Paleoproterozoic juvenile magmatism within the northeastern sector of the São Francisco paleocontinent: Insights from the shoshonitic high Ba-Sr Montezuma granitoids.

Samuel Moreira Bersan\textsuperscript{a,d*}, Alice Fernanda de Oliveira Costa\textsuperscript{b}, André Danderfer Filho\textsuperscript{b}, Francisco Robério de Abreu\textsuperscript{c}, Cristiano Lana\textsuperscript{b}, Glaucia Queiroga\textsuperscript{b}, Craig Storey\textsuperscript{d}, Hugo Moreira\textsuperscript{d}

\textsuperscript{a}Universidade Federal de Ouro Preto, Programa de Pós-graduação, Departamento de Geologia, Campus Morro do Cruzeiro, Ouro Preto, MG CEP 35400-000, Brasil.

\textsuperscript{b}Universidade Federal de Ouro Preto, Departamento de Geologia, Campus Morro do Cruzeiro, Ouro Preto, MG CEP 35400-000, Brasil.

\textsuperscript{c}Sustain Geologia Ltda. Teresa M. Valadares 503/502, Belo Horizonte, MG. CEP 30575-160, Brasil.

\textsuperscript{d}University of Portsmouth, School of Earth and Environmental Sciences, Burnaby Building, Burnaby Road, Portsmouth, PO1 3QL, UK

* Corresponding author. E-mail address: samuelbersan@gmail.com (S. Bersan).
Abstract

New, integrated petrographic, mineral chemistry, whole rock geochemical, zircon and titanite U-Pb geochronology, and zircon Hf isotopic data from the Montezuma granitoids, as well as new lithogeochemical results for its host rocks represented by the Corrego Tingui Complex, provides new insights into the late- to post-collisional evolution of the northeastern São Francisco paleocontinent. U-Pb zircon dates from the Montezuma granitoids spread along the Concordia between ca. 2.2 Ga to 1.8 Ga and comprise distinct groups. Group I have crystallization ages between ca. 2.15 Ga and 2.05 Ga and are interpreted as inherited grains. Group II zircon dates vary from 2.04 Ga to 1.9 Ga and corresponds to the crystallization of the Montezuma granitoids, which were constrained at ca. 2.03 Ga by the titanite U-Pb age. Inverse age zoning is common within the ca. 1.8 Ga Group III zircon ages, being related to fluid isotopic re-setting during the Espinhaco rifting event. Zircon $\varepsilon_{Hf}(t)$ analysis show dominantly positive values for both Group I (–4 to +9) and II (–3 to +8) zircons and $T_{DM}^2$ model ages of 2.7–2.1 Ga and 2.5–1.95 Ga, respectively. Geochemically, the Montezuma granitoids are weakly peraluminous to metaluminous magnesian granitoids, enriched in LILES and LREE, with high to moderate Mg# and depleted in some of the HFSE. Their lithochemical signature, added to the juvenile signature of both inherited and crystallized zircons, allowed its classification as a shoshonitic high Ba-Sr granitoid related to a late- to post-collisional lithosphere delamination followed by asthenospheric upwelling. In this scenario, the partial melting of the lithospheric mantle interacted with the roots of an accreted juvenile intra-oceanic arc, being these hybrid magma interpreted as the source of the Montezuma granitoids. The Córrego Tinguí Complex host rocks are akin to a syn- to late-collisional volcanic arc granitoids originated from the partial melting of ancient crustal rocks. The results presented in this study have revealed the
occurrence of juvenile rocks, probably related to an island arc environment, that are exotic in relation to the Paleo- to Neoarchean crust from the São Francisco paleocontinent's core.

**Keywords:** Zircon U-Pb-Hf; Titanite U-Pb; High Ba-Sr; Late- to post-collisional; São Francisco paleocontinent.
1. Introduction

Understanding Paleoproterozoic magmatic events has global significance as it informs the evolution of palaeocontinents and represents the recycling of the first continental crust formed during the Archean (e.g., Silva et al., 2002; Heilbron et al., 2010; Zhao et al., 2011; Cioffi et al., 2016; Wang et al., 2016; Patersson et al., 2018). In central Brazil, the São Francisco craton and associated marginal orogens registers several important Archean–Paleoproterozoic tectono-magmatic events playing an important role in the formation of the South American continental crust. (e.g., Barbosa and Sabaté, 2004; Heilbron et al., 2010; Cioffi et al., 2016; Cruz et al., 2016; Moreira et al., 2018).

Despite most of the continental crust formation being linked to the end of arc and collisional stages of magmatism (Hawkesworth et al., 2009), post-collisional magmas with dual mantle and crustal geochemistry also represent an important contribution to crustal growth processes (Couzinie et al., 2016).

Events of granitoid generation associated with a late to post-collisional tectonic settings are commonly related to a hybrid environment, with different proportions of interaction between mantle and crustal derived magmas (e.g. Bonin, 2004; Moyen et al., 2017). Consequently, some late- to post-collisional granitoids, classified as shoshonitic or high Ba-Sr granitois, have a dual mantle-crust chemical signature whose petrogenetic process are linked to the partial melting of a subduction related matassomatized mantle, with latter crustal assimilation and contamination (Bonin, 2004; Fowler et al., 2008; Goswami and Bhattacharyya, 2014; Clemens et al., 2017; Moyen et al., 2017).

The São Francisco Craton consists of a stable crustal segment not affected by the Neoproterozoic collisional and accretionary processes related to the Gondwana supercontinent construction (Almeida, 1977; Alkmim et al., 1993). As a result, several Neoproterozoic orogenic belts partly reworked its margins, being the Araçuaí orogen
developed at its eastern edge (Fig. 1; Almeida, 1977; Alkmim et al., 2006). The São Francisco paleocontinent represents the Archean nuclei and Paleoproterozoic magmatic arcs amalgamated during the early Orosirian that integrate the basement of both the São Francisco craton and its marginal orogens (Noce et al., 2007; Heilbron et al., 2010; Degler et al., 2018). The so-called Rhyacian–Orosirian orogeny is marked by the production of enormous volumes of granitoids between ca. 2.35 Ga and 2.08 Ga, which were variably deformed mainly during collisional processes (Silva et al., 2002; Noce et al., 2007; Heilbron et al., 2010; Cruz et al., 2016; Silva et al., 2016), followed by extensive ca. 2.08–1.85 Ga late- to post-collisional magmatism (Santos Pinto et al., 1998; Barbosa et al., 2012; Cruz et al., 2016).

Despite recent work on the granitoid rocks that integrate the deformed segments from the São Francisco paleocontinent exposed within the Araçuaí orogen basement (e.g., Silva et al., 2002, Noce et al., 2007; Heilbron et al., 2010; Cruz et al., 2016; Silva et al., 2016; Degler et al., 2018), there are many questions still to be answered. This paper, based on new petrographic, lithogeochemical, geochronological (U-Pb in zircon and titanite) and isotopic (Hf in zircon) data from the Montezuma granitoids and its host rock, the Córrego do Tingui Complex (Knauer et al., 2007, 2015), presents the record of a high Ba-Sr juvenile magmatism at ca. 2.03 Ga constituting a new element added to the crustal growth of the São Francisco paleocontinent.

2. Geological Setting

The São Francisco paleocontinent is composed by several Archean nuclei, including the Quadrilátero Ferrífero, Gavião, Serrinha, Jequié, Guanhães and Itacambira-Monte Azul, being commonly represented by a sodic association of tonalite-trondhjemite and granodiorite complexes (TTG) and associated greenstone belts, and potassic rich granitoids (e.g. Barbosa and Sabaté, 2002; Noce et al., 2007; Romano et al., 2013;
Throughout the Paleoproterozoic, these blocks were accreted through collisional processes that resulted in the building of several orogenic belts with associated cordilleran and juvenile magmatic arcs, including the Itabuna-Salvador-Curaçá, Mineiro, Mantiqueira, Juiz de Fora and the Western Bahia, whose ages vary from Siderian to Orosirian (ca. 2.5–1.9 Ga; Barbosa and Sabaté, 2002, 2004; Noce et al., 2007; Heilbron et al., 2010; Teixeira et al., 2015; Cruz et al., 2016; Degler et al., 2018; Moreira et al., 2018; Fig. 1B). These Rhyacian to Orosirian collisional processes were responsible for the construction and consolidation of the São Francisco paleocontinent.

In addition, rifting events occurred after the assemblage of the São Francisco paleocontinent, giving rise to intra-plate anorogenic magmatism (ca. 1.75 Borrachudos and São Timóteo granitoids; Lobato, 1985; Dussin, 1994; Fernandes et al., 1994; Silva et al., 1995; Chemale et al., 1997; Silva et al., 2002; Lobato et al., 2015; Magalhães et al., 2018) and deposition of the cover units from the Espinhaço and Macaúbas supergroups (Danderfer and Dardenne, 2002; Danderfer et al., 2009, 2015; Costa and Danderfer, 2017) (Figs. 1–3). At the end of the Neoproterozoic, parts of the Archean-Paleoproterozoic rocks were reworked within the Araçuaí orogen during the Brasilian/Pan-African orogeny (Almeida, 1977; Pedrosa-Soares et al., 2001; Alkmim et al., 2006). Thus, the sector investigated here represents the extension of the São Francisco paleocontinent inside the Araçuaí orogen (Fig. 1).

At the northeastern portion of the São Francisco paleocontinent, here it is highlighted the events recorded in the Gavião and Itacambira-Monte Azul nuclei. The first one consists of Archaen gneissic-migmatitic TTG terranes, meta-volcanosedimentary sequences and potassic granitoids intruded by Paleoproterozoic granitoids, represented by twenty-nine intrusive massifs that vary in shape, size and lithgeochemical
characteristics with crystallization ages from ca. 2.38 Ga to 1.85 Ga (Cruz et al., 2016 and references therein). Recently, Cruz et al. (2016) separated these granitoids into pre- to syn-collisional (ca. 2.35–2.06 Ga) and late- to post-collisional (ca. 2.05–1.90 Ga) groups based on their geochronological and lithogeochemical signatures, and deformation characteristics. This Paleoproterozoic magmatism, as proposed by these authors, was related to the development of a cordilleran continental arc, the Western Bahia Magmatic Arc (WBMA, Fig. 2), in response to the collision between the Gavião and Jequié nuclei from ca. 2.3 Ga.

The Itacambira-Monte Azul nucleus can be understood as the southward continuation of the western Gavião nucleus overprinted by the Neoproterozoic Araçuaí orogeny and is also represented by Archean gneissic-migmatitic TTGs and high-k calc-alkaline granitoids (Silva et al., 2016; Bersan et al., 2018a; Figs. 1, 2). These rocks are associated with the Riacho dos Machados meta-volcanosedimentary sequence of unknown age, as well as the Paleoproterozoic granitoids of the Paciência and Catolé suites whose evolution is connected to the WBMA post-collisional stages (Silva et al., 2016; Bersan et al., 2018b; Sena et al., 2018; Figs. 1, 2).

The gneisses from Córrego Tinguí Complex area, host of the Montezuma granitoids, are located in the southern region of the Gavião nuclei, where it is exposed as a basement window (Silva et al., 2016), and is bounded by Archean TTG gneisses and Tonian supracrustal rocks of the Macaúbas Supergroup (Costa and Danderfer, 2017). It outcrops in a N–S trending structural high (Peixoto, 2017) and is ca. 15 km in width and ca. 60 km in length encompassing an area of ca. 350 km² (Figs. 2, 3).

2.1. Previous studies on the Córrego Tinguí Complex and Montezuma granitoids area
Knauer et al. (2007) first described the Corrego Tingui Complex as an association of equigranular to porphyritic granitoid rocks and migmatized banded gneisses, locally affected by varying intensities of Neoproterozoic tectonic deformation. The Córrego Tinguí Complex was earlier considered to be Archean (Knauer et al., 2007), however recent U–Pb zircon ages obtained by Silva et al. (2016) from banded biotite gneiss with “in situ” pockets of anatetic leucosome constrained its crystallization age at 2.14 Ga (Fig. 3). Based on their litogeochemical (data not available) and isotopic signatures ($\varepsilon_{Nd}$ of $-6.85$ and $T_{DM}$ of 3.31 Ga), Silva et al. (2016) classified these rocks as a syn-collisional granitoid with significant involvement of a Paleoarchean crustal source.

As proposed by Knauer et al. (2015), the Córrego Tingui banded gneisses are intruded by granitoids that were affected by different degrees of tectonic deformation, sorting from slightly foliated to mylonitic granitoids. In the scope of this work, these deformed granitoids were named Montezuma granitoids, due to its proximity to the Montezuma town (Fig. 3). However, as also stated by Knauer et al. (2015), the outcrops are rare and poorly preserved which preclude the identification of field relation between them. In this work, we use the chemical signature (high K$_2$O and Ba-Sr) and the occurrence of accessory titanite or muscovite to distinguish and classify the rocks as belonging to the Córrego Tingui Complex (low Ba-Sr and lower in K$_2$O, absence of titanite and presence of muscovite) and the Montezuma granitoids (high Ba-Sr, high K$_2$O, titanite occur as accessory phase). During field investigations, neither xenoliths nor mafic microgranular enclaves (MMEs) were observed within the Montezuma granitoids.

3. Analytical methods

New twelve lithochemical analyses were obtained from the granitoids that compose the Córrego Tingui Complex and the Montezuma granitoids. Among these, four (T7B, VM-82, T2B and T1A) were chosen for EPMA mineral chemistry analyses and two were
selected for zircon U-Pb analysis (VM-82 and T1C). However, zircons from sample T1A are metamitic and the results are highly discordant, showing no reliable age (see the results in the Supplementary files). LA-ICP-MS titanite U-Pb dating was performed in the same VM-82 sample dated by zircon U-Pb geochronology. In situ zircon MC-ICP-MS Hf isotopic analyses were performed for all dated zircon crystals from sample VM-82. For details about the procedures, used techniques and equipments, detection limits and standards applied for chemical and geochronological analyses, please refers to supplementary material (Supplementary file Methods).

4. Results

4.1. Sampling, petrography and mineral chemistry

The main outcrops are scattered and sparse. The field relationships among the different geological stations are therefore assumed. In this study we described and sampled different outcrops of the high Ba-Sr Montezuma granitoids (T2A, T2B, T2C, T3A, T3B, T5, T7A, T7B and VM82) and the Córrego Tinguí Complex granitoids (T1A, T1B, T1C). Fig. 3 shows the locations of 12 samples collected, including the sample used for U-Pb dating and Hf isotopic analysis (VM82).

The Córrego Tinguí Complex rocks (Fig. 4A–C) are medium to coarse-grained gneissified granodiorites to monzogranites, that have main mineralogy consisting of plagioclase (38%–40%), quartz (30%–33%) and alkali-feldspars (18%–20%) with minor biotite (~8%) and white-mica (2%–4%) (Fig. 4B, C). Zircon, apatite and opaque minerals are the common accessory phases. Quartz is anhedral, with sizes varying from 2 mm to 5 mm and show undulose extinction in some sections. Plagioclase ($X_{An}$: 4.30%–11.98%; $X_{Ab}$: 87.39%–95.26%) is medium to coarse-grained anhedral to subeuhedral crystals with composition varying from oligoclase to albite (Figs. 4B, C, 5A). They can have polysynthetic twinning (Fig. 4B) and are cloudy in some thin-
sections due to their breakdown into sericite (Fig. 4C). The alkali-feldspars are
dominantly microcline, and its orthoclase component ($X_{Or}$) ranges from 90.23% to
96.98% (Fig. 5A). They occur either as smaller or larger (up to 1 cm) crystals in which
inclusions of plagioclase and biotite may occur (Fig. 4B). Biotite is the only mafic
mineral and occurs as small to medium euhedral and subeuhedral blades within the
interstices of quartz and feldspars crystals (Fig. 4B, C). The biotite from Corrego Tinguí
granitoids plot in the field of ferro-biotite and are characterized by low TiO$_2$ contents
(average of 2.23 wt.%) and medium MgO (average of 8.83 wt.%) with average Mg/(Fe$^T$
+ Mg) ratio of 0.44 (Fig. 5B–E; Supplementary Table 1). White mica is commonly
described as sericite, being related to the weathering and breakdown of plagioclase
crystals. However, it is also observed as euhedral to subhedral crystals associated with
biotite or plagioclase (Fig. 4B, C; sample T1A). According to the division established
by Miller et al. (1981) most of the analyzed white-mica from sample T1A falls in the
field of secondary mica. However, some of them plot within the transition field of
secondary and primary micas, as show in Fig. 5F. The accessory minerals are euhedral
to subhedral and occur associated with biotite or plagioclase.

The Montezuma granitoids are equigranular to porphyritic biotite monzogranites with
minor granodiorite and quartz-monzonite. These rocks are highly to slightly foliated
(Fig. 4D–N), with some protomylonitic to mylonitic members (Fig. 4D–F). Its main
mineralogy consists of plagioclase (30%–40%), alkali-feldspars (20%–50%), quartz
(10%–30%), biotite (5%–20%), with secondary calcite, white-mica and chlorite
reaching values up to 5%. Zircon, apatite, epidote, titanite and opaque minerals are the
common accessory phases, while allanite was observed in few of the analysed thin-
sections (Fig. 4E–O). Quartz occurs as small anhedral crystals with undulose extinction
intimately associated with the feldspar-biotite groundmass (Fig. 4H, K, O). For the
Montezuma granitoids, feldspar mineral chemical analyses were done only for the dated VM-82 sample. Biotite analyses were made from three samples with distinct whole rock MgO content: T7A (less differentiated with MgO~3.2 wt.%), VM-82 (MgO~1.8 wt.) and T2B (MgO ~1 wt.%). Plagioclase from sample VM-82 is essentially oligoclase in composition ($X_{An}$: 15.85%–20.46%; $X_{Ab}$: 78.78%–82.92%) and occurs as fine to medium grained anhedral to subhedral grains that show polysynthetic twinning (Figs. 4K, 5A). Alkali-feldspars ($X_{Or}$ = 89.04%–93.62%; $X_{Ab}$ = 6.37%–10.44%) are subhedral, medium to coarse grained, and dominantly classified as microcline with minor perthite, which may contain inclusions of plagioclase and biotite (Fig. 4H, K, L, O). The concentration of BaO and SrO in plagioclase (average BaO and SrO of 0.028% and 0.088%, respectively) and alkali-feldspar (average BaO and SrO of 0.63% and 0.090%, respectively) crystals from sample VM-82 are higher than those obtained for the Córrego Tinguí granodiorites (plagioclase average: BaO = 0.009%, Sr = 0.000%; alkali-feldspar average: BaO = 0.414%; SrO = 0.006%; Supplementary Table 1). Biotite is again the only mafic mineral phase and in deformed granitoids defines the protomylonitic to mylonitic foliation. Biotites from the less differentiated sample T7A (Fig. 4F) have higher MgO (average of 12.39 wt.%), lower FeO (average of 15.53 wt.%), and therefore higher Mg# (average 0.59), than the biotites from samples VM-82 (average MgO, FeO and Mg# are respectively 9.44 wt.%, 20.44 wt.% and 0.45) and T2B (average MgO, FeO and Mg# are respectively 7.72 wt.%, 21.27 wt.% and 0.39). These biotites are classified as magnesio-biotite (sample T7A) and ferro-biotite (samples VM-82 and T2B; Figs. 4F, K, L, O, 5B, C). In the FeO$^T$/FeO$^T$+MgO vs. MgO digram (after Zhou, 1986) they plot in between mantle-crustal mixed source and purely crustal source, whereas the biotite of the Córrego Tinguí Complex plot within the crustal source field (Fig. 5D). Moreover, the FeO–MgO–Al$_2$O$_3$ biotite discrimination
diagram (after Abdel-Rahman, 1994) suggests a calc-alkaline magma related to subduction for the Montezuma granitoids; the Córrego Tinguí biotites plot mostly in the collisional peraluminous related magmatism field (Fig. 5E). Accessory minerals are euhedral to subhedral and commonly associated with biotite or plagioclase. Titanite commonly occurs as large euhedral crystals with similar size to the main phase minerals (quartz, feldspar and biotite), sometimes included in feldspars crystals (Fig. 4K, L, M).

4.2. Whole rock major and trace elements

The twelve major and trace element compositions obtained for the Córrego Tinguí Complex and Montezuma granitoids are listed in Table 1. Classification diagrams are presented in Fig. 6. The Montezuma granitoids plot mostly within the quartz-monzonite field in the Middlemost (1985) TAS diagram with only two more evolved samples potting in the granite field; the three analyzed samples for the Córrego Tinguí Complex plot within the granite field in this diagram (Fig. 6A). In the K₂O vs. SiO₂ diagram, the Montezuma granitoid samples plot in the shoshonitic series field, whereas the Córrego Tinguí rocks have lower concentrations of K₂O, plotting in the transition area between the medium to high-K calc-alkaline fields (Fig. 6B). The shoshonitic affinities of the Montezuma granitoids are also attested by its high Th/Yb, Ce/Yb and Ta/Yb ratios (Fig. 6C; Pearce, 1982). The samples have a weakly peraluminous to metaluminous character (Fig. 6D) with Montezuma granitoids being classified as alkali to alkali-calcic, while Córrego Tinguí Complex samples plot in the calc-alkalic field (Frost et al., 2001, Fig. 6E). All samples show magnesian affinities (Frost et al., 2001; Fig. 6F) with 100×Mg# varying from 35 to 55 for the Montezuma granitoids and 33 to 42 for the Córrego Tinguí Complex (Table 1).

The analyzed samples have intermediate to high SiO₂ contents (61.58–74.35 wt.%) and moderate Al₂O₃ concentrations (14.12–16.89 wt.%). K₂O, Na₂O and CaO contents are
variable, ranging from 3.15–5.81 wt.%, 2.91–4.54 wt.% and 1.09–2.84 wt.%, respectively (Table 1, Fig. 7). Montezuma granitoids are enriched in K₂O and CaO and impoverished in Na₂O (Figs. 6B, 7). Thus, the K₂O/Na₂O ratios are higher in the Montezuma granitoids (1.19<K₂O/Na₂O<1.68) than in the Corrego Tinguí Complex ones (0.69<K₂O/Na₂O<0.85). Montezuma granitoids are enriched in Fe₂O₃ (2.51–5.14 wt.%), MgO (0.9–3.44 wt.%), TiO₂ (0.37–0.86 wt.%) and P₂O₅ (0.10–0.36 wt.%) when compared to the Córrego Tinguí Complex rocks, where the concentration of these oxides varies of 1.34–1.58 wt.%, 0.35–0.53 wt.%, 0.17–0.22 wt.% and 0.03–0.06 wt.%, respectively (Table 1; Fig. 7). The Montezuma granitoids have relatively low Rb (average of 149 ppm) and high concentrations of Ba (2357–1271 ppm), Sr (1022–374 ppm), Zr (335–275 ppm), Th (22–64 ppm), Y (23–44 ppm) and V (90–20 ppm) than Córrego Tinguí samples (Table 1; Fig. 7).

There is a tendency for all granitoids to display a fractionated chondrite-normalized REE patterns, with enrichments in light rare earth elements (LREE) and depletion in heavy rare earth elements (HREE) (Fig. 8A). Some of the analyzed Montezuma granitoids samples (T7B, VM-82 and T2B) have variable Ce anomalies probably related to post-magmatic processes. Thus, to correct these values, we applied geometric interpolation from normalized REE values. The corrected values are indicated by asterisks in Table 2 and plotted as dashed lines in Fig. 8A. The (La/Yb)₅ ratios vary between 10 and 54 for the Montezuma granitoid samples. The Córrego Tinguí Complex samples are depleted in REE, having higher (La/Yb)₅ ratios (64–7; Table 1). Also, the Montezuma granitoids have higher ΣREE (up to 708 ppm), while the ΣREE for the Córrego Tinguí Complex samples are lower than 150 ppm. All samples record a negative Eu anomaly. However, it is noted that the less differentiated samples from the
Montezuma granitoids have higher Eu/Eu* ratios (~0.85) and only a slightly negative anomaly (Fig. 8A; Table 1).

Primitive mantle normalized incompatible trace element patterns for all samples are characterized by enrichment in large-ion lithophile elements (LILE) over the high field-strength elements (HFSE; Fig. 8B). Nb, Ta, P, and Ti troughs are a common feature (Fig. 8B). Ba troughs are observed for the more differentiated Montezuma samples and for the Córrego Tinguí granitoids (Fig. 8B).

4.3. Zircon U–Pb dating

A total of ninety-four analyzes were carried out in sixty-three zircon grains extracted from sample VM82 (UTM 766990/8317190). The zircons are translucent to opaque and vary from light to dark brown. These grains are euhedral to subhedral, prismatic, have high Th/U ratios (0.12–1.68) and vary in size from 50–100 µm (wide) to 100–400 µm (long). The CL images reveal different textural types of zircons (Fig. 9A). Most of the investigated crystals are single-growth-zone grains with clear oscillatory zoning or oscillatory-zoned zircons with an inherited core, typical of igneous origin. Sometimes, zircon grains are either euhedral with no obvious zoning or blurred in CL. Complex textures characterized by convoluted zones and bright irregular domains were also observed in some zircons. All the U-Pb results are presented in Supplementary Table 2.

The reported dates show a wide temporal variation, spreading along the Concordia between Rhyacian to Statherian ages. The zircons have $^{207}\text{Pb}/^{206}\text{Pb}$ dates ranging between 2359 ± 27 Ma and 1759 ± 20 Ma and comprise at least three distinct clustered populations with weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 2123.3 ± 9.8 Ma (upper intercept age at 2128 ± 11 Ma), 1972.2 ± 9.1 Ma and 1823 ± 15 Ma (Fig. 9A, B). In general, the dates between ca. 2.24 Ga and 1.95 Ga were obtained in zircons with oscillatory zoning pattern, although some zircons with convolute zoning and metamict texture also yield
these ages. For the $^{207}\text{Pb}/^{206}\text{Pb}$ ages below ca. 1.9 Ga, the zircon grains are structureless and blurred with lots of fractures and, sometimes, are related to inverse age zoning (i.e., younger cores than rims). Therefore, most of the young ages do not reflect the primary magmatic age but represent degrees of incomplete or complete resetting of older zircon grains.

4.4. Titanite U–Pb dating and Zr-in-titanite temperatures

Backscatter electron analysis of titanite grains reveals a majority of homogenous grains; sector zoning was only observed in a few crystals (Fig. 9C). Titanite grains from sample VM-82 are euhedral to sub angular and brownish in colour. Twenty-one grains were analyzed and fifteen yielded a concordia age of 2036 ± 8.7 Ma (after $^{204}\text{Pb}$ correction based on the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 2051 ± 13 Ma obtained from the uncorrected data; Fig. 9C). Three analyses are slightly discordant, with two of them defining a discordia that intercepts the concordia at 1789 ± 100 Ma (Fig. 9B).

The Zr-in-titanite temperatures were calculated using the method of Hayden et al. (2008). Although zircon and quartz are commonly observed to coexist with titanite in the analyzed samples, rutile does not coexist with titanite. Thus, the activation energy of TiO$_2$ ($\alpha$TiO$_2$) is lower than 1. Given the absence of P–T–t–x modelling for the Montezuma granitoids, we considered $\alpha$TiO$_2$ = 0.5 and pressure estimation of 1.0 GPa for all data. The obtained temperatures vary from 712 °C to 766 °C (average of 740 °C) for the 2036 Ma concordant titanite grains; for the discordant titanite on the ca. 1.8 Ga discordia line the temperatures are 703 °C and 492 °C.

4.5. Zircon Hf isotopes

Almost all the zircon domains that have the most concordant U-Pb ages were also measured for their Hf isotope compositions and the results are listed in Supplementary Table 4 (the calculation formula and the relevant constant used in calculations are
presented in the foot note of this table). The $\varepsilon_{\text{Hf}}(t)$ values were calculated using the zircon $^{207}$Pb/$^{206}$Pb ages. A summary of the Hf isotope results are show in Table 2.

The $^{176}$Hf/$^{177}$Hf$_{(t)}$ ratios for sample VM82 show a wide range from 0.281325 to 0.281785 (Fig. 10A). For the oldest zircons, showing dates between ca. 2.15 Ga and 2.05 Ga, the $^{176}$Hf/$^{177}$Hf$_{(t)}$ varies from 0.281325 to 0.281669 (Fig. 10A and Supplementary Table 4). The $\varepsilon_{\text{Hf}}(t)$ for this group of ages are dominantly positive, varying from 0 to +8.87, with only one sample giving a negative $\varepsilon_{\text{Hf}}(t)$ value ($\varepsilon_{\text{Hf}}(t) = -4.11$; Fig. 10B and Supplementary Table 4). As observed for the oldest zircons, a broad variation of the $^{176}$Hf/$^{177}$Hf$_{(t)}$, between 0.281443 and 0.281724 (Fig. 10A and Supplementary Table 4), is also typical for the ca. 2.04–1.9 Ga zircons; positive values of $\varepsilon_{\text{Hf}}(t)$ (+1.14 to +8.17) are also predominant, with four spots having negative $\varepsilon_{\text{Hf}}(t)$ values (−0.12 to −3.06; Fig. 10B and Supplementary Table 4). For the youngest zircons, with dates between ca. 1.86 Ga and 1.76 Ga, the $^{176}$Hf/$^{177}$Hf$_{(t)}$ is slightly higher and has a narrow range between 0.281638 and 0.281785, with $\varepsilon_{\text{Hf}}(t)$ varying from +0.45 to +5.48; Fig. 10 and Supplementary Table 4).

5. Discussion

5.1 - Assessment on the degree of weathering and element mobility

The presence of secondary chlorite, sericite, carbonate and epidote in the granitoid samples may indicate some degree of post-magmatic alteration or weathering. As show in chondrite-normalized REE diagram (Fig. 8A), Ce anomalies are also described for some of the analyzed samples, and may also be an indication of post-magmatic supergene processes (Cotton et al., 1993). To verify the degree of weathering of the Montezuma and Córrego Tinguí Complex granitoid rocks, we use the chemical index of alteration (CIA; molar $[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{CaO}^*+\text{Na}_2\text{O}+\text{K}_2\text{O})]$; Nesbitt and Young, 1982)
and the MFW diagram proposed by Ohta and Arai (2007). The CIA values vary between 49 and 53 (Table 1) and are within the range of fresh granitoids suggested by Nesbitt and Young (1982). The MFW diagram also indicates that these rocks experienced low degrees of weathering (considering a cut-off value of $W = 30\%$), since their position close to, or overlapping with, the igneous trend in the MFW diagram of Ohta and Arai (2007), suggests limited alteration and/or LILE (Large Ion Lithophile Elements) mobility (Supplementary Fig. 1).

5.2. **Age and isotopic constraints of the Montezuma granitoids**

Three main zircon age group populations between Rhyacian to Statherian were obtained for Montezuma granitoid sample VM-82 (Fig. 9). Group I comprise zircon grains with clearly igneous oscillatory zoning and ages ranging from 2.15 Ga to 2.05 Ga with a mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2.12 Ga. Most zircons from Group II are also characterized by igneous oscillatory zoning and have crystallization ages between 2.04 Ga and 1.9 Ga with weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1.97 Ga. Group III comprises the youngest group of zircons, averaging 1.82 Ga. These zircons are structureless and metamictization is commonplace. Aditionally, some of the grains have reverse core and rim ages, similar to those presented by Gerdes and Zeh (2009) and interpreted as fluid controlled zircon alteration.

Due to the spread of U-Pb ages in the Concordia diagram, the $^{176}\text{Hf}/^{177}\text{Hf}_{(t)}$ ratios were used to investigate coupling or decoupling between the U-Pb and Lu-Hf systems, i.e, if this range of U-Pb ages are related to multiple Pb-loss events (Gerdes and Zeh, 2009). As show in figure 10A, the three discrete groups of zircons have a distribution of $^{176}\text{Hf}/^{177}\text{Hf}_{(t)}$ ratios, although overlap between the groups exists, that is not expected for younger ages related to Pb-loss. Also, if the younger age defined by the Group II zircons were related to the process of lead-loss from the ca. 2.12 Ga Group I zircons, it...
would be expected a decrease in the Pb content from the older to the younger ages. However, as shown in Supplementary Fig. 2, the counts (CPS) of both $^{206}$Pb and $^{207}$Pb are similar or even higher for the younger group of zircon. Thus, it is unlikely that dates between 2.04 Ga and 1.9 Ga obtained for Group II zircons are related to some lead-loss that affected the ca. 2.12 Ga Group I zircons.

Reconciling the crystallization age of this rock with three sub to concordant distinct groups of ages is not a straightforward task. On the other hand, titanite is potentially a good candidate to clarify this issue. Firstly, the titanite from sample VM-82 seems to be igneous, being euhedral and texturally in equilibrium with the main mineralogical assemblage (quartz, feldspars and biotite; Fig. 4K–M). Second, the large size of the titanites (Fig. 4L, M), the absence of metamorphic reaction texture in thin sections with biotite or Fe-Ti oxides, and the presence of zircon inclusions (bright response in BSE image; Fig. 9C), plausibly suggests an igneous origin for such crystals. The large size of some titanites is consistent with then avoiding Pb-loss after interaction with fluids that altered the zircons at ca. 1.8 Ga. Moreover, two discordant titanites yield an intercept age similar to the youngest group of zircons (Fig. 9B). Also, there are no corroded borders or other textures in the titanite crystals indicative of an inherited origin for these grains. Thus, among such a complex group of ages for a single rock, the authors are inclined to suggest a crystallization age at approximately 2.03 Ga for this granitoid, given the Concordia age provided by titanite after common lead correction and the oldest zircon ages of Group II (Fig. 9A). Therefore, we interpret that the older group of zircons represent inherited contributions assimilated by the magma, and the younger group is related to later hydrothermal metasomatic alteration. Also, the main metamorphic event that affected the Montezuma granitoids are Neoproterozoic in age, since its foliations are subparallel to the Neoproterozoic tectonic fabric described in the
surrounding Proterozoic supracrustal sequences. Thus, if these titanites were related to
the metamorphic event that causes its deformation, we should expect ages of ca. 600-
500 Ma.

The inherited zircon grains from group I reflect an important contribution and/or
incorporation of a heterogeneous and dominantly juvenile Paleoproterozoic ancient
crust for the Montezuma granitoids magma (Fig. 10B). Combined with the juvenile Hf
signature of most of the Group I zircons, the lack of inherited Archean zircons and
average $T_{DM}$ ages at 2.27 Ga within the Montezuma VM-82 sample is a contrasting
feature, since its surrounding Paleoproterozoic granitoids of the WBMA have a
considerable Archean contribution indicated by the presence of inherited grains and
whole-rock Sm-Nd signatures (Figs. 2, 3; Cruz et al., 2016; Silva et al., 2016 and
references there in). Therefore, it is unlikely that these grains were captured from the
WBMA continental crust. Possible sources for these inherited zircons are the ca. 2.17 to
2.10 juvenile granitoids from the Mineiro belt (eg. Barbosa et al., 2015; Moreira et al.,
2018) or the ca. 2.15 Ga and 2.08 Ga Juiz de Fora/Pocrane complexes rocks (Degler et
al., 2018), southern São Francisco paleocontinent (Fig. 1), which have the same range
of ages and similar Hf isotopic signature (Fig. 10). Despite that, the heterogeneous ($\varepsilon_{Hf}$
of +8.14 to –3.06) but dominantly juvenile signature of group II zircons (Fig. 12B),
interpreted as the crystallization age of the Montezuma granitoids, points to a mixed
source with some degree of mantle input, since their $\varepsilon_{Hf}(t)$ can be as high as the
inherited zircons. If its source was only related to melting of a relatively homogeneous
ancient crust, it would be expected to yield lower and less variable $\varepsilon_{Hf}(t)$ values, and not
within the same range as observed. The crystallization age estimated for the Montezuma
granitoids coincides with the timing of major late- to post-collisional magmatism and
orogenic collapse that was followed by a period of slow cooling and final stabilization
of the São Francisco paleocontinent continental mass at ca. 1.9 Ga (Heilbron et al., 2010; Cruz et al., 2016; Silva et al., 2016; Aguilar et al., 2017).

In the São Francisco paleocontinent, similar ages to the group III zircons are related to the Espinhaço rift related Statherian (ca. 1.75 Ga) A-type granitoids (Borrachudos Suite and Lagoa Real Complex; Dussin, 1994; Fernandes et al., 1994; Silva et al., 1995; Chemale et al., 1997; Dussin et al., 1997; Silva et al. 2002; Lobato et al., 2015; Figs. 1, 2), as well as some mafic to acid volcanic rocks associated with the Espinhaço rifting basal units (Danderfer et al, 2009; Danderfer et al., 2015; Costa et al., 2017; Moreira, 2017; Fig. 3). This rifting event affected almost the entire eastern part of the São Francisco paleocontinent and disturbed the isotopic record of Group III zircons, causing isotopic re-setting and inverse age zoning. The imprints of this rifting event on zircons from Paleoproterozoic granitoids was also noticed by Degler et al. (2018) for juvenile rocks of the Juiz de Fora/Pocrane complexes.

**5.3. Classification of the Montezuma granitoids**

Granitoid rocks are commonly classified according to their affinity to I, S, M and A-types. These classifications are mainly based on the mineralogical and geochemical characteristics of the granitoid rock, and may further be linked to the nature of source rocks or to the tectonic setting (Pitcher, 1997).

The lithochemical composition of the Montezuma granitoids show that these rocks are slightly peraluminous to metaluminous and characterized by moderate to high concentrations of some major oxides (MgO, CaO, K₂O, TiO₂ and P₂O₅), with relatively high Mg# (35–55), for values of SiO₂ ranging of ca. 61–70 wt.%. Moreover, they are enriched in LILEs (Ba and Sr that reaches concentrations higher than 1000 ppm), as well as in REE and in some of the transition elements (Zr, Y and V). Although the Montezuma granitoids share some similar features with A-type granitoids, such as the
K₂O, Zr, Nb and Ce concentrations, their low SiO₂ and 10,000×Ga/Al ratios (<2.6), as well as their magnesian affinity, contrasts with the typical A-type signature (Figs. 6F, 11A, B; Whalen et al., 1987; Frost et al., 2001).

Regarded as a distinct group of granitic rocks, Tarney and Jones (1994) proposed the high Ba-Sr granitoid group, which is characterized by unusual trace element contents, as high K/Rb, Ba (>500 ppm), Sr (>300 ppm; Ba+Sr >1500 ppm) and light REEs; relatively low Rb/Sr ratios, Nb, Ta and heavy REEs. As previously described, the chemical signature obtained for the Montezuma granitoids, such as its high Ba, Sr and LREE contents along with low abundance of HREE and its (La/Yb)_N (18.07–53.76) and Sr/Y (22–35) ratios, are similar to the high Ba-Sr granitoids (Tarney and Jones, 1994; Fowler et al., 2008; Fig. 11C). The Montezuma granitoids have a shoshonitic affinity (Fig. 6B, C) and share characteristics (e.g. their relatively high K₂O/Na₂O ratios and high P₂O₅, ΣREE and LREE/HREE ratios, Ba, Sr, and Zr) of late- to post-collisional shoshonitic type granitoids (Jiang et al., 2002; Goswami and Bhattacharyya, 2014; Clemens et al., 2017). Thus, the Montezuma granitoids can be classified as high Ba-Sr shoshonitic granitoid. Some chemical characteristics of the Montezuma granitoids resemble the signature of Archean granitoids from the sanukitoid series (Laurent et al. 2014), a characteristic also presented by other shoshonitic granitoids (Fig. 11E; Goswami and Bhattacharyya, 2014; Clemens et al., 2017). However, despite the relatively high Mg#, the high K₂O and K₂O/Na₂O ratios, togheter with the lack of Ni and Cr analyses in this study, make it difficult to classify these rocks as typical sanukitoid-like granitoids.

High Ba–Sr and shoshonitic granitoids can be formed by similar processes (e.g. Tarney and Jones, 1994; Fowler et al., 2008; Goswami and Bhattacharyya, 2014; Clemens et al., 2017). According to Tarney and Jones (1994), the generation of high Ba–Sr
granitoids can be related to partial melting of subducted ocean islands or ocean plateaus; partial melting of underplated mafic rocks; or partial melting of lithospheric mantle that had been metasomatized by asthenosphere-derived carbonatitic melts. Some authors attributed their origin to the partial melting of the mafic lower crust (with residual garnet) (Ye et al., 2008; Choi et al., 2009) or to AFC products of mantle-derived appinitic magmas (Fowler et al., 2001, 2008). For the shoshonitic type granitoids, Jiang et al. (2002) proposed two different mechanisms of generation: involvement of subducted oceanic crust sediments into the mantle source; or partial melting of subducted oceanic crust sediments or metasediments of the thickened continental lower crust in the process of late-orogenic slab break-off or lithospheric thinning. According to Jiang et al. (2006), Jiang et al. (2012), Goswami and Bhattacharyya (2014) and Clemens et al. (2017), partial melting of an enriched lithospheric mantle, metasomatized by slab-derived fluids or hybridized by continental slab-derived melts could explain the signature of some shoshonitic type granitoids. Partial melting of a lower crustal incompatible-element enriched amphibolite source is also proposed for the generation of shoshonitic granitoids (Bitencourt and Nardi, 2004). So, although the origin of both high Ba–Sr and shoshonitic granitoids are not well constrained, and there is a lot of discussion about their genesis, they are believed to be related to a late to post-collisional tectonic setting.

The São Francisco paleocontinent was in a late- to post-collisional setting during the early Orosirian, precluding a source related to partial melting of subducted ocean islands or plateaus. Also, the Montezuma granitoids have low Sr/Y (Fig. 11D), which also precludes any relation to adakite-like granitoids generated by the partial melting of thickened lower crust.
The lack of field evidence of the interaction between basic and acid granitic magmas (e.g. evidence of magma mingling and mafic enclaves) within the Montezuma granitoids coupled with the abundance of inherited zircon grains may suggest granitic melts extracted from juvenile crustal sources only. However, the Mg# values of the Montezuma granitoids reaches values of 55, which are relatively higher than those expected for a mafic lower crustal source (Rapp and Watson, 1995; Rapp et al., 1999).

The high Mg# coupled with a juvenile εHf isotopic signature indicate that the primary magma of the Montezuma granitoids are at least partly derived from, or interacted with, a mantle source. In addition, a mantle-crust mixed magmatic source is also indicated by its biotite compositions (Fig. 5D), which are consistent with the interpretation of a mantle-crust mixed origin. In this case, the enrichment in incompatible elements may indicate either some crustal contamination during or after the magma emplacement or that its source was already enriched, metasomatized by fluids or melts during previous subduction events. The process of crustal contamination does not seem to be a controlling factor, since the concentration in incompatible elements of the less differentiated Montezuma granitoids are higher than its host rocks. Thus, it is more reasonable to interpret that its source was already enriched in those elements.

The alkali-calcic to alkalic, high-K to shoshonitic affinities of the Montezuma granitoids preclude that they are classical arc magmas. The main geochemical features of the Montezuma granitoids are similar to late- to post-collisional suites affected by prior subduction events with later metasomatism of the lithospheric mantle. The late- to post-collisional nature of these rocks is supported by the tectonic discrimination diagram of Pearce et al. (1984) (Fig. 11F).

The ratios between fluid/melt-mobile and fluid/melt-immobile trace elements can be used to evaluate the importance of subduction fluids (enrichment in Ba, Sr and Nb, for
example) and/or sediment melts (enrichment in Th and LREE) in the metasomatism of its source. The low Th/Nb ratios of the Montezuma granitoids point to a contribution from slab-derived fluids (Fig. 12A). However, Nebel et al. (2007) proposed that fluid-dominated arc environments have low Th/Yb ratios (commonly <1), whereas arc settings dominated by subducted sediments have high Th/Yb ratios. The Montezuma granitoids have high Th/Yb ratios (8.34–11.59), indicative of a significant contribution from sediments in its metasomatized source (Fig. 12B). The role of sediment melt in its source is also highlighted by the relatively high La/Sm ratio and low Ba/Th ratio (Labanieh et al., 2012; Fig. 12C). In this case, due to the dominantly juvenile signature of the Montezuma granitoids, the time between source metasomatism and extraction has to be relatively short.

As discussed above, the lack of Archean inheritances, together with Hf model ages below ca. 2.5 Ga (with the exception of one zircon grain for which the its Hf model age is 2.69 Ga) and its dominantly juvenile signature strongly suggest that the source of the Montezuma granitoids were generated without contribution from the Archean continental margin of the São Francisco paleocontinent, possibly related to an intra-oceanic setting. The Hf model ages obtained for the inherited zircons are within the range to those obtained for the 2.35 Ga TTG’s and 2.13 Ga sanukitoids from the Mineiro belt (Moreira et al., 2018) as well as for the 2.20–1.97 Ga intra-oceanic Juiz de Fora/Pocrane complexes (Heilbron et al., 2010 and Degler et al., 2018). However, the Montezuma rocks plot within the continental arc field in the Th/Yb vs. Nb/Yb diagram (after Condie and Kröner, 2013; Fig. 12D). Some authors argue that oceanic arcs can evolve to continental arcs when they are accreted to a continental margin (ex. Draut et al., 2009; Condie and Kröner, 2013; Cioffi et al., 2016). In this case, the accreted oceanic arc becomes thicker and starts to melt its roots, generating granitoids with a
continental arc-like signature (Draut et al., 2009; Condie and Kröner, 2013; Cioffi et al., 2016). Therefore, we suggest here that the Montezuma granitoids were a delayed response to a delamination process resulting from the interaction of a subcontinental mantle wedge and the roots of an accreted island arc, possible associated with a late-orogenic slab break-off or lithospheric thinning tectonic setting that was followed by the cratonization of the São Francisco paleocontinent. Alternatively, due to the complex U-Pb zircon and titanite results, these rocks could also represent a shoshonitic association related to a Paleoproterozoic mature arc. In this case, its crystallization age would have to be represented by the ca. 2.12 Ga Group 1 zircons, being the youger Group II zircon and the titanite dates related to a younger overprinting event. However, as presented above, our U-Pb data do not favor this interpretation, although, chemically, it is also a valid hypothesis.

The more differentiated samples from the Montezuma granitoids (samples T2B, T2C and T2A) were probably derived from fractional crystallization of the less differentiated Montezuma granitoids, mainly controlled by feldspar, biotite, apatite and Fe-Ti oxides fractionation (more pronounced Eu anomalies, enrichment in Rb and Ba and Sr troughs; negative correlation of major and trace elements; Figs. 7, 8). Also, its lower Mg#, relatively higher A/CNK and biotite chemical signature are more crustal like, pointing to a minor participation of the mantle and, perhaps, contribution of sediments in the evolution of these samples.

An alternative explanation for the abundant inherited zircons, the heterogeneous $\varepsilon$Hf and the relatively high concentrations in Th within the Montezuma granitoids is that these grains are linked to subducted sediments (mélanges) created by the erosion of a juvenile intra-oceanic arc that were first recycled by the slab-derived melts into the
mantle wedge above the subducting slab and then extracted by the Montezuma source melt (e.g.: Jiang et al., 2012; Marschall and Schumacher, 2012; Cruz-Uribe et al., 2018).

5.4 - Classification of the Córrego Tinguí Complex granitoids

The Córrego Tinguí Complex rocks chemically correspond to a magnesian, slightly peraluminous, calc-alkaline, medium- to high-K acid–silicic series and resemble a volcanic arc-like signature (Figs. 6, 11F). Although the occurrence of a small amount of muscovite and its slightly peraluminous signature resembles S-type granites, its relatively high Na$_2$O and low K$_2$O/Na$_2$O ratios (0.69–0.85) and the absence of other Al-rich minerals (such as cordierite and/or garnet) are more akin to an I-type signature. These rocks plot in the hybrid granites field in the Laurent et al. (2014) ternary classification diagram, where TTG field overlaps the biotite-two-mica granites field (Figure 11E). Indeed, the Córrego Tinguí granitoids share some characteristics with Archean TTG, such as: calc-alkaline, slightly peraluminous, silica-rich signature; low contents of ferro-magnesian oxides (FeO$^T$ + MgO + MnO + TiO$_2$ ~2 wt.%), Y (< 5.3 ppm), Yb (~0.3 ppm), HFSE and low K$_2$O/Na$_2$O ratios; and its fractionated REE pattern (64 ≤ (La/Yb)$_N$ ≤ 97) and relatively high Sr/Y ratios (26–35). Although their Sr/Y ratios resembles some TTGs, the Sr concentration (140–170 ppm) is too low compared to typical TTGs (usually higher than 300 ppm; Martin et al., 2005; Laurent et al., 2014). Thus, we interpret that the Córrego Tinguí rocks may represent syn-to-late collisional volcanic arc magmatism originated from the partial melting of ancient TTG-like rocks from the Gavião nuclei. Also, its biotite composition is suggestive of collisional crustal source magma (Fig. 5D, E). It is possible that these rocks resembles to the sample dated by Silva et al. (2016) at 2140 ± 14 Ma, being in this case related to a collisional setting within the São Francisco paleocontinent. Also, its chemical signature indicates the reworking of ancient basement rocks, pointing to a similar isotopic composition to the
obtained by Silva et al. (2016), in which negative $\varepsilon_{\text{Hf}}$ value of –6.85, coupled with a 
depleted mantle model age of 3.31 Ga, could be related to the reworking of Archean 
TTG’s from the Porteirinha Complex. However, for further constraints on the evolution 
of the Córrego Tingúí Complex granitoids new isotopic studies are required.

5.5. Implications for the Paleoproterozoic evolution of the eastern São Francisco 
paleocontinent

The Siderian to Orosirian accretionary to collisional tectonic evolution of the eastern 
São Francisco paleocontinent is well constrained in its northern and southern domains 
(Fig. 1; Alkmim and Teixeira, 2017; Barbosa and Barbosa, 2017; Heilbron et al., 2017; 
Teixeira et al., 2017). In its southern domain at least three magmatic arcs were 
developed and/or accreted to the former Archean São Francisco paleocontinent (Fig. 1): 
the ca. 2.35–2.1 Ga Minas orogeny (Mineiro belt) that is composed of a set of 
individual juvenile and continental arc systems, each one comprising metaigneous rocks 
and associated supracrustal sequences (Ávila et al., 2010, 2014; Seixas et al., 2012, 
2013; Barbosa et al., 2015; Teixeira et al., 2015; Moreira et al., 2018); the ca. 2.20-2.05 
Ga Mantiqueira Complex, which represents a continental magmatic arc with significant 
Achaean crustal inheritance (Silva et al., 2002; Noce et al., 2007; Heilbron et al., 2010); 
the ca. 2.20–1.95 Ga, dominantly juvenile, Juiz de Fora/Pocrane intra-oceanic arc 
(Heilbron et al., 2010; Novo, 2013; Degler et al., 2018). In the northern domain, which 
encompasses the granitoids described in this work, most of the Paleoproterozoic 
collisional to post-collisional magmatic rocks resemble an active continental arc, defined 
by Cruz et al (2016) as the WBMA (Fig. 2), although the authors suggests the 
possibility of a juvenile source mixed with Archean crust at ca. 2.0 Ga. Due to its 
similarities to the Mantiqueira arc, Cruz et al. (2016) proposed that both the WBMA 
and Mantiqueira arcs, based on their isotopic signatures and Archean inheritance,
represents a single continental magmatic arc developed at the eastern boundary of the São Francisco paleocontinent. On the other hand, these authors also have suggested the presence of a Rhyacian juvenile accretion episode within the WBMA, based on less negative $\varepsilon$Nd signature of some late- to post-collisional granitoids, which allowed them to bring up the possibility of a linkage with the Mineiro belt granitoids.

The results obtained in this work, added to the isotopic results of Silva et al. (2016), show that the Córrego Tinguí granitoids are akin to the WBMA and Mantiqueira arcs, representing a continental-like signature whose source is related to the reworking of ancient Archean crust. However, as an exception of previous studies developed in this area, the ca. 2.13 Ga zircon inherited ages from the Montezuma granitoids record an important event of juvenile magmatism. The data obtained here suggest that the Montezuma granitoids source was originated at distance from the Archean São Francisco paleocontinent margin, probably in an intra-oceanic setting, since no Archean inheritance was observed. As discussed above, all these features likely suggest the juvenile rocks from the Mineiro belt or Juiz de Fora/Pocrane complexes as a potential source.

Hereby, the Montezuma granitoids are interpreted as a consequence of post-collisional delamination of subducting lithosphere, inducing asthenospheric upwelling that caused partial melting and interacted with a juvenile lower crust, represented by the roots of an island arc that might be represented either by the juvenile rocks from the Mineiro belt or the Juiz de Fora/Pocrane arc. Consequently, the interaction of these magmas resulted in the intermediate to acid magma of the Montezuma granitoids.

Shoshonitic granitoids of almost similar age (ca. 2.05 Ga) and similar nature (high-K, Mg#, Ba and Sr) are common to the west of the Montezuma granitoids, within the western Gavião and Itacambira-Monte Azul nuclei (e.g., Paciencia and Guanambi...
suites; Fig. 2). These rocks are also related to a late- to post-collisional tectonic system associated with the partial melting of metasomatized lithospheric mantle due to delamination of subducting lithosphere (Rosa et al., 1996; Rosa, 1999; Bersan et al., 2018). However, despite the similarities between these rocks and the Montezuma granitoids, they show an evolved isotopic signature, with negative $\varepsilon_{\text{Hf}}$ (–10.88 to –7.5; Rosa, 1999; Silva et al., 2016) and $\varepsilon_{\text{Hf}}$ (–16.8 to –18.5). Consequently, even with a similar tectonic situation, the contrasting isotopic signature points to a complex scenario involving two different sources for the setting of these Paleoproterozoic shoshonitic high Ba-Sr granitoids. Thus, we envisage the process of double subduction zones with the same polarity as proposed by Noce et al. (2007) for the southern São Francisco paleocontinent, similar to the geodynamic model proposed by Eglinger et al. (2018) for post-collisional potassic magmatism with contrasting isotopic source within the West African craton (Guinea), for the evolution of the studied post-collisional granitoids (Fig. 13). We also consider, as already stated by Mascarenhas (1979) and Barbosa et al. (2013), that the Gavião nuclei is characterized by distinct Archean paleoplates (Guanambi-Correntina block to the west, and Gavião block to the east) that collided together during the early stages of the Siderian–Orosirian accretionary to collisional tectonic evolution. In the proposed model, the sources from which the Montezuma granitoid magmas have been extracted were enriched by juvenile subducted sediments (with some participation of fluids) derived from an island arc (similar to the Mineiro belt or Juiz de Fora/Pocrane complexes), whereas the Paciencia and Guanambi suite sources were enriched with participation of Archean components from a continental arc developed at eastern margin of the São Francisco paleocontinent (Fig. 13A). This accretionary to convergent context occurred between ca. 2.35 Ga and 2.08 Ga (Cruz et al., 2016; Barbosa and Barbosa, 2017; Heilbron et al., 2017). By this time, the collision
between the intra-oceanic arc-like and the continental arc may have thickened the lithosphere along the margin of the São Francisco paleocontinent. The Corrego Tingui Complex granitoids would have been generated during this collisional event. From ca. 2.08 Ga to ca. 1.9 Ga, a late- to post-collisional regime started to operate, and the processes of slab break-off and lithospheric delamination triggered the partial melting of lithospheric mantle and the roots of the ancient crust to produce the potassic magmas (Fig. 13B). However, the connections and relations between the WBMA and the juvenile sector of the Montezuma granitoids deserves further study in order to better constrain the tectonic evolution of the São Francisco paleocontinent. Another question still to be answered is how this predominantly Paleoproterozoic juvenile segment may be surrounded by the Archean Gavião nuclei (Fig. 2).

6. Conclusions

Our focused study of the Montezuma granitoids and its host rocks, the Corrego Tingui Complex, situated in the northeastern part of the São Francisco paleocontinent provides new, significant insights for the post-collisional magmatism in this tectonic domain. Some of the most salient conclusions of this study are as follows:

(i) The Montezuma zircon U-Pb dates spread along the Concordia from ca. 2.2 Ga to ca. 1.8 Ga and can be divided into three different groups: Group I zircons are interpreted as inherited and have a mean $^{207}\text{Pb}^{206}\text{Pb}$ age of 2.12 Ga; Group II zircon ages vary from 2.04 Ga to 1.9 Ga and the oldest zircon grains from this group, with mean $^{207}\text{Pb}^{206}\text{Pb}$ age of 2026 Ma, are interpreted as the crystallization age of the Montezuma granitoids; Group III comprises the youngest group of zircons, averaging of 1.82 Ga, and are interpreted as fluid controlled zircon alteration related to the Espinhaco rifting event that affected the eastern border of the São Francisco paleocontinent.
Titanite dates constrain the Montezuma granitoids crystallization age at 2.036 Ga.

Magmas of the Montezuma granitoids are enriched in LREEs and LILEs, depleted in HFSE, with high to moderate Mg# and dominantly positive $\varepsilon_{\text{Hf}}(t)$ values without Archean zircon inheritance. These geochemical and isotopic signatures allow its classification as a hybrid post-collisional high Ba-Sr shoshonitic granitoid related to the process of subducting lithosphere delamination followed by asthenospheric upwelling that caused partial melting of the roots of an accreted juvenile intra-oceanic arc.

The Córrego Tinguí Complex is akin to syn- to late-collisional volcanic arc magmatism originated from the partial melting of ancient TTG-like crustal rocks.

The Montezuma granitoids, together with other post-collisional high Ba-Sr shoshonitic rocks that occur in to the west of the study area reveal a complex scenario involving two contrasting isotopic sources for the setting of these Paleoproterozoic granitoids.

Acknowledgements

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Figure captions:

Figure 1 – (A) Geotectonic contextualization of the São Francisco craton in the context of western Gondwana, highlighting the main Archaean nuclei (modified from Alkmim et al. 2006). (B) Simplified geological map of the São Francisco craton and Araquã orogen highlighting the Archaean and Paleoproterozoic assemblage referred as the São Francisco paleocontinent (modified from Cruz et al., 2016; Silva et al., 2016; Bersan et al., 2018). Archaean nuclei: 1 – Quadrilátero Ferrífero area; 2 – Gavião; 3 – Jequié; 4 – Serrinha; 5 – Itacambira-Monte Azul; 6 – Guanhães. Paleoproterozoic arcs: a – Mineiro belt (Minas orogeny); b – Mantiqueira Complex; c – Juiz de Fora Complex; d – Pocrane Complex; e – Western Bahia Magmatic Arc.

Figure 2 – Simplified geological map of the Itacambira-Monte Azul Block and southwestern Gavião nuclei (modified from Cruz et al., 2016 and Silva et al., 2016).

Figure 3 – Geological map of the study area (after Costa and Danderfer, 2017) with samples location.

Figure 4 – Field aspects and photomicrographs showing textures and mineralogy of the Córrego Tingui Complex granitoids (A–C) and Montezuma granitoids (D–O). (A) Field aspec of the samples T1A to T1C location. (B and C) Photomicrographs from granodiorites with anhedral plagioclase associated with quartz, biotite and wite-mica. Note that most of the plagioclase crystals are sericitized. (D and E) Highly foliated Montezuma granitoids with proto- to mylonitic texture. (F) Photomicrograph from sample T7A showing that the foliation is marked by the align of Biotite crystals, with K-feldspars and microcline being the main porfiroblasts. Quartz and plagioclase occur as small anhedral grains. (G and E) Field and thin-section aspect of the unfoliated granodioritic sample T3B, with secondary epidote associated with biotite. (I and J) Slighty foliated outcrops from samples T5 and VM-82 respectively. (K) Thin-section from sample VM-82 showing larger crystals of alkali-feldspars and plagioclase with quartz and biotite constituting a fine grained matrix for these monzogranites. Note in the center of the image the presence of a euhedral titanite. In (L and M), note the large
euhedral to subhedral titanite crystals within the main mineralogy of sample VM-82. Note that these grains have no inclusions of Fe-Ti oxides. (N and O) Outcrop and thin-section aspect of a quartz-monzonite from sample T2B. In (O), epidote occurs associated with biotite and most of the plagioclase shows a cloud aspect due to sericitization. Qtz – quartz; Mc – microcline; Kfs – K-feldspar; Pl – plagioclase; Bt – biotite; Wm – witticite; Ttn – titanite; Ep – Epidote.

Figure 5 – Plots of mineral chemistry for feldspars (A), Biotite (B–E) and muscovite (F). See text for further explanations and references.

Figure 6 – Geochemical classification diagrams for Montezuma and Córrego Tinguí Complex granitoids (references in the text).

Figure 7 – Harker diagram for the Montezuma and Córrego Tinguí Complex granitoids.

Figure 8 – (A) Chondrite-normalized REE patterns. (B) Primitive mantle-normalized trace element spider diagram. Normalizing values for chondrite and primitive mantle are from Boynton (1984) and McDonough and Sun (1995), respectively.

Figure 9 – (A) Representative zircons CL images and $^{207}$Pb/$^{206}$Pb weighted mean ages from sample VM-82. Note the complex structures and the inverse zoning in the ca. 1.8 Ga zircons. (B) Concordia diagram for LA-ICP-MS zircon and titanite U-Pb dating from sample VM-82. (C) Representative BSE-SEM images and Concordia age diagram of the analyzed titanite.

Figure 10 – Hf isotope data for zircons from sample VM-82. (A) $^{176}$Hf/$^{177}$Hf$_{(t)}$ vs. apparent $^{207}$Pb/$^{206}$Pb date illustrating the three groups of zircon populations identified. (B) Plot of $\varepsilon_{Hf}(t)$ vs. U-Pb ages.

Figure 11 – Tectonic and geochemical discriminant diagrams from Montezuma and Córrego Tinguí Complex granitoids. (A and B) I, S and A-type granitoids diagram proposed by Whalen et al. (1987). (C) High Ba-Sr granitoids discrimination diagram after Tarney and Jones (1994). (D) Sr/Y vs. Y diagram after Drummond and Defants (1990). (E) Ternary classification diagram from Laurent et al. (2014). (F) Rb vs. Y+Nb diagram of Pearce et al. (1984); the post-collisional field is from Pearce (1996).

Figure 12 – (A–C) Ratios between fluid/melt-mobile and fluid/melt-immobile trace elements can be used to evaluate the importance of subduction fluids and/or sediment melts in the source metasomatism. Fields in (B) are after Laurent et al. (2011). (D) Pearce and Peate (1995) Th/Yb vs. Nb/Yb diagram with the boundary between felsic igneous rocks from oceanic and continental arcs from Condie and Kröner (2013).

Figure 13 – Schematic model for the evolution of magmatism and the generation of two contrasting groups of post-collisional shoshonitic high Ba-Sr granitoids within the northeastern sector of the São Francisco paleocontinent. See text for discussions. (A) Pre- to sin-collisional stage with two subduction zones with the same polarity being responsible for the contrasting nature of mantle metasomatism between the eastern and western sectors. (B) Post-collisional stage, where the processes of slab break-off and lithospheric delamination triggered the partial melting of the previously metasomitized lithospheric mantle. CC – Continental crust; OC – Oceanic crust; JC – Juvenile crust; SCLM – Subcontinental lithospheric mantle.
Supplementary files captions:


Supplementary figure 2 – Diagram of $^{207}$Pb/$^{206}$Pb age versus $^{207}$Pb and $^{206}$Pb counts per second.

Supplementary figure 3 – Scanned thin-sections described in this study.

Supplementary table 1 – Mineral chemistry data.

Supplementary table 2 – Zircon LA-ICPMS U-Pb isotopic data.

Supplementary table 3 – Titanite LA-ICPMS U-Pb isotopic and trace elements data.

Supplementary table 4 – Zircon Lu-Hf isotopic data.
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<td>(^{207}\text{Pb}/^{206}\text{Pb} \text{ age (Ga)})</td>
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<td>III - re-setting ages with inverse zoning</td>
<td>1.90–1.76</td>
<td>0.2816376–0.2817849</td>
<td>+0.46 to +5.48</td>
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This study:
- Zircons with $^{206}\text{Pb}^{207}\text{Pb}$ ages between ca. 2.15 Ga and 2.05 Ga
- Zircons with $^{206}\text{Pb}^{207}\text{Pb}$ ages between ca. 2.04 Ga and 1.9 Ga
- Zircons with $^{206}\text{Pb}^{207}\text{Pb}$ ages below ca. 1.9 Ga
- Filled circles - zircons with oscillatory zoning
- × Pocrame complex granitoids from Degler et al. (2018)
- × Juiz de Fora complex granitoids from Degler et al. (2018)
- △ Mineiro belt: Resende Costa orthogneiss from Teixeira et al. (2015)
- △ Mineiro Belt: Lagoa Dourada TTG's and Alto Maranhão sanukitoid from Moreira et al. (2018)
- △ Mineiro belt: Metagranitoids from Barbosa et al. (2015)
2.36 Ga to 2.09 Ga accretionary to collisional stage

Continental arc (with Archaean inheritance)

Juvenile intra-oceanic arc

Juiz de Fora/Pocrane complexes or Mineiro belt?

Western Gavião nuclei (Guanambi-Correntina block)

SCLM metasomatism

Juvenile sediment input

2.08 Ga to 1.90 Ga late to post-collisional stage

Paciencia and Guanambi suites

Montezuma granitoids

Delamination

Astheno sphere inflow

Slab break-off

SCLM metasomatized by Archaean sediments

SCLM metasomatized by juvenile sediments
- Cârano Tingui Complex
- Montevideo granitoids
- Shoshonitic granitoids from Clemens et al. (2014)
- Shoshonitic granitoids from Goowami and Bhattacharyya (2014)
- ca. 1.75 Ga Bomachudos and Lagoa Real A-type granitoids
Group I zircons with $^{207}$Pb/$^{206}$Pb ages between ca. 2.25 Ga and 2.05 Ga
Group III zircons with $^{207}$Pb/$^{206}$Pb ages below ca. 1.9 Ga
Group II ircons with $^{206}$Pb/$^{238}$Pb ages between ca. 2.04 Ga and 1.9 Ga
Titanite dates
Three zircon populations were obtained for the Montezuma granitoid.
Titanite U-Pb age constrain the crystallization age of the Montezuma granitoid at ca. 2.03 Ga.
Late- to post-collisional shoshonitic high Ba-Sr granitoid in the northeastern São Francisco paleocontinent.
Lack of Archean inheritance and positive $\varepsilon_{Hf}(t)$ signature.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: