tectonic unit of the MP (Fig. [1\)](#page-1-0) is the RB that is generated from the closure of the Adamastor Ocean due to the interaction between the San Francisco, Paranapanema, Rio de la Plata, Luis Alves, Congo, and Kalahari cratons during Gondwana assembly (Fig. [1a](#page-1-0)).

The Coastal Terrane (CoT) of the RB (Fig. [1](#page-1-0)b) includes the Oriental Domain, which was defned by Heilbron et al. ([2004,](#page-25-0) [2008\)](#page-25-1) and Tupinambá et al. ([2012\)](#page-26-0), the Paranaguá/ Iguape Domains (Cury et al. [2008;](#page-25-2) Passarelli et al. [2004](#page-25-3)),

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<span id="page-1-0"></span>**Fig. 1 a** Reconstruction of West Gondwana after Heilbron et al. ([2008\)](#page-25-1), Vaughan and Pankhurst ([2008\)](#page-26-4), Frimmel et al. [\(2011](#page-25-8)) and Cordani et al. ([2013\)](#page-24-2). Cratons shown in grey: *A* Amazonia, *C* Congo, *K* Kalahari, *LA* Luis Alves, *P* Paranapanema, *SF* São Francisco, *WA* West Africa. Brasiliano–Panafrican belts (ringed): *Bo* Borborema, *Rp* Rio Preto, *A* Araguaia, *Aç* Araçuaí, *P* Paraguai, *B* Brasilía, *R* Ribeira, *DF* Dom Feliciano, *Pa* Pampean, *H* Hoggar, *D* Dahomey, *Ro* Rockelides, *O* Oubangides, *Ta* Tanzania, *WC* West Congo, *Ka* Kaoko, *Da* Damara, *K/Z* Katangan/Zambezi, *Kl* Katanga-Luflian Arc, *M* Mozambique, *G* Gariep, *S* Saldania. Location of the northern Mantiqueira Province is shown. **b** General outline of the Northern Domain of the Mantiqueira Province (Brazil–Uruguay). Simplifed from Basei et al. [\(1999](#page-24-3), [2000\)](#page-24-4), Heilbron et al. ([2004\)](#page-25-0), Tupinambá

and the Mongaguá Domain (Passarelli et al. [2016\)](#page-26-1). These areas are very important to understand the regional tectonics, because it offers an opportunity to discuss about the Curitiba and Paranaguá Domains (Siga Jr et al. [1995\)](#page-26-2) that are situated in the south and belongs to the Oriental Domain (Heilbron et al. [2010\)](#page-25-4) in the north.

The Mongaguá Complex (MC) initially named as Mongaguá Domain by Passarelli ([2001\)](#page-25-5) is composed of mainly gneiss–migmatitic and granitic rocks of Itariri Suite (IS) and Areado and ROP plutons, with Paleoproterozoic-to-Neoproterozoic ages (Passarelli et al. [2016\)](#page-26-1). The term Complex is used here as defned by the International Stratigraphic Guide (Murphy and Salvador [1999\)](#page-25-6) as a "lithostratigraphic unit composed of diverse types of any class or classes or rocks… and characterized by irregularly mixed lithology or by highly complicated structural relations". The MC is limited by Cubatão Shear Zone to the northwest and by the Itariri Shear Zone to the south.

The MC granitoids have been correlated with the Rio Negro magmatic arc in the Rio de Janeiro State and with Paranaguá Domain in the Paraná State (Passarelli et al. [2008,](#page-25-7) [2019\)](#page-26-3). Magma mingling features have already

et al. ([2007\)](#page-26-5) and Passarelli et al. [\(2011](#page-26-6)). 1. Quaternary and Terciary sediments; 2. Paraná Basin (PB). Mantiqueira Province—Northern Domain: Brasília Belt (BB): 3. Socorro-Guaxupé nappe. Ribeira Belt (RB): 4. Andrelândia Terrane (A); 5. Juiz de Fora Terrane (JF); 6. Paraíba do Sul Terrane (PS); 7. Embu Terrane (E); 8. Apiaí Terrane (Ap); 9. Coastal Terrane (Co)—Coastal, Cambuci, Italva Domains, Rio Negro/Mongaguá/Paranaguá-Iguape Domains, Iguape Metassediments. 10. Cabo Frio Terrane (CF); 11. Piên Magmatic Arc (P); 12. Curitiba Terrane (C). Foreland units: 13. S. Francisco Craton and Cover (SF). 14. Luis Alves Terrane (LA). States of Brazil: ES-Espírito Santo, RJ-Rio de Janeiro, MG-Minas Gerais, SP-São Paulo, PR-Paraná

been identifed in the ROP by Passarelli [\(2001](#page-25-5)) and Pas-sarelli et al. [\(2004](#page-25-3)). These authors provide some isotopic and U–Pb TIMS zircon data on granite of the ROP with strong isotope inheritance, showing inaccurate lower intercept ages around 580 Ma, TDM Nd age of 1729 Ma,  $\varepsilon$ Nd = -10.7, and initial <sup>87</sup>Sr/<sup>86</sup>Sr of 0.708. Preliminary LA-ICP-MS analyses on ROP granite give inconclusive ages around 560 Ma (Passarelli et al. [2016\)](#page-26-1).

The main aim of this study is to report new petrographic, isotopic, and geochemical data of two lithotypes from the ROP to decipher their petrogenetic processes and possible emplacement environment.

Field evidence for magma mingling and isotopic mixing suggestion is presented where dioritic microgranular enclaves are surrounded by monzogranitic rocks. The interaction between two magmas of contrasting composition and physical properties generates several structures and textures preserved in the ROP. Textures can be interpreted with respect to efective magmatic processes at the time the magma chamber was active.

# **Geological context**

The NE–SW-trending MP was generated during the Neoproterozoic Brasiliano–Panafricano Orogeny associated with the evolution of Western Gondwana assembly. Among the several belts diachronically developed in this province, the largest one is the RB that is situated in southeastern Brazil. It consists of several tectonic domains, limited either by thrust or by transpressive shear zones (Figs. [1b](#page-1-0), [2\)](#page-2-0) and a subduction-to-collisional belt developed consequently of the collision between the São Francisco, Paranapanema, Luís Alves, and Congo cratons and the assembly of West Gondwana during the Neoproterozoic (e.g., Brito Neves et al. [1999](#page-24-5), [2014](#page-24-6); Trouw et al. [2000](#page-26-7); Campanha and Brito Neves [2004;](#page-24-7) Basei et al. [2010](#page-24-8)). The northern and central RB comprise the Occidental, Paraíba do Sul-Embú, Oriental (CoT or Serra do Mar Terrane) and Cabo Frio terranes (Campos Neto [2000;](#page-24-9) Heilbron et al. [2004;](#page-25-0) Schmitt et al. [2004;](#page-26-8) Tupinambá et al. [2012\)](#page-26-0). Apiaí, Embú, and Curitiba terranes compose the southern RB

(Campos Neto [2000](#page-24-9); Basei et al. [2009;](#page-24-10) Siga Jr et al. [2011a,](#page-26-9) [b](#page-26-10)), whereas the Lancinha-Cubatão and Itariri shear zones separate the supracrustal terranes to the north (Embu and Apiaí terranes) from the granite-gneissic migmatitic terranes to the south, including the CoT and Curitiba Terrane (CRT) (Fig. [1b](#page-1-0)). In addition, the Itariri Shear Zone (ISZ) separates the CRT from the MC-CoT (Fig. [2](#page-2-0)).

#### **Coastal Terrane (CoT): central and northern RB**

In the central RB, the CoT comprises the (1) Costeiro Complex, which contains orthogneisses and ortho-derived migmatite, para-derived migmatitic rocks, and amphibolite unit and calc-silicatic rocks; (2) syn-tectonic peraluminous and metaluminous granitic rocks, and (3) charnockitic rocks (Ubatuba Charnockite). The timing of diatexite melt crystallization is constrained at 584 Ma and 575 Ma with inherited cores of 770 Ma and 635 Ma. Amphibolitic rocks with ages between 650 and 550 Ma is interpreted as metamorphic events and ages of ca. 800–750 Ma as the crystallization age of the mafc protolith. The high-grade metasedimentary



<span id="page-2-0"></span>**Fig. 2 a** Tectonic sketch of the Mongaguá Complex (MC) adjacent terranes and main shear zones of the Southern RB with red polygon showing the location of the study area. **b** Simplifed map of the MC with the main units: Itariri Suite, Areado, and Ribeirão do Óleo Plutons

rocks with maximum depositional age at 670–650 Ma; Ediacaran (587–562 Ma) I and S-type granites, late Ediacaran charnockitic rocks (ca. 560–565 Ma); Cambrian (ca. 500 Ma), quartz Monzonites, and Cretaceous alkaline rocks. (Janasi et al. [2003](#page-25-9); Azevedo Sobrinho et al. [2011;](#page-24-11) Meira [2014](#page-25-10); Meira et al. [2014](#page-25-11), [2015](#page-25-12)).

In the Northern RB, the CoT, identified as Oriental Terrane (Heilbron et al. [2004](#page-25-0), [2008,](#page-25-1) [2017\)](#page-25-13), is made up of Tonian-to-Ediacaran juvenile intra-oceanic to immature continental arc-related rocks of the Costeiro Domain (Serra da Prata and Rio Negro complexes) and Neoproterozoic high-grade metasedimentary successions (Italva and São Fidélis Groups). The Costeiro domain, contains a distal passive margin succession of ca. 1000–760 Ma (lower units of the São Fidelis Group) intruded by the Neoproterozoic Rio Negro and Serra da Prata magmatic arcs of ca. 840–605 Ma. In a back arc setting, the São Fidélis and Italva basins deposited at ca. 840–605 Ma. Porphyritic syn-collisional granites (590–560 Ma), syn-collisional leucogranites and S-type to hybrid charnockites (ca. 580 Ma), late-collisional granites and charnockites (ca. 560 Ma), and post-collisional biotite granite (510–480 Ma) is also recognized in this terrane. A distinctive characteristic of this terrane is the absence of a Paleoproterozoic or older basement assemblage (Heilbron et al. [2017](#page-25-13)).

#### **Coastal Terrane (CoT): southern RB**

The MC is composed of granite and gneiss–migmatitic rocks including the IS and Areado and ROP plutons. The IS is mainly composed of monzogranite, granodiorite, and tonalite, some of which have a gneiss–migmatitic aspect. The Areado pluton contains monzogranite and some tonalitic rocks. The ROP is made of predominant granites and quartz microdiorites.

Isotopic data obtained on rocks of the IS, the Areado, and ROP plutons (Passarelli et al. [2014a](#page-26-11)) led to a better characterization of the MC (south of CoT), and revealed important diferences with the lithotypes defned at the CoT to the north.

The IS includes medium-to-high-K monzogranites, granodiorites, and biotite tonalites, locally migmatitic. LA-ICP-MS geochronology of zircons provide U–Pb ages of 745 Ma in protomylonitic tonalite, and two age clusters of 640–630 Ma and 612 Ma in magmatic zircons and their overgrowths, respectively. Inherited cores provide ages of 2.2–2.1 Ga, 1.8 Ga, 1.2–1.1 Ga, and 790 Ma (Passarelli et al. [2014a](#page-26-11)). U–Pb monazite ages around 600 Ma indicate a thermal event in the area, which recorded in zircon rims. Paleoproterozoic ages around 2150 Ma, until undetected in this terrane, were found in the mesosome of migmatites, and represent minor basement remnants. The zircon data suggest that the IS granites crystallized in several magmatic pulses derived mainly from a Paleoproterozoic (2.2–1.8 Ga) source, which is a normal age for the South American basement rocks. On the other hand, the origin of Mesoproterozoic zircon ages (1200–1100 Ma) also observed in the Itariri rocks that are not so easy to explain since rocks with these ages have not so far been reported in any part of southern Brazil. The Namaqua rocks from southwestern Africa are the best candidates for the protoliths of the Itariri granites (Passarelli et al. [2016](#page-26-1)). The IS had been already associated with the 790–600 Ma Rio Negro Complex (Tupinambá et al. [2012\)](#page-26-0) of Oriental Terrane in the central sector of the RB by Passarelli et al. [\(2004,](#page-25-3) [2008,](#page-25-7) [2011](#page-26-6)).

The record of Cryogenian magmatism (ca. 700 Ma) is also observed in the Areado pluton that presents local gneissic features. Paleoproterozoic basement (2150 Ma) is preserved as roof-pendants in the central part of the body. Inherited zircon cores in the Areado granite provide ages of 2.2–2.1 Ga, 1.8 Ga, and 860 Ma (Passarelli et al. [2016](#page-26-1)).

The ROP pluton presents well-characterized magma mingling features and apparently intrudes all units of the MC, although no contacts between the units were observed in the feld. First, LA-ICP-MS analyses in the monzogranite of ROP provide ages around 560 Ma, and interpreted as the possible crystallization age of this body, although zircon with 610 Ma is also present (Passarelli et al. [2014b](#page-26-12)). Inherited zircon cores provide ages of 2.2–2.1 Ga, 700 Ma, and 645 Ma.

The study area is located in south-central portion of the MC, southern part of the RB. The ROP crop out north of the ISZ. It has a restricted expression in the area with exposure of around  $9 \text{ km}^2$ , and its long axis is oriented approximately N30E (Fig. [2\)](#page-2-0). The monzogranite and diorite rocks of the ROP present an N80W to E–W main foliation with moderate dip (40°–60°) towards NE and contain a biotite and feldspar lineation with moderate plunges (54°) to N50W, possibly infuenced by the ISZ kinematics (see Passarelli et al. [2011](#page-26-6)).

The IS, Areado, and ROP rocks have geochemical characteristics which point to the contribution of diferent crustal sources during the generation of these magmas. This fnding is quite similar to studied rocks of southern Brazil.

# **Petrography of ROP**

Petrographic studies were done on two main outcrops (K-54 and K-194) along the Oil Brook where the outcrops are slight or no weathered. The ROP was defned at northeast of the Itariri city where it is observed a clear interaction between acid and intermediate rocks. The acid rock is represented by biotite monzogranite medium grey-bluish coloring, fnely foliated. These rocks have hypidiomorphic, inequigranular texture, and are fne-to-medium grained. The intermediate rocks of dioritic composition have dark grey in colour and are fnely foliated as well.

The ROP shows evidence of both magmatic and solidstate flow. Structures of magmatic flow are well preserved, and are defned by macro- and microscopic structures such as aligned intermediate enclaves, euhedral K-feldspar megacrysts (Fig. [3a](#page-4-0)–c), and mafc minerals. Biotite crystals defne a steeply plunging mineral lineation. The evidence of solid-state fow is better identifed in thin sections, which is described latter.

Mingling structures consist of laterally discontinuous intermediate sheets with cuspate edges alternating with irregular elongate and fame-like shape enclave swarms (Fig. [3](#page-4-0)a–c). Normally near the magma's interaction, porphyritic textures with euhedral alkali feldspar megacrysts (10–45 mm) are found (Fig. [3](#page-4-0)c). Medium-to-coarse-grained quartz-feldspathic veins (Fig. [3](#page-4-0)d) and sheets form ptygmatic folds with axial plane roughly parallel to main foliation (Fig. [3e](#page-4-0)).

Biotite monzogranite (Fig. [4](#page-5-0)) composed of quartz, microcline, oligoclase, and biotite, whereas titanite, zircon, apatite, and rare sulphides as accessory minerals. Secondary minerals are sericite, epidote, chlorite, muscovite, and opaque oxide minerals. The colour index varies between 15 and 20. Foliation is defned by orientation of biotite crystals and the quartz segregations (Fig. [4](#page-5-0)a, sample K-54A; Fig. [4b](#page-5-0), sample K-190A). Quartz crystals usually occur as polycrystalline aggregated with polygonised contacts. They tend to segregate in strips, but typically do not form ribbons. They do not show undulating extinction.

Microcline crystals are sometimes microperthitic and often are recrystallized (Fig. [4](#page-5-0)c, sample K-190A). Plagioclase crystals are commonly saussuritised. Biotite has light yellow-to-strongly reddish brown pleochroism. It alters to chlorite. Chlorite and muscovite crystals usually have welldeveloped shapes.

The evidence of solid-state flow in the monzogranite includes recrystallized aggregates of quartz and K-feldspar and elongated lenses of biotite (Fig. [4a](#page-5-0), b).

Suggestion of a "submagmatic flow" (Paterson et al. [1989\)](#page-26-13) or grain-supported flow (Vernon [2000](#page-26-14)) is evidenced by quartz-flled fractures in K-feldspar (Fig. [4](#page-5-0)c)



<span id="page-4-0"></span>**Fig. 3** Outcrop type of monzogranite and microdiorite mingling— Ribeirão do Óleo Pluton. **a** Note the higher concentration of K-feldspar phenocrysts nearby mafc material. **b** Mafc sheets with cuspate edges alternating with irregular elongate and fame-like shape enclave swarms and 'waterfall' of K-feldspar phenocrysts. **c** Detail of biotite monzogranite with euhedral K-feldspar phenocrysts. **d**, **e** Ptygmatic folds (highlighted) on medium-to-coarse-grained quartz-feldspathic veins. Location of samples for geochronology and geochemical studies is shown. Monzogranite: sample 1 (K-54A) and sample 2 (K-190A). Quartz microdiorite: sample 3 (K-190B)



<span id="page-5-0"></span>**Fig. 4** Photomicrographs of Ribeirão do Óleo biotite monzogranite in XZ sections. **a**, **b** Foliation is expressed mainly by segregated bands of quartz and aligned biotite crystals. **c** K-feldspar recrystallization

and recrystallized K-feldspar with very discrete exsolution lamellae (Fig. [4c](#page-5-0)).

Some evidences of magma mingling in thin sections of granite samples are mantles or coronas (Fig. [4d](#page-5-0), sample K-190A) that may be formed by difusion-limited reactions in dissolution boundary layers (Stimac and Pearce [1992](#page-26-15)). Other evidences like a rounded and embayed crystal form are rare in quartz and K-feldspar.

Intermediate rock (sample 3, K-190B) is dioritic, composed of plagioclase, quartz, alkali feldspar, hornblende, and biotite, with titanite, zircon, and apatite as accessory phases. Epidote is the main secondary mineral. Colour index reached about 50%.

A folded foliation (Fig. [5](#page-6-0)a) is defned by mafc minerals and strong dynamic recrystallized quartz (Fig. [5b](#page-6-0)). This deformation led to defection of mafc agglomerates, and to folding which affected biotite, hornblende, and sometimes epidote crystals (Fig. [5](#page-6-0)a). Myrmekites are common. Inclusions of biotite within hornblende and of hornblende within biotite are common substitution features.

The elongated intermediate enclaves enclosed in a fnely foliated acid material possibly have deformed by solid-state

and fractures flled by quartz. **d** Quartz commonly supports coronas of biotite. Mineral abbreviations: bi, biotite; Kf, K-feldspar; pl, plagioclase; qz, quartz

deformation, due to a series of microstructures such as: (1) recrystallized aggregates of quartz and plagioclase (Fig. [5c](#page-6-0)); (2) myrmekite replacing K-feldspar, very local fame perthite, anastomosing foliations, shear bands (Fig.  $5d$  $5d$ ); (3) undulose extinction, and recrystallization of minerals to fner aggregates (Fig. [5](#page-6-0)b, d); (4) irregular borders and lens-like shapes of hornblende crystals (Fig. [5a](#page-6-0), b, e, f).

Mantles or coronas of hornblende and biotite (Fig. [5e](#page-6-0)), and mafc clots (Fig. [5](#page-6-0)f) in dioritic material also are typical textures whose origin can be explained in terms of magma mingling. However, suggestion of a "submagmatic fow" is not evidenced in this rock.

## **Cumulate layers of K‑feldspar megacrysts**

Near the contacts between quartz microdiorite and granite, there is a strong concentration of euhedral, centimetric phenocrysts of K-feldspar (Fig. [3a](#page-4-0)–c). Notably, the feldspars cumulate are clustered near the intermediate rock and are also present as xenocrysts in intermediate enclaves. Feldspar crystals may be partly or completely physically incorporated into enclaves before the enclaves



<span id="page-6-0"></span>**Fig. 5** Photomicrographs of Ribeirão do Óleo quartz microdiorite, sample 3 (K-190B). **a** Folded foliation. **b** Quartz dynamic recrystal-

lization. **c** Recrystallization of plagioclase. **d** Shear bands with dextral

solidifed (Vernon [1991\)](#page-26-16), as shown in Fig. [3](#page-4-0)a representing incipient, local magma mingling that occurred just before consolidation of the accumulated enclaves (Vernon and Paterson [2006](#page-26-17)). Accumulation of crystals seems to be particularly common in granites showing evidence of magma mingling, which may be related to magma flows promoted by replacement of magma chambers (Vernon and Paterson [2006](#page-26-17)). In ROP, the evidences supporting physical

movement. **e** Quartz crystal bordered by a corona of hornblende and biotite. **f** Mafic clot. Mineral abbreviations: hb, hornblende; bi, biotite; Kf, K-feldspar; pl, plagioclase; qz, quartz; ep-epidote

accumulation of concentrations of K-feldspar megacrysts and not in situ growth (Paterson et al. [2005](#page-26-18)) include: (a) clustering of megacrysts in much greater modal proportions than is likely from the magma composition (Fig. [6\)](#page-7-0); (b) imbrication of megacrysts (Fig.  $6$ ); (c) no evidence of adjustment around megacrysts even so many of them are in contact; (d) dike-like concentrations of megacrysts (Fig. [6](#page-7-0)) that in some places intrude other units with fewto-no megacrysts.

<span id="page-7-0"></span>**Fig. 6** Outcrop-type of monzogranite and microdiorite mingling—Ribeirão do Óleo Pluton. Thin feldspathic veins in mafc material (1), sometimes with complex folded structures (2). Concentration of medium– fne-grained K-feldspathic aggregates near the granitediorite contact (3). K-feldspar cumulates with imbrication of phenocrysts up to 10 cm (4). Near of most K-feldspar cumulates, small enclaves or mafc clots in granite occur (5)



# **Analytical techniques**

This work presents feld and petrography, whole-rock geochemical and isotopic data, and LA-ICP-MS U–Pb and Lu–Hf data in zircon obtained from the intermediate and acid rocks from the ROP. All data were obtained at the facilities of the Núcleo de Apoio à Pesquisa (NAP)—Geoanalytic Laboratories—Geoscience Institute—São Paulo University, and of the Geochronological Research Centre (CPGeo), University of São Paulo, Brazil.

# **Mineral concentration**

The concentration of the heavy mineral fraction for U–Pb analysis was conducted at the Mineral Separation Laboratory of the CPGeo, Brazil. The separation procedures were carried out as described by Passarelli et al. ([2009\)](#page-25-14).

# **LA‑ICP‑MS analyses**

The procedures used for in situ analysis of U–Pb in zircon by LA-ICP-MS were described by Sato et al. ([2009](#page-26-19), [2012\)](#page-26-20) and Matteini et al. ([2010\)](#page-25-15). The instruments used were an Excimer 193 nm laser coupled to a Thermo Scientifc™ NEPTUNE™ MC-ICP-MS with a multi-collector array, installed at the CPGeo–IGc-USP laboratory. Analytical techniques for in situ Hf isotopic analyses in zircon have been described in detail by Wu et al. [\(2006\)](#page-26-21) and Sato et al. ([2009](#page-26-19)).

Between 30 and 50 zircon grains were dated per sample. The grains were mounted in 2.5 cm-diameter epoxy discs. The discs were polished sufficiently to expose the internal structures of the grains. All analyses are checked against zircon (GJ-1). Laser spot sizes used ranged from 20 to 32 μm (U–Pb analysis) to 47 μm (Hf analysis) and depth of crater  $~\sim 10$  μm. Each spot analysis took ca. 40 s. The complete procedures follow those outlined in Košler et al. ([2002](#page-25-16)) and Košler and Sylvester [\(2003](#page-25-17)).

Isotope analyses were carried out on sites previously selected by cathodoluminescence (CL) microscopy studies to identify the best areas and beam spot sites in zircon grains. The analytical data were processed off-line using the data reduction program "R" (Siqueira et al. [2014\)](#page-26-22). All fnal ages and plots were processed using the IsoplotEx software (Ludwig [2012](#page-25-18)).

The methodology for the determination of trace elements and REE in zircon grains performed in the NAP—Geoanalytic Laboratories with laser ablation associated with Quadrupole Inductively Coupled Plasma Mass Spectrometry (LA-Q-ICP-MS) is described in Andrade et al. [\(2014\)](#page-24-12).

#### **Whole‑rock chemical and isotopic analyses**

In total, three samples (two acid and one intermediate rock) were analysed. Bulk chemical X-ray fuorescence spectrometer analyses were performed using fused glass beads to determine the major and minor element compositions, and pressed pellets were used to determine the trace-element abundances. A computer program was used to calculate background, interference, mass absorption, and root mean square. 169 and 114 reference samples were used for calibration of major and minor elements, respectively, as specifed in Mori et al. ([1999\)](#page-25-19). Quality control used one or two standards used in the calibration, but treated as unknowns. Trace-element and REE abundances were determined by the ICP-MS and the analytical procedure described by Navarro et al. [\(2008\)](#page-25-20).

A Finnigan MAT 262 multi-collector thermal ionization mass spectrometer (TIMS) was used to obtain Sr–Nd and Rb–Sr whole-rock isotope analyses at the CPGeo-IGc-USP. Nd crustal residence ages (TDM) were calculated following the depleted mantle model of DePaolo [\(1981\)](#page-25-21), and a twostage Nd isotope evolution model was used for the calculation of the TDM of DePaolo et al. ([1991](#page-25-22)). εNd(*t*) values were calculated by using U–Pb zircon ages. Neodymium crustal residence ages (TDM) were calculated following the depleted mantle model of DePaolo [\(1981\)](#page-25-21), and a two-stage Nd isotope evolution model was used for the calculation of the TDM of DePaolo et al. ([1991](#page-25-22)). εNd(*t*) values were calculated using U–Pb zircon ages.

#### **Results**

#### **Major and trace elements**

A total of three samples (1 quartz microdiorite and 2 monzogranite) from the ROP were collected for wholerock major and trace-element composition analyses. The results are given in Table S1. The quartz microdiorite has  $SiO<sub>2</sub>$  contents 59.10 wt%, K<sub>2</sub>O contents 3.33 wt%,  $Na<sub>2</sub>O<sub>3</sub>$  contents 3.69 wt%, CaO contents 5.42 wt%, and  $Al_2O_3$  contents 15.31 wt%, exhibiting a metaluminous feature  $(A/CNK = 0.78$  (Fig. [7a](#page-8-0)). In addition, quartz microdiorite is characterized by high MgO contents 4.06 wt% with Mg-number (Mg#) of 55 [Mg# =  $100 \times (Mg^{2+})$  $(Mg^{2+} + Fe^{2+}))$ . The monzogranite samples record values of  $SiO_2 = 66.35 - 70.52 \text{ wt\%}, K_2O = 3.56 - 3.92 \text{ wt\%},$  $Na_2O_3 = 4.16-4.53$  wt%,  $MgO = 1.26-1.33$  wt%, and  $Mg# = 42.19 - 47.77$ . They display peraluminous feature  $(A/CNK = 1.00-1.04)$  (Fig. [7a](#page-8-0)). All the samples plot in the subalkaline series and discriminated as granite and diorite in the total vs alkali (TAS) diagram (Fig. [7b](#page-8-0)) and high-K calc-alkaline series in  $SiO_2-Ka_2O$  diagram (Fig. [7c](#page-8-0)).



gram after Maniar and Piccoli ([1989\)](#page-25-23), based on the Shand's index; **b** SiO<sub>2</sub>  $\times$  K<sub>2</sub>O after Peccerillo and Taylor [\(1976\)](#page-26-23); **c** TAS classifcation diagram of the granitoids using the classifcation of Cox et al. ([1979\)](#page-25-24)

<span id="page-8-0"></span>**Fig. 7 a** A/CNK  $\times$  A/NK dia-

The chondrite-normalized rare-earth element (REE; McDonough and Sun [1995\)](#page-25-25) plots of the new data (Table S1) are shown in Fig. [8.](#page-9-0) The quartz microdiorite displays enrichment in light REE (LREE;  $(La/Sm)_{CN} = 5.56$ ) and a depleted HREE patterns  $(Gd/Yb)<sub>N</sub> = 3.52$ , with no Eu anomalies (Fig. [8a](#page-9-0)). The monzogranite samples also show enrichment in LREE (Fig. [8b](#page-9-0);  $(La/Sm)_{CN} = 5.52-6.64$ ) and a depleted HREE patterns  $(Gd/Yb)<sub>N</sub> = 2.94–3.64$ , which also show no Eu anomalies (Fig. [8](#page-9-0)b). On the primitive mantle-normalized spidergram (Fig. [8b](#page-9-0)), the samples exhibit high concentrations of Rb, Th, and Pb. They also show characteristics of negative anomalies of Nb, P, and Ti, which might be associated with the magmatic differentiation of plagioclase residual.

#### **Sm–Nd and Rb–Sr isotopic data**

The whole-rock Nd and Sr isotope compositions are listed in Tables S2 and S3 for the Ribeirão do Óleo Pluton. The two monzogranite samples have relatively consistent<sup>143</sup>Nd/<sup>144</sup>Nd ratios ranging from 0.5117 to 0.5118, whereas one dioritic sample shows 0.5118, corresponding to  $_{eNd}(t)$  values of  $-7.83$  to  $-10.66$  at t=600 Ma. In addition,  ${}^{87}Sr/{}^{86}Sr$  initial ratios display the values of ca. 0.708 for the monzogranite and 0.706 for the quartz microdiorite.

#### **Zircon U–Pb (LA‑ICP‑MS) geochronology**

Zircon crystals were studied using conventional optical microscopy and CL imaging. All CL images were produced from a split screen on an FEI Quanta 250 Scanning Electron Microscope (SEM) and XMAX CL detector (Oxford Instruments) at the Laboratory of High-Resolution Geochronology of the Institute of Geosciences of the University of São Paulo (GeoLab-IGc-USP). For description details of the optical and electronic imagery, see Sato et al. ([2014](#page-26-24)).

Usually, bright CL image indicates U-poor domains with a well-ordered crystal lattice and dark CL image indicates U-rich domains. Primary internal zircon structures can be observed by the CL images, but important secondary features were also observed in zircons from Ribeirão do Óleo granite.

#### **External and internal morphology**

The zircon crystals of the ROP monzogranite are normally transparent, sub-euhedral and short-to-long prismatic grains (2:1–7:1) with an average 3:1. The pyramidal faces are under-developed (Fig. [9](#page-10-0)a–c). Inclusions of other minerals and some degree of fracturing are very common. In optical microscopy, magmatic zonation can be observed through conspicuous growth zones (Fig. [9c](#page-10-0)).

The zircon crystals of the ROP microdiorite are normally transparent, sub-euhedral and medium-to-long prismatic grains with an average 4:1. The pyramidal faces are underdeveloped (Fig. [9d](#page-10-0), e). Widespread inclusions and fracturing occur. In optical microscopy, magmatic zonation also can be observed through visible growth zones (Fig. [9e](#page-10-0)).

The most common pattern in analysed crystals identifed by CL imaging is the oscillatory/sector zoning that represents the heterogeneous distribution of trace elements (Hoskin [2000\)](#page-25-26) and presence of possibly xenocrystic inherited cores. Figure [10](#page-11-0) shows selected zircon CL images from monzogranite and quartz microdiorite, respectively.

As shown in Fig. [10a](#page-11-0), zircons from the monzogranite (sample 1—K-54A) display growth zoning (oscillatory or sector zoned), usually darker (weak CL) than the inherited core (exception of zircon 14). Blurred primary zones are also common. In the sample 2—K-190A, the inherited core is either brighter or darker than rims (Fig. [10](#page-11-0)b). Rare homogeneously textured zircon crystals occurred (zircon 20 Fig. [10](#page-11-0)a; zircons 1, 3, 16 Fig. [10](#page-11-0)b). Presence of transgressive zones of recrystallization, local development of convolute zoning, and complex growth zoning with possible local intermediate resorption in zircon occur in the inherited cores (zircons 5, 11, 12, 13, 24, 25 and 30, Fig. [10](#page-11-0)a; zircons 4, 8, 9, 16, 17, 18, 21, Fig. [10b](#page-11-0)).

Mostly of the zircon crystals of the quartz microdiorite exhibit low CL intensity (Fig. [10](#page-11-0)c) with exception of xenocrysts or inherited cores (see explanation on item 5.3.2). Magmatic growth oscillatory zoning, blurred primary zones

<span id="page-9-0"></span>**Fig. 8 a** Chondrite-normalized (Nakamura [1974](#page-25-27)) REE distribution patterns; **b** primitive mantle-normalized multi-element plot (Sun and McDonough [1989](#page-26-25)) of ROP samples. Legend is the same of Fig. [7](#page-8-0)





<span id="page-10-0"></span>**Fig. 9** Transmitted light images showing external morphology variations of zircon crystals from biotite monzogranite (**a**–**c**) and microdiorite (**d**, **e**) of ROP. Monzogranite: **a** sample 1 (K-54A); **b** sample 2

(zircons 1, 2, 3, 4, 6, 10, 12, 16, 20, Fig. [10c](#page-11-0)), with presence of possibly xenocrystic inherited cores (zircons 6, 8, 9, 11, 12, 15, 16, 20, Fig. [10](#page-11-0)c), and transgressive zones of recrystallization (zircons 1, 3, 6, 16, Fig. [10c](#page-11-0)) are observed. Development of local convolute zoning is rare (zircon 1 and 11, Fig. [10c](#page-11-0)). Homogeneously textured zircon crystals are not rare (zircons 8, 12 and 16, Fig. [10c](#page-11-0)). Low-luminescent metamorphic rim is present in samples 2 and 3 (Fig. [10](#page-11-0)b, c).

#### **U–Pb zircon dating**

The result of the LA-ICP-MS U–Pb analysis is given in Tables [1](#page-12-0), [2](#page-14-0) and [3](#page-15-0). The data are presented as Concordia age with 1 sigma, decay-constant errors, MSWD and probability (of concordance) are indicated. The U–Pb analyses were performed in two samples of the foliated biotite monzogranite (sample 1 and 2—Fig. [3\)](#page-4-0) and in one sample of the quartz microdiorite enclaves (sample 3—Fig. [3](#page-4-0)). Concordant zircon age dispersion is observed in both rocks of the ROP and

(K-190A); **c** detail of zircon crystals with magmatic zonation (sample 2, K-190A). Microdiorite: **d** sample 3 (K-190B). **e** Detail of zircon crystals with magmatic zonation

only with the joint investigation with the CL images of the analysed zircon grains was possible to interpret the diferent sets of concordant ages. Only analyses with sub-concordant passing a<10% discordancy test were considered. Systematic age variation between cores and rims is clearly shown in analysed zircon grains.

**Monzogranite** Thirty-three zircons of sample 1 (K-54A) have a relatively narrow range in Th/U ratios (0.24–1.07) but a wide range in Th (55–2613 ppm) and U (74–4019 ppm) contents (Table [1\)](#page-12-0). This sample is located a quite distance (ca. 3 meters) from the enclaves (Fig. [3\)](#page-4-0) and displays an interval between ca. 700 and 550 Ma of concordant ages (Fig. [11](#page-16-0)a, b). Two diferent sets of data of spot analyses with oscillatory zoning provide ages of 586 Ma (zircons 16, 27 and 28 Fig. [10](#page-11-0)a) and 613 Ma (zircons 4, 6 and 20 Fig. [10](#page-11-0)a) are interpreted as autocrysts and antecrysts, respectively.

Cores (possibly xenocrysts) (spots 1.1, 7.1, 8.1, 9.1 Fig. [10](#page-11-0)a) provide ages of 645 and 690 Ma, where spot 8.1



<span id="page-11-0"></span>**Fig. 10** Cathodoluminescence (CL) images of zircon grains: spot locations for U–Pb (red circles), Hf (green circles) analyses,  $^{206}Pb^{238}U$  ages in Ma are shown. The underlined numbers indicating

the spots are shown. Zircon internal structures are discussed in the text. **a** Biotite monzogranite sample 1 (K-54A); **b** biotite monzogranite sample 2 (K-190A); **c** quartz microdiorite sample 3 (K-190B)

although located on the edge of the crystal must have caught in depth part of the zircon core. In addition, inherited cores of Paleoproterozoic age of  $2.21 \pm 0.42$  Ga (Fig. [11a](#page-16-0)) were dated (spots 2.2 and 17.2—Fig. [10](#page-11-0)a).

The larger set of data provide a Concordia age of 556 Ma (Fig. [11b](#page-16-0)), although this age corresponds to a range of concordant ages between 570 and 540 Ma. This interval corresponds to analyses on: darker rims, usually with high Th and U contents, with mainly sector zoning and probably represents late and/or hydrothermal zircons.

The second dated sample (K-190A) is located in an area closer to the intermediate enclaves (Fig. [3\)](#page-4-0). Twenty-three zircons of sample 2 have a relatively wide range in Th (24–605 ppm) and U (48–637 ppm) contents, but a relatively narrow range in Th/U ratios (0.29–1.24). The exceptions on Th/U ratios between 0.02 and 0.12 (spots 1.2, 8.1, 9.1, 12.1, 14.1 and 18.1) are discussed later (Table [2\)](#page-14-0).

An interval between ca. 650 and 600 Ma of concordant ages is record (Fig. [11](#page-16-0)c). However, based on CL images, four diferent groups of ages can be identifed: 601 Ma, 613 Ma, 627 Ma, and 647 Ma.

The crystallization age  $601 \pm 4$  Ma (Fig. [11](#page-16-0)c) of the sample 2 is defned by the autocrysts with magmatic oscillatory zoned domains (spots 2.1, 19.1, 21.1 Fig. [10b](#page-11-0)).

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Relative homogeneous zircon cores with high CL intensity (spots 3.1, 7.7, 11.1, 13.1, 16.1—Fig. [10b](#page-11-0)) provide an age of  $613 \pm 5$  Ma (Fig. [11c](#page-16-0)). Darker zoned mantle (spots 5.1, 8.1, 17.1, 20.1, 22.1—Fig. [10b](#page-11-0)) of possibly zircon cores provides an age of  $627 \pm 2$  Ma.

The age of  $682 \pm 3$  Ma was obtained mainly on sector zoning rims and mantles (spots 9.1, 10.1, 14.1, 18.1—Fig. [10b](#page-11-0)) and in one zircon core (spot 1.1—Fig. [10b](#page-11-0)). Unzone cores enclosed by planar zoned or unzone mantles (spots 1.2, 12.1 and 15.1—Fig. [10b](#page-11-0)), normally with low Th/U values, with thin discrete darker non-dated rims provide an age of  $647 \pm 4$  Ma, probably from a late-stage magmatic or metamorphic episode of the 682 Ma xenocrysts.

Xenocryst with age around 788 Ma shows heterogeneous core (spot 6.1—Fig. [10b](#page-11-0)) surrounded by sector and oscillatory zoning mantle with fne darker rim. Inherited nuclei with discordant Paleoproterozoic age were dated (spot 23.1—Fig. [10](#page-11-0)b).

**Quartz microdiorite** The 20 analysed zircons of sample 3 (K-190B) can be divided into main three groups regarding the CL intensity and Th and U contents: (1) xenocrysts with normally high CL intensity (grains 1, 3, 6, 7, 8, 12, and 16—Fig. [10c](#page-11-0)) with a relatively narrow range in Th (16–

<span id="page-12-0"></span>



334 ppm) and U (50–363 ppm) contents and a reasonably wide range in Th/U ratios  $(0.11-1.21)$ ;  $(2)$  low CL intensity crystals (grains 2, 10, 13, 14, 17, 18, 19 and 20—Fig. [10](#page-11-0)c) with a relatively wide range in Th (108–1590 ppm) and U (526–1136 ppm) contents and a reasonably wide range in Th/U ratios (0.15–1.40); (3) darker rims (spots 4.1, 5.1, 9.1, 11.1, 15.2) with a relatively wide range in Th (11–657 ppm) content, narrow range in U (357–841 ppm) content, and a wide range in Th/U ratios (0.08–1.20) (Table [3\)](#page-15-0).

The crystallization age of the quartz microdiorite is recorded in autocrysts (spots 13.1, 15.2, 18.1, 19.1, 20.1— Fig. [10](#page-11-0)c) at  $623.7 \pm 2.3$  Ma (Fig. [11d](#page-16-0)). Ages of 655 Ma (spots 4.1, 5.1, 10.1—Fig. [10c](#page-11-0)) are recorded in darker rims and mantle of possibly antecrysts and may be interpreted as a result of the hypothetical frst magma pulse. An older age of 680 Ma (spots 2.1, 9.1—Fig. [10c](#page-11-0)) is recorded in darker rim of inherited cores.

Paleoproterozoic and Mesoproterozoic ages (Fig. [11d](#page-16-0)) are recorded both in xenocrysts (zircon crystals 1, 3, 7, 8, 12, 16—Fig. [10c](#page-11-0)) or inherited core (zircon 15—Fig. [10](#page-11-0)c).

#### **Lu–Hf analysis of zircon**

All Lu–Hf analyses were carried out by LA-ICP-MS at points as close as possible of U–Pb spot analyses always in the same CL sector of the zircon crystal (Fig. [10](#page-11-0)a) making more robust the correlation of *ε*Hf and Hf  $T_{DM}$  values at the time of crystallization (Fig. [12a](#page-17-0)). Zircon Hf T<sub>DM</sub> model ages are usually referred to as crust formation ages (Hawkesworth and Kemp [2006\)](#page-25-28). The Lu–Hf isotope compositions for 11 grains from sample 1 (K-54A) are summarized in Table [4.](#page-18-0) Typically, average 176Lu/177Hf ratios are very low, ranging from 0.000498 to 0.002009.

Zircon crystals from K-54A monzogranite show mean values of the  $176$ Hf/<sup>177</sup>Hf(*t*) isotopic composition ranging from 0.281899 to 0.282020, that corresponds to a total vari ation of about five  $\varepsilon$ -units  $[\varepsilon Hf(t) = -17.26$  to  $-12.51]$ .

An average of Hf  $T_{DM}$  model ages of 2.38 Ga, and  $\epsilon Hf(t)$ values around −14.7 were acquired on zircons of ages of the last period of the magmatic pulse of the pluton (group 2.3–2.4 Ga, Fig. [12a](#page-17-0)). Exception of zircon 19.1 with older Hf  $T_{DM}$  model age (2.5 Ga) and more  $\epsilon Hf(t)$  negative value  $(-17.02)$ , values were very similar to zircon 6.1 (Fig. [10](#page-11-0)a) of 618 Ma (group 2.5–2.6 Ga, Fig. [12](#page-17-0)a). One spot represent ing older age (705 Ma) provide considerably less negative  $\text{eff}(t)$  of  $-4.56$  and much younger Hf  $T_{DM}$  model ages of 1.86 Ga (Fig. [12a](#page-17-0)). In broad spectrum, an overall decrease in εHf from the oldest to the youngest magmatic pulse is observed (Fig. [12b](#page-17-0)).

The negative  $\epsilon Hf(t)$  values suggest derivation from a source with much lower Lu/Hf ratio than the chondritic reservoir, i.e., the sources of zircon crystals for the monzo granite have clearly crustal afnities. The igneous protolith



<span id="page-14-0"></span> $\underline{\textcircled{\tiny 2}}$  Springer



<span id="page-15-0"></span>Table 3 Results of U-Pb LA-ICP-MS dating of zircons on quartz microdiorite of ROP—sample 3 (K-190B) **Table 3** Results of U–Pb LA-ICP-MS dating of zircons on quartz microdiorite of ROP—sample 3 (K-190B)

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<span id="page-16-0"></span>**Fig. 11** LA-ICP-MS zircon U–Pb concordia diagram for the ROP. All given ages are Concordia ages or, when specified, mean <sup>238</sup>U/<sup>206</sup>Pb ages. *P* probability of concordance. Paleoproterozoic inheritances are given in mean 238U/206Pb ages. The **a** U–Pb plot of zircon crystals from the ROP monzogranite—sample 1 (K-54A). **b** Detail of Neoproterozoic zircon crystals from the ROP monzogranite—sample

of this granite probably were added to the continental crust in Siderian times as indicated by the zircon Hf model ages.

#### **Trace elements in zircon**

The result of the trace-element analysis is given in Table [5.](#page-19-0) 12 spots in 9 investigated zircon crystals from sample K-54A of the ROP monzogranite were analysed. For the calibration procedure, two glass standards NIST610 were used. After each group of six scan lines (rasters-R), a quality control analysis of the zircon standard ZR 91500 was made, and to fnalize the analyses of each sample, a single analysis of the glass standard NIST 612 and two more analyses of the NIST 610 standard were made (Table [5\)](#page-19-0). The following images were made of analysed zircons from sample 1 (location on Fig. [3](#page-4-0)) showing the spots of the raster lines (Fig. [13\)](#page-20-0). The

1 (K-54A) (see text for explanation). **c** U–Pb plot of zircon crystals from the ROP monzogranite—sample 2 (K-190A) (see text for explanation). Data-point error ellipses are 2*σ*. **d** U–Pb plot of zircon crystals from the ROP quartz microdiorite—sample 3 (K-190B) (see text for explanation)

spot diameter was 25 μm. The other spots are the sites of analyses of U–Pb and Hf.

Zircons from the monzogranite have relatively high Th/U ratios (0.24–1.07—Table [1](#page-12-0)) indicating a magmatic origin (Rubatto [2002;](#page-26-26) Hoskin and Schaltegger [2003\)](#page-25-29). Just one Th/U ratio of 0.08 was observed in the raster 6 of the zircon-8 rim (Zr-8—Fig. [13c](#page-20-0); Table [5\)](#page-19-0). The zircon crystals have high concentrations of Th and U (Table [5](#page-19-0)), generally varying from 240 ppm to 820 ppm and 600 ppm to 2200 ppm, respectively. An exception is two analyses, the zircon-7 rim with 6615 ppm of Th and 7354 ppm of U and zircon-8 with 60 ppm of Th.

Hafnium shows concentrations varying within the range of 1.3–2.0 wt%. Y exhibits high concentrations in analysed zircons varying between 800 and 5400 ppm. The Nb/Ta ratios vary from 2 to 8 and the highest value is found in the



 $(b)$ Age  $x \in Hf(t)$  $-4$  $-6 -8$  $-10 -12 -14$  $-16$  $-18$ 500  $550$ 600 650 700 (Ma)

<span id="page-17-0"></span>**Fig. 12** Hf isotope composition of zircon crystals from the ROP monzogranite (sample 1, K-54A): **a** εHf(*t*) versus intrusion age diagram. The evolution trends were calculated for a 176Lu/177Hf of 0.0113. *DM*

depleted mantle evolution line, *CHUR* chondritic uniform reservoir. **b** Plot of <sup>206</sup>Pb/<sup>238</sup>U zircon ages versus  $\epsilon Hf(t)$ 

youngest zircon (Zr 7-spot 7.2—518 Ma, Fig. [10](#page-11-0)a) that is enriched in all REE comparative with other zircons.

The REE geochemistry of zircons and its chondritenormalized REE patterns show depleted light REE and enriched heavy REE, some positive Ce, and weak negative Eu anomalies, although some zircons did not show Eu anomaly (Table [5;](#page-19-0) Fig. [14](#page-21-0)a). The REE patterns show that the incorporation of most REE correlates with younger zircons and possibly with a hydrothermal event.

The data obtained of ratios of REE concentrations in the zircon crystals versus the REE content in the host rock (sample 1, K-54A) show that the HREEs are strongly concentrated by the zircons, with high partition coefficients, varying from 100 to 3000 (Table [6,](#page-22-0) Fig. [14b](#page-21-0)). The LREEs, however, have much lower coefficients, mostly in the range of 1–20. U and Y are preferred in the zircon structure in relation to Th, Ta, and Nb, which is refected in their higher partition coefficients (Table  $6$ ). Ta is preferred in relation to Nb, typical from non-A-type granites (Table [6\)](#page-22-0).

In  $(Sm/La)_N$  vs. La (Fig. [14](#page-21-0)c) and Ce/Ce\* vs.  $(Sm/La)_N$ (Fig. [14d](#page-21-0)), diagrams widely used to discriminate magmatic from hydrothermal zircons, most zircons analysed plot close to the "hydrothermal" feld defned by Hoskin ([2005](#page-25-30)), or even into others hydrothermal felds compiled from several magmatic and hydrothermal zircons by Zhong et al. [\(2018](#page-27-0)).

In a broad sense, a positive correlation between zircon Th/U and Ti-in zircon temperature and between Th/U and  $Zr/Hf$  is observed (Fig. [15](#page-22-1)a–c). This indicates that higher temperature crystallization in less fractionated magmas is associated with elevated zircon Th/U ratios. Also, the positive correlation between Ti-in-zircon temperature and zir-con Th/U (Fig. [15a](#page-22-1)) and  $(Th_{(ziron/rock)}/U_{(ziron/rock)})$  (Fig. [15](#page-22-1)c)

suggest that cooler more fractionated melts containing more U in the zircon crystals, due to the less-incompatible nature of U in relation to Th (e.g., Kirkland et al. [2015\)](#page-25-31). The raster 3 of Zr-7 (Fig. [13b](#page-20-0)) that represents probably an age of ca. 518 Ma (spot 7.2—Fig. [10](#page-11-0)a) is usually out of the trends.

# **Discussion**

Finely foliated biotite monzogranite and quartz microdiorite compose the ROP of the MC-CoT. Magma mingling features is observed by feld evidence (Figs. [3](#page-4-0), [6\)](#page-7-0) and petrographic analyses (Figs. [4,](#page-5-0) [5\)](#page-6-0). Physical accumulation of K-feldspar megacrysts in clusters with no evident boundary, highlighting the occurrence of instabilities that change considerably these mineral proportions are also supported by petrographic studies. The physical accumulation by mingling of K-feldspar megacrysts resulted in concentrations in irregular patches and dike-like bodies with difuse boundaries (Figs. [3](#page-4-0)a, b, [6\)](#page-7-0) are also found as suggested by Paterson et al. [\(2005\)](#page-26-18).

Magmatic fow in ROP is mainly represented by alignment and imbrication of undeformed euhedral K-Feldspar crystals and elongation of microdiorite enclaves consistent with rotation of crystals in a melt phase (Vernon [2000](#page-26-14)). On the other hand, evidences of solid-state fow are found, possible under infuence of the high-angle ductile shear zones that limit the MC. Folded foliation, quartz dynamic recrystallization, recrystallization of plagioclase, and shear bands are typical microstructures in microdiorite, and a foliation expressed by segregated bands of quartz and aligned biotite crystals and K-feldspar recrystallization is



<span id="page-18-0"></span>The spot number is the same as the U–Pb analysis

The spot number is the same as the U-Pb analysis

observed in monzogranites. Additionally, microstructures in ROP monzogranite indicate fracturing of K-feldspar crystals in the presence of melt (Fig. [4](#page-5-0)c). As postulated by Bouchez et al. ([1992](#page-24-13)), fracturing resulted from concentration of stress at contacts between grains when the granite contains submagmatic nature. The presence of a submagmatic fow in monzogranites suggests that the crystallization of this pluton undergone to some strain. Conversely, the grain flow is not observed in quartz microdiorite. The implications for the observed deformations and the emplacement chronology of the two bodies are discussed in the following item.

The irregular elongate and flame-like shape enclave swarms indicate the relative fow direction between the acid and intermediate magmas (Fig. [3a](#page-4-0), b), suggesting that both acid and the intermediate magmas were melted during fow.

In a polycyclic terrane where reworking of the continental crust is evident (Table [7](#page-23-0)), the high-precision U–Pb zircon dating provides signifcant U–Pb age range (556–613 Ma and 601–627 Ma on monzogranite and 624–655 Ma on quartz microdiorite, Fig. [11](#page-16-0)), refecting prolonged timescales of zircon crystallization and long magma residence times. According to Samperton et al. ([2017](#page-26-27)), such age heterogeneity may indicate prolonged crystallization between the temperatures of zircon saturation and rock solidifcation, stressing the condition of considering zircon as a zoned, dynamic archive.

The discrimination of autocryst, antecryst, and xenocryst in terranes with complex crustal histories is a hard work, but the CL images analyses allow us make some interpretations. Nevertheless, as pointed out by Miller et al. ([2007](#page-25-32)), the line between xenocryst and antecryst could be indistinct. Table [7](#page-23-0) presents a resume of some available ages of IS and Areado pluton of the MC along with the ages reported in this work, which discriminate the origin of zircon crystals.

A late-stage magmatic episode of the ROP monzogranite of 556 Ma is given by spots in darker rims with sector zoning, although several pulses of zircon crystallization are recorded through several time spam, i.e., 627 Ma; 613 Ma, 601 Ma, and 586 Ma. The initial crystallization of the older intermediate material is constrained at ca. 655 Ma and the fnal crystallization age around 624 Ma.

In contrast to usual magmatic zircon, the weak CL (apart from inherited zircon cores or xenocrysts), the enrichment of REE in darker rims (Zr 32-R1; Zr 7-R3; Zr8-R5; Zr12-R9; Figs. [13,](#page-20-0) [14](#page-21-0)a), the distribution on  $(Sm/La)<sub>N</sub>$  vs. La and Ce/  $Ce^*$  vs.  $(Sm/La)<sub>N</sub>$  diagrams (Fig. [14](#page-21-0)c, d), and variable Th/U ratios suggest that the ROP analysed zircons may contain domains of hydrothermal origin (Hoskin [2005;](#page-25-30) Harley et al. [2007](#page-25-33); Wang et al. [2016](#page-26-28); Zhong et al. [2018](#page-27-0)). Nevertheless, more detailed zircon geochemistry to diferentiate magmatic and hydrothermal zircons is necessary to make this interpretation unequivocal.



<span id="page-19-0"></span>Table 5 Trace element and REE (ppm) data  $(\pm 1\sigma)$  for zircon crystals from the ROP biotite monzogranite—sample 1 (K-54A) 1 3**Table 5** Trace element and REE (ppm) data (±1*σ*) for zircon crystals from the ROP biotite monzogranite—sample 1 (K-54A)



<span id="page-20-0"></span>**Fig. 13** Transmitted light (left) and cathodoluminescence images (right) of analysed zircon crystals—sample 1 (K-54A) by ICP-MS for trace elements. In the fgure are represented the raster number with

Th/U ratios values in parentheses and the zircon number (same of Fig. [10a](#page-11-0)). The green and yellow lines correspond to the rasters spots (scan lines)

Thus, the observed feld relations and the older U–Pb zircon ages of the quartz microdiorite suggest that the monzogranite emplacement started probably during the mediumto-fnal stages of crystallization of the quartz microdiorite, and this one could react as a fuid with which the granite could mingle.

A common feature of the granites in the MC is the Paleoproterozoic and Neoproterozoic inheritances (Table [7](#page-23-0)). The Rhyacian inheritance (spots 2.2, 17.2, Fig. [10a](#page-11-0)) is quite typical in the monzogranites of the ROP and is also registered in inherited zircons of IS and in basement roof pendants in the Areado Pluton (Passarelli et al. [2016\)](#page-26-1). Osirian inheritance of 2.0 Ga is found in quartz microdiorite and in monzogranite—sample 2 (spot 23.1, Fig. [10](#page-11-0)b; spots 1.1, 7.1, 15.1 and 16.1, Fig. [10c](#page-11-0)). Statherian inheritance (1.72–1.79 Ga) is only found in quartz microdiorite zircon crystals (spots 3.1, 6.1, 8.1, 8.2 and 12.1, Fig. [10](#page-11-0)c) and is not found in MC rocks (Table [7\)](#page-23-0).

Ages around 790 Ma are found in xenocrysts of the ROP monzogranite and the IS rocks. On the other hand, ROP monzogranite xenocrysts of ca. 645 Ma could refect the Itariri magmatism.

Possibly co-mingling and exchange of xenocrysts with ages between 680 and 700 Ma occurred mainly between the quartz microdiorite (spots 2.1, 9.1—Fig. [10c](#page-11-0)) and monzogranite sample 2 (spots 1.1, 9.1, 10.1, 18.1—Fig. [10](#page-11-0)b) of ROP. These xenocrysts may be incorporated from host rocks of the MC (Areado Granite and IS—Table [7](#page-23-0)).

Additionally, the diference of ages between the two samples of monzogranite may suggest that a hybrid zone was formed between the two magmas, and the sample 2, with older ages, may represent a hybrid monzogranite. The Nd and Sr isotopic data seem to corroborate this proposition.

In the conventional εNd vs.  $87$ Sr/ $86$ Sr isotope variation diagram (Fig. [16](#page-23-1)a); along with the data for oceanic island basalts and MORB sample major reservoirs in the mantle, and data from MC rocks, no trend in the ROP data is evident. Nevertheless, the isotope data display a consistent shift away from likely oceanic isotope signatures, with lower εNd and higher  ${}^{87}Sr/{}^{86}Sr$  values indicate a characteristic of the continental crust feld-enriched quadrant (Fig. [16](#page-23-1)a). This behavior is in accordance with the features and ages observed in the zircons that clearly indicate the participation of the crust in its generation. Additionally, we can consider that the Sr and Nd isotope ratios for ROP rocks are distinctly less radiogenic than those of the other units of the MC.

Isotope-element mixing diagrams provide some insight into the processes and origins of Sr–Nd isotopic signatures in the ROP. These samples show a linear correlation when they are plotted in  $1/\text{Sr}$  vs.  $87\text{Sr}/86\text{Sr}$  and considered that the correlation observed in Rb–Sr isotope evolution diagram is probably due to two component mixing (Fig. [16b](#page-23-1)). A binary mixing array between a low-Sr concentration more radiogenic  $87$ Sr/ $86$ Sr (∼0.715) end-member (monzogranite sample 1) with a high-Sr, less radiogenic (∼ 0.708) source (quartz microdiorite sample) probably represents a mechanical mixing (monzogranite sample 2).

In the conventional Nd isotope-element mixing diagram (Fig. [16](#page-23-1)c) the Nd data suggest also a binary mixing array between a less negative εNd, high Nd concentration source (quartz microdiorite sample) with a more negative εNd and low Nd concentration (monzogranite sample 1). Mechanical mixing probably controls the mixing array.

Moreover, the new data from the MC combined with the literature data (charnockitic rocks; Picanço [1994](#page-26-29); Picanço et al. [1998](#page-26-30); Pavan [2017](#page-26-31)) from the Itatins Complex (Curitiba Terrane) were plotted in Sr evolution diagram (Fig. [16d](#page-23-1)). Despite the similarity of the ROP REE pattern with those rocks originated from charnockite fusion, the ROP rocks are plotted below the evolution lines of the Itatins Complex charnockitic



<span id="page-21-0"></span>**Fig. 14 a** Chondrite-normalized averaged REE patterns from ROP monzogranite zircons of sample 1 (K-54A) (data from Table [5](#page-19-0)). Chondrite values are from Taylor and McLennan ([1985\)](#page-26-32). **b** Zircon/ rock partition coefficients from ROP monzogranite zircons with mov-ing average (data from Table [6](#page-22-0)). **c**, **d**  $(Sm/La)<sub>N</sub>$  vs. La and Ce/Ce<sup>\*</sup>



vs. (Sm/La)N diagrams. The outlined areas represent the "magmatic" (blue) and "hydrothermal" (green) feld defned by Hoskin [\(2005](#page-25-30)). Others magmatic (light grey) and hydrothermal (dark grey) felds are from the compilation made by Zhong et al. ([2018\)](#page-27-0)

rocks, therefore, not being genetically related to them. However, it can be suggested that the granites of ROP may have derived from reworking of IS rocks of the MC.

The analysed samples from ROP belong to a high-K calcalkaline series. Granites are slightly peraluminous and quartz microdiorite sample is metaluminous. ROP REE pattern suggests some similarity with A-type post-orogenic rocks, although the REE partition coefficients in zircon crystals are typical from non-A-type granites.

# **Tectonic implications**

Several episodes of amalgamation and subsequent diachronous collision of the terranes and microplates during the closure of the Adamastor Ocean were already postulated by several authors (e.g., Basei et al. [2000](#page-24-4), [2009](#page-24-10); Heilbron et al. [2008;](#page-25-1) Brito Neves et al. [1999](#page-24-5), [2014](#page-24-6) among others).

<span id="page-22-0"></span>**Table 6** Zircon/rock partition coefficients of REEs, Y, Th, U, Nb, and Ta from the ROP biotite monzogranite—sample 1 (K-54A)





*R* raster and equivalent zircon crystals from Figs. [10](#page-11-0) and [13](#page-20-0)

<span id="page-22-1"></span>**Fig. 15 a** Ti-in zircon temperature versus Zircon Th/U (sample 1-monzogranite). **b** Zircon Th/U versus Zr/Hf zircon. **c** Plot of fractionation factor  $(Th_{(zircon/rock)}/U_{(zircon/rock)})$  versus Ti-in-zircon temperatures. R: raster. The rasters and equivalent zircon crystals are shown in Fig. [15](#page-22-1) and Tables [5](#page-19-0) and [6](#page-22-0)



Domain of MC/origin of zircon crystals	Autocrysts crystallization ages	Antecrysts		Neoproterozoic inheritance Paleo-Mesoproterozoic inherit- ance
Itariri Suite <sup>a</sup>	745 Ma: 640–630 Ma: 620–612 Ma; 603 Ma	Not available	790 Ma	2.2–2.1 Ga; 1.8 Ga; 1.2–1.1 Ga
Areado Pluton <sup>a</sup>	700 Ma; 2150 Ma	Not available	860 Ma	2.2–2.1 Ga; $1.8$ Ga
ROP monzogranite (K-54A— sample 1)	556 Ma (570–540 Ma)		613 Ma: 580 Ma 690 Ma: 645 Ma	$2.21$ Ga
ROP monzogranite $(K-190A$ —sample 2)	601 Ma		631 Ma; 627 Ma 788 Ma; 682 Ma; 647 Ma (metamorphic rim)	$1.9$ Ga
ROP quartz diorite (K-190B— sample 3)	624 Ma	655 Ma	684 Ma	2.0 Ga: 1.7 Ga

<span id="page-23-0"></span>**Table 7** Main U–Pb geochronological data of the Mongaguá Complex units

a Data from Passarelli et al. ([2014a,](#page-26-11) [2016\)](#page-26-1)



<span id="page-23-1"></span>**Fig. 16 a**  $\epsilon N d_i$ —(<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>i</sub> diagram (modified after White [2015](#page-26-33)) for the ROP rocks with initial ratios calculated for 600 Ma: MORB mid-ocean ridge basalts and BSE–bulk silicate Earth are shown. The mantle sources of MORB and the mantle end-members EMI (enriched mantle type I) and EMII (enriched mantle type II) are from Zindler and Hart ([1986\)](#page-27-1). **b** Sr isotope-element mixing diagram. **c** Nd isotope-element mixing diagram. **d** Sr evolution diagram for the

MC rocks and charnockitic rocks from the Itatins Complex (Curitiba Terrane). Legend for **a**–**c**: dark-blue square=monzogranite sample 1 (K-54A); light-blue square=monzogranite sample 2 (K-190A); red circle=microdiorite sample-3 (K-190B). Black symbols are of studied rocks of the MC (data from Tables [2](#page-14-0) and [3\)](#page-15-0): triangle=Itariri Suite; circle=Areado Pluton

The juxtaposition of Curitiba Terrane (CRT) and Paranapanema craton took place at ca. 630–605 Ma, and of the Luis Alves and CRT was already fnished around 590 Ma (Basei et al. [2009](#page-24-10)). The docking of CoT and adjacent terranes may be occurred subsequently.

One of the deformation phases identifed in the Itariri Shear Zone possibly represents an extensional movement resulting from stress release of the juxtaposition of the Embu and Curitiba terranes (Passarelli et al. [2011\)](#page-26-6). Additionally, the wedge confguration of the CoT between the Embu and Curitiba terranes is due to the sinistral Itariri shear zone movement (Passarelli et al. [2019](#page-26-3)) which is constrained around 580 Ma (Passarelli et al. [2011,](#page-26-6) [2019\)](#page-26-3).

The presence of magma mingling/mixing is a common feature in the 580 Ma late- to post-collisional magmatism of the RB (Pedrosa-Soares and Wiedemann-Leonaros [2000](#page-26-34); Medeiros et al. [2001;](#page-25-34) Gualda and Vlach [2007](#page-25-35); Meira [2014](#page-25-10); Machado et al. [2016\)](#page-25-36), resulting from the intrusion of hot mafc magma into colder felsic magma. On the other hand, the ROP was generated from melting of crustal rocks due the interaction with older hotter mafc magmas at the base of the crust.

The slightly older microdiorite (655–624 Ma) and 613–586 Ma monzogranite in addition to the observed grain-supported fow only in monzogranite and solid-state deformation in both rocks suggest that the initial phases of the mafc magmatism took place under no strain or at an extensional event. Moreover, the continuous closure of the Adamastor Ocean and juxtaposition of the terranes associated with magmatic underplating provided high temperatures of the continental crust for a long-term late orogenic period generating the monzogranite of the ROP under a main compressive tectonic regime.

# **Conclusions**

- Magma mingling between slightly older quartz microdiorite and biotite monzogranite is evidenced in the ROP, where the emplacement of the monzogranite started probably during the medium-to-fnal stages of crystallization of the quartz microdiorite.
- A hybrid zone between the two magmas is suggested by Nd and Sr isotopic data and by LA-ICP-MS U–Pb zircon geochronology.
- The petrographic analyses indicate syn-tectonic characteristics of the ROP, involving submagmatic and solidstate deformation.
- The petrographic and isotopic analyses indicate that the ROP was produced from partial melting of older crustal rocks, originated probably by underplating of mafc magmas responsible for providing high temperatures of the continental crust during a protracted orogenic evolution of the RB.
- An accurate analysis of LA-ICP-MS U–Pb ages and zircon internal structures allows us to determine a reasonable origin of zircon crystals and the sequence of several magmatic pulses and post-magmatic events over an extended time of 655–556 Ma.

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