TONALITE-TRONDHJEMITE AND LEUCOGRANODIORITE-GRANITE SUITES FROM THE RIO MARIA DOMAIN, CARAJÁS PROVINCE, BRAZIL: IMPLICATIONS FOR DISCRIMINATION AND ORIGIN OF THE ARCHEAN Na-GRANITOIDS

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Abstract

The Mesoarchean Na-granitoids exposed in the Rio Maria domain, southeastern Amazonian craton, are represented by tonalite-trondhjemite and leucogranodiorite-granite suites. The 2.98–2.92 Ga tonalite-trondhjemites are the most voluminous rock type in the Rio Maria domain and host 2.86 Ga leucogranodiorite-granite plutons. These rocks share common geochemical characteristics, such as relatively high Al_2O_3 and Na_2O and low Yb and Y contents, as well as the behavior of the REE. However, based on an extensive geochemical data set, it is possible to show that the leucogranodiorite-granites have higher K₂O, Ba, Sr, and Rb and lower CaO contents than the tonalite-trondhjemites. The latter are compositionally similar to typical tonalite-trondhjemite-granodiorite (TTG) series and probably originated from partial melting of garnet amphibolites, derived from tholeiitic rocks or from metabasalts of the Identidade greenstone belt, at pressure conditions suitable to produce high, medium, and low La/Yb tonalite-trondhjemite groups. The leucogranodiorite-granite show geochemical affinity with the Transitional TTG of the Yilgarn craton and are related to the Hybrid granitoid group. The ambiguous geochemical character of the Rio Maria leucogranodiorite-granite suite, which shares some characteristics that are typical of the tonalite-trondhjemite rocks and others more commonly observed in the sanukitoid suites, may be related to complex processes involving TTG and sanukitoid magmas. The discrimination of these two Na-granitoid groups helps us estimate the true volume of TTG magmatism in the Rio Maria domain and in understanding the dynamics of petrogenetic processes in the terrane at the end of the Archean.

Keywords: Amazonian craton, Carajás province, Rio Maria domain, tonalite-trondhjemite, leucogranodioritegranites.

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INTRODUCTION

Tonalites and trondhjemites are the dominant granitoids in Archean terranes and key rocks in the development of Earth's early continental nuclei (Barker & Arth 1976). In early works granodiorites were also included in this group, which led to the TTG-suite terminology (Jahn et al. 1981; also called TTD, tonalite-trondhjemite-dacite, by some workers). Granodiorite-granite associations are also a widespread voluminous constituent of Archean cratons. Tonalite-trondhjemite-granodiorites, however, are better known and are the oldest felsic components of cratons, forming the gneissic basement of preserved Archean continental crust (Barker & Arth 1976, Barker 1979, Kröner et al. 2000, Martin et al. 2005, Moyen et al. 2007, Champion & Smithies 2007, Almeida et al. 2011, Moyen & Martin 2012, Laurent et al. 2013, 2014). The Archean granites were typically emplaced in the late stages of many Archean crustal evolution cycles, but not all potassic granites are Neoarchean (Champion & Smithies 2007, Almeida et al. 2010, 2013).

Increasing knowledge of Archean granites has led to the identification of important geochemical contrasts among these rocks, which can be calc-alkaline, alkaline, or even strongly peraluminous (Day & Weiblen 1986, Bourne & L'Heureux 1991, Sylvester 1994, Champion & Sheraton 1997, Frost *et al.* 1998, Champion & Smithies 2001, Moyen *et al.* 2003, Laurent *et al.* 2014). Such diversity suggests that they were produced by contrasting petrogenetic processes in various geodynamic settings (Moyen *et al.* 2003, Laurent *et al.* 2014).

A new Archean granite group has only recently been introduced into the literature (Champion & Smithies 2007, Almeida et al. 2010, 2013, Laurent et al. 2014). These rocks share some geochemical characteristics with typical Archean TTG suites and are composed of leucogranodiorites and leucomonzogranites with high (La/Yb)_N ratios and no significant negative Eu anomaly. However, when compared to TTGs sensu stricto, they have higher LILE contents, show strong enrichment in K₂O and Rb, with increasing differentiation, and tend toward more siliceous compositions (68-77% SiO2; Champion & Smithies 2001, 2003). These rocks are widespread in many Archean terranes and are either contemporaneous (e.g., GG suites of the Wyoming Province; Frost et al. 2006) or postdate (e.g., 2.61 Ga granites of the western Dharwar craton, Jayananda et al. 2006; Pilbara craton, Champion & Smithies 2007; North China craton, Yang et al. 2008; Kaapvaal craton, Laurent et al. 2013; Amazonian craton, Almeida et al. 2010, 2013) true TTGs. The term "transitional TTGs"

was proposed to describe a group of granites initially identified in the Pilbara and Yilgarn cratons (Champion & Smithies 2001, 2003). More recently, Laurent *et al.* (2014) defined these rocks as belonging to a Hybrid granitoid group, which are formed through interaction (*e.g.*, metasomatism, mingling, or mixing) between magmas or sources related to TTG, sanukitoid, or granitic rocks.

Tonalite-trondhjemite (granodiorites are extremely rare) and leucogranodiorite-granite suites have been identified in the Archean Rio Maria domain in the southern part of the Carajás province, the largest Archean domain of the Amazonian craton (Leite 2001, Dall'Agnol et al. 2006, Vasquez et al. 2008, Almeida et al. 2010, 2011). These rocks were not affected by earlier events and generally preserve their original igneous structures and textures (Althoff et al. 2000, Leite 2001, Souza et al. 2001, Guimarães et al. 2010, Almeida et al. 2010, 2011, 2013). Therefore, it is possible to study in detail their primary magmatic compositions and the petrogenesis of their magmas. In this paper, we propose ways to discriminate between the Rio Maria leucogranodiorite-granite and TTG suites and compare them with analogous granitoids from other Archean cratons.

GEOLOGICAL SETTING

The Rio Maria domain is located in the southern part of Carajás province (DOCEGEO 1988, Dall'Agnol *et al.* 2006, Vasquez *et al.* 2008), the largest Archean province of the Amazonian craton identified so far (Fig. 1a). It was included in the Central Amazonian province by Tassinari & Macambira (2004) and is considered an independent tectonic province (Santos 2003).

Based on the age and nature of the supracrustal sequences, age of the magmatic and deformational events, nature of the granitoid series, and tectonic setting, the Carajás province has been divided into two Archean tectonic domains: (1) the Mesoarchean (3.0-2.86 Ga) Rio Maria domain and (2) the Neoarchean Carajás domain, composed mostly of 2.76-2.55 Ga metavolcanic rocks, banded iron formations, and granitoids (Machado et al. 1991, Macambira & Lafon 1995, Barros et al. 2001, Dall'Agnol et al. 2006). Feio (2012) proposed that the northern part of the Carajás domain corresponds to the Neoarchean Carajás basin and defined the Transition sub-domain in its southern part. The cratonization of both the Rio Maria and Carajás domains occurred at the end of the Archean and they were later affected by intrusions of Paleoproterozoic A-type granites (Dall'Agnol et al. 2005).



FIG. 1. (a) Location of the studied area in the Amazonian craton; (b) geological map of the Rio Maria domain.

Although tonalite-trondhjemite and leucogranodiorite-granite associations have also been recognized in the Transition sub-domain (Gomes & Dall'Agnol 2007, Feio 2012), this paper will focus on the sodic granitoids that occur in the Rio Maria domain (Figs. 1b, 2). The rock types of this domain (Fig. 2) are similar in their broad aspects to those found in other Archean terranes around the world, being composed of greenstone belts and a variety of late-Archean granitoids (Dall'Agnol et al. 2006). The former gave ages of 2.97 to 2.9 Ga (Fig. 2) and consist of metaultramafic (komatiites) and metamafic (basalts and gabbros) rocks and subordinate intermediate to felsic rocks, with intercalations of metagraywackes, all grouped into the Andorinhas supergroup (Souza et al. 2001). The oldest granitoids are represented by tonalite-trondhjemite suites formed between 2.98-2.92 Ga (Arco Verde, Caracol, and Mariazinha tonalites and Mogno trondhjemite; DOCEGEO 1988, Althoff et al. 2000, Souza et al. 2001, Leite et al.

2004, Dall'Agnol et al. 2006, Guimarães et al. 2010, Almeida et al. 2011). The contact relationships between these rocks and the greenstone sequences are not exposed, but enclaves of greenstone belts have been found in these granitoids. The oldest tonalitetrondhjemite suites were intruded by: (1) The Rio Maria sanukitoid suite (~2870 Ma; Oliveira et al. 2009, 2011), composed dominantly of granodiorites, with associated mafic and intermediate rocks, forming enclaves in the granodiorites or locally small bodies. These rocks are intrusive in the greenstone belts and in the older tonalite-trondhjemite series and are crosscut by the Água Fria trondhjemite (Leite et al. 2004). (2) A minor occurrence of younger tonalite-trondhjemite granitoids exposed in the Xinguara area, represented by the Água Fria trondhjemite. It was dated at ca. 2860 Ma and is intrusive in the Caracol tonalitic complex and coeval with the Xinguara potassic leucogranite (Leite et al. 2004). (3) The Archean leucomonzogranite and leucogranodiorite suite (~2.87-2.86 Ga;



FIG. 2. Geochronological overview of the available data for the Archean units of the Rio Maria domain. Data sources: (1) Pimentel & Machado (1994); (2) Macambira & Lancelot (1996); (3) Rolando & Macambira (2003); (4) Vasquez et al. (2008); (5) Almeida et al. (2011); (6) Leite et al. (2004); (7) Almeida (unpublished data); (8) Dall'Agnol et al. (1999); (9) Almeida et al. (2013); (10) Althoff et al. (2000); and (11) Lafon et al. (1994). Guarantã suite, Grotão granodiorite, and similar granitic rocks; Almeida *et al.* 2010, 2013). (4) The potassic leucogranites of calc-alkaline affinity (\sim 2.87–2.86 Ga), represented by the Xinguara (XG) and Mata Surrão (MSG) granitic plutons and by small granitic stocks (Fig. 2). The last shearing deformational event identified in this terrane occurred at around 2.86 Ga (Althoff *et al.* 2000, Souza *et al.* 2001, Leite *et al.* 2004), and thereafter the Rio Maria domain remained stable until the emplacement of the 1.88 Ga A-type granites and associated dikes.

TONALITE—TRONDHJEMITE SUITES

Almeida *et al.* (2011) discussed in detail the main geologic, petrographic, and geochemical characteristics, as well as geochronological data for the tonalite–trondhjemite suites from the Rio Maria domain.

Geochronological and geological characteristics

Almeida *et al.* (2011) identified three tonalite– trondhjemite magmatic events: (1) 2.96 ± 0.02 Ga (the oldest rocks of the Arco Verde tonalite and Mogno trondhjemite); (2) 2.93 ± 0.02 Ga (Caracol tonalitic complex, Mariazinha tonalite, and the youngest rocks of the Arco Verde tonalite); and (3) $2.86 \pm$ 0.01 Ga (Água Fria trondhjemite).

The Rio Maria tonalite-trondhjemite suites are large batholiths, weakly to strongly foliated, and commonly show compositional banding (Arco Verde tonalite and Mogno trondhjemite). However, they also form individual plutons (Caracol tonalitic complex, Mariazinha tonalite, and Água Fria trondhjemite). The intensity of deformation increases in the vicinity of shear zones, where mylonitic textures occur. On the other hand, away from the intensely deformed zones, igneous textures are generally well preserved (Althoff et al. 2000; Fig. 3). The tonalite-trondhjemite rocks from the Rio Maria domain usually have E-W trending, non-penetrative foliations that dip 70-90° southward, except for the Mariazinha pluton, which has conspicuous NE-SW to N-S foliations (Fig. 1b). These rocks contain microgranular quartz-dioritic and greenstone belt enclaves and are cut by the Rio Maria sanukitoid (Althoff et al. 2000, Almeida et al. 2008, 2011). Potassium-rich veins and coarse-grained leucogranodiorites appear forming agmatitic structures (Fig. 3).

The youngest tonalite-trondhjemite rocks (Água Fria trondhjemite) display NW-SE to WNW-ESE compositional banding with subvertical dip and include tonalitic enclaves that may represent xenoliths of older tonalite-trondhjemite series. The Água Fria trondhjemite is crosscut by granitic veins, but the compositional banding of the trondhjemite is deformed together with concordant leucogranitic veins from the Xinguara pluton, suggesting that both units are approximately coeval (Leite 2001). This evidence is reinforced by the age of 2864 ± 21 Ma (Leite *et al.* 2004) obtained for the Água Fria trondhjemite, which is almost coincident with that of the Xinguara pluton.

Petrography

The rocks of the Rio Maria tonalite–trondhjemite suites have been classified as tonalites or trondhjemites (*cf.* Le Maitre 2002), with granodiorites being extremely rare (Fig. 4). Gray, equigranular, mediumto coarse-grained, or seriated rocks are dominant in these units. A typical feature is the igneous banding, which is indicated by alternating dark (biotite and accessory minerals) and light (plagioclase and quartz) layers.

The primary mineralogies of the tonalite-trondhjemite units are similar and are dominated by calcic oligoclase, quartz, and biotite as the main minerals. Hornblende rarely occurs as an accessory mineral. Zircon, allanite, apatite, magnetite, epidote, and titanite are the primary accessory phases, while white mica, chlorite, epidote (replacing plagioclase), hematite, goethite, pyrite, and chalcopyrite are secondary phases.

Geochemistry

The great majority of the tonalite-trondhjemite rocks from the Rio Maria domain show SiO₂ contents >66 wt.% (Fig. 5), belong to the high-Al group (Barker & Arth 1976), have geochemical affinities with rocks of the sub-alkaline and calc-alkaline series, and plot in the medium-K series domain. In the classification of Barker (1979), these rocks are tonalites and trondhjemites with rare granodiorites (Fig. 6a). They are poor in ferromagnesian oxides $(Fe_2O_3 + MgO + MnO + TiO_2 mostly \leq 5\%; Fig. 5h),$ are meta to peraluminous (A/CNK values between about 0.9 and 1.1; Fig. 6b), and have low K₂O/Na₂O ratios (generally <0.5; Fig. 6c) and moderate to low Mg# (<0.45). The sodic character of these granitoids is demonstrated in the K-Na-Ca plot in Figure 6d (Barker & Arth 1976, Martin 1994). In the P-Q diagram of Debon & Le Fort (1988), the samples mostly plot in the tonalite field (Fig. 6e).

The Rio Maria tonalite-trondhjemite suites display low concentrations of compatible transition elements (Ni, Cr, and V), relatively low HFSE (Nb, Ta, Zr, Y, and Hf), and variable LILE contents, with low Rb and moderately high Sr and Ba (Fig. 7; Almeida *et al.* 2011).

Based on La/Yb and Sr/Y ratios, Almeida *et al.* (2011) distinguished three TTG groups (Figs. 8a-c and



FIG. 3. (a) Field relationship showing tonalite from the Arco Verde tonalite crosscut by leucogranodiorite from the Guarantã pluton. (b) Foliated, porphyritic, and pink leucogranodiorite from the Guarantã pluton. Note the oriented alkali feldspar phenocrysts, which define a WNW–ESE trending subvertical foliation. (c) Hand sample of the medium-grained equigranular tonalite.

9): (1) high La/Yb ratio TTGs: characterized by high $(La/Yb)_N$ and $(Sr/Y)_N$ ratios and the absence of a significant negative Eu anomaly; (2) medium La/Yb ratio TTGs: displaying slight fractionated REE patterns, being also devoid of significant negative Eu anomalies, and showing intermediate $(Sr/Y)_N$ ratios; and (3) low La/Yb ratio TTGs: characterized by flat HREE patterns, moderate to pronounced negative Eu anomalies, and low $(Sr/Y)_N$ ratios.

Almeida *et al.* (2011) suggested that the high-La/ Yb TTG group may have been derived from magmas generated at relatively high pressures (>1.5 GPa) from sources that left garnet and amphibole as residual phases, whereas the magmas that originated the medium-La/Yb group may have formed under intermediate pressure conditions (\sim 1.0–1.5 GPa), but still in the garnet stability field. As for the low-La/Yb group, with low Sr/Y and Nb/Ta ratios, the authors suggested that its rocks may have crystallized from magmas generated at relatively low pressures (\sim 1.0 GPa) from an amphibolitic source that left plagioclase as a residual phase. According to Almeida *et al.* (2011), these three geochemical groups are not directly linked to the three episodes of TTG generation. Therefore, a TTG unit can be composed of rocks from different groups.



FIG. 4. QAP and Q-(A + P)-M diagrams for the tonalite-trondhjemite and leucogranodiorite-granite suites from the Rio Maria domain.

LEUCOGRANODIORITE-GRANITE SUITES

Almeida *et al.* (2010, 2013) discussed in detail the geologic, petrographic, and geochemical data, and the petrogenesis of these suites.

Geochronological and geological characteristics

The leucogranodiorite-granite rocks from the Rio Maria domain are represented mainly by the Guarantã suite, which includes three plutons (the Guarantã granite as well as the Azulona and Trairão granodiorites). Furthermore, small granitic stocks and the Grotão granodiorite are similar to the rocks of the Guarantã suite and, consequently, they are included in the same Archean granitoid group. The rocks of the Guarantã suite crosscut the oldest tonalite-trondhjemite suite (Fig. 3a), which is strongly deformed, and large shear zones are present in the contacts between the Guarantã suite and its country rocks. The plutons are elongated along the dominant regional trend and their rocks display a widespread, well-developed, WNW-ESE trending and subvertical foliation associated with a subhorizontal stretching lineation (Althoff *et al.* 2000, Dias 2009), except for the Trairão granodiorite, as these plutons are exposed in low-relief areas. They all give moderate to low radiometric responses. Crystallization ages of 2870 ± 16 Ma and 2869 ± 12 Ma were recently obtained by U-Pb LA-MC-ICP-MS (Almeida *et al.* 2013) for the Guarantã and Trairão plutons, respectively.

Petrography

The plutons of the Guarantã suite are composed of coarse-grained, pink or pinkish gray, and porphyritic granodiorites and monzogranites (Fig. 3b), with mafic mineral content usually lower than 7 vol.% (Fig. 4). Potassium-feldspar phenocrysts (5–20 mm) are set in a medium- to fine-grained matrix composed of quartz, plagioclase, microcline, biotite, epidote, and accessory minerals. Moreover, in some samples, these K-feldspar phenocrysts show a strong preferential orientation (Fig. 3b). In all plutons, biotite, generally associated with magmatic epidote, is the most abundant ferromagnesian phase. The primary accessory mineral assemblage includes zircon, apatite, allanite, titanite,



FIG. 5. Major-element Harker diagrams (wt.%) for tonalite-trondhjemite and leucogranodiorite-granite suites from the Rio Maria domain. Samples from late-Archean granitoids from the Pietersburg block and Limpopo mobile belt, South Africa (Laurent et al. 2014) are also plotted for comparison.



FIG. 6. Geochemical plot showing the distribution of the samples of the tonalite-trondhjemite and leucogranodiorite-granite suites from the Rio Maria domain. (a) Normative feldspar triangle (O'Connor 1965). The fields are those drawn by Barker (1979). (b) [Al₂O₃/(CaO + Na₂O + K₂O)]mol *versus* [Al₂O₃/(K₂O + Na₂O)]mol diagram (Shand 1950). (c) K₂O/Na₂O *versus* SiO₂ diagram. (d) K–Na–Ca triangle (Barker & Arth 1976). (e) P–Q diagram from Debon & Le Fort (1988).



FIG. 7. Harker plots for selected trace elements for the tonalite-trondhjemite and leucogranodiorite-granite suites from the Rio Maria domain. Samples from late-Archean granitoids from the Pietersburg block and Limpopo mobile belt, South Africa (Laurent *et al.* 2014) are also plotted for comparison.

and magnetite, while chlorite, zoisite, and white mica occur as secondary minerals.

Geochemistry

These rocks span a narrow compositional range (SiO₂ contents between 68.2 and 75.8 wt.%; Fig. 5). Almost all analyzed samples show relatively high Al₂O₃ (14 to 16 wt.%; Fig. 5e) and are poor in ferromagnesian elements (Fe₂O_{3t} + MgO + TiO₂ + MnO = 1.2 to 5.0 wt.%; Fig. 5h). Moreover, their MgO and Na₂O contents vary from 0.2 to 1.4 wt.% (mean 0.45 wt.%; Fig. 5b) and from 4.0 to 5.4 wt.% (Fig. 5g), respectively; their Mg# values are moderate to high

(mostly 0.30–0.48; mean 0.36) and their FeO_t/(FeO_t + MgO) ratios are usually lower than 0.8 (not presented). Beyond that, these samples have moderate K_2O/Na_2O values (normally between 0.5–1.0; Fig. 6c), are metaluminous to peraluminous (Fig. 6b), and consist mostly of granodiorites and monzogranites, as shown in the P–Q diagram of Debon & Le Fort (1988) (Fig. 6e). These rocks follow a classical calc-alkaline trend in the K–Na–Ca triangle (Fig. 6d) and plot mainly in the trondhjemite and granite fields in the An–Ab–Or normative diagram (Fig. 6a).

The trace elements of the leucogranodiorite–granite suites show a considerable spread in Harker diagrams (Fig. 7). Barium and Sr contents are variable, but



FIG. 8. Chondrite normalized (Evensen *et al.* 1978) REE patterns for (a, b, c) tonalite-trondhjemite and (d, e, f) leucogranodiorite-granite suites from the Rio Maria domain, and (g) TTGs and (h) hybrid granitoids from the Pietersburg block and Limpopo belt (Laurent *et al.* 2014).

generally high (697–1962 ppm and 212–861 ppm, respectively; Fig. 7a, b), while their Rb contents are low to moderate (57–193 ppm, generally <130; Fig. 7c). These granites are depleted in HFSE (Zr, Hf, Y, Nb, and Ta) when compared to A-type or alkaline granites (Whalen *et al.* 1987, Eby 1992, Sylvester 1994). Additionally, their Zr contents tend to be lower than those found in similar Archean granites as well as those of the tonalite–trondhjemite from Rio Maria (Fig. 7d).

In general, the leucogranodiorite–granite rocks from the Rio Maria domain show fractionated REE patterns (Fig. 8d, e). Analogous to the tonalites– trondhjemite suites, it is also possible to identify three main types of granites in the Guarantã suite on the basis of their REE patterns (Fig. 8d–f): (1) high La/Yb granites: marked by high (La/Yb)_N ratios (normally >42) and absence of an Eu anomaly or only a small negative or positive Eu anomaly (Eu/Eu* = 0.85– 1.22), and concave shape of the HREE patterns; (2) medium La/Yb granites: this group is dominant and their rocks display less fractionated REE patterns [16 < (La/Yb)_N < 46] than the high La/Yb granites, with no or slight Eu anomalies (0.70–1.06); and (3) low La/ Yb granites: this granite group is characterized by flat HREE patterns [8 < (La/Yb)_N < 24; generally <14] and the presence of a slight negative Eu anomaly (Eu/ Eu* = 0.68–0.91; with an isolated sample showing 1.30).

The low La/Yb granites have higher Y and lower Sr contents compared to the other granite groups (Fig. 9). The concave shape of the HREE patterns shown by the samples of the high La/Yb group suggests that hornblende was probably an important fractionating phase during the evolution of these rocks.



FIG. 9. (a) La/Yb *versus* Sr/Y and (b) La/Yb *versus* Yb diagrams used to discriminate the different groups of TTG and leucogranodiorite–granite suite rocks from the Rio Maria domain. Samples from late-Archean granitoids from the Pietersburg block and Limpopo mobile belt, South Africa (Laurent *et al.* 2014) are also plotted for comparison.

DISCUSSION

Comparison between the Rio Maria tonalite– trondhjemite and leucogranodiorite–granite suites

The tonalite-trondhjemite suites are composed essentially of tonalites and trondhjemites with very scarce associated granodiorites. Their modal compositions are generally not superposed with those of the leucogranodiorite-granite rocks in the QAP plot (Fig. 4). These leucogranodiorite-granite rocks are coarsegrained pink or pinkish gray porphyritic rocks (Fig. 3b), whereas the tonalite-trondhjemite rocks are gray and show equigranular, medium- to coarse-grained textures (Fig. 3c).

The geochemical contrasts between the leucogranodiorite–granites and the tonalite–trondhjemites of the Rio Maria domain are clear, defining distinct fields in several plots (Figs. 5a, c, d, f, h, 6, 7a–c). For example, the leucogranodiorite–granites have higher K₂O, Ba, Sr, and Rb contents (Figs. 5d, 7a–c) and lower CaO contents (Fig. 5c) compared to the tonalite– trondhjemites. Moreover, the relative depletion in Fe₂O₃ + TiO₂ + MnO + MgO of the leucogranodiorite–granites also distinguishes these rocks from the tonalite–trondhjemites (Fig. 5h).

In the A/NK versus A/CNK diagram of Shand (1950), both leucogranodiorite–granites and tonalite– trondhjemites fall in the transition from the metaluminous to the peraluminous fields. However, the tonalite–trondhjemite group shows higher A/NK ratios than the leucogranodiorite–granite group (Fig. 6b). In the Ab–An–Or diagram, the analyzed samples from the tonalite-trondhjemite suite plot in the limit between the trondhjemite and tonalite fields, whereas the samples from the leucogranodiorite-granite suites plot in the transition between the trondhjemite and granite fields (Fig. 6a). In addition, because of their low normative anorthite content, the leucogranodiorites of the latter group do not plot in the granodiorite field in this diagram. The P-Q diagram (Fig. 6e; fields of Debon & Le Fort 1988) looks more suitable for the geochemical discrimination of the studied suites, where the leucogranodiorite-granite rocks fall in the granodiorite and granite fields, and the tonalitetrondhjemite rocks plot in the tonalite field (Fig. 6e).

In terms of REE behavior, the three distinct REE patterns identified in the leucogranodiorite-granite suites (Fig. 8) were also observed in the tonalitetrondhjemite suites (Almeida et al. 2010). The high, medium, and low La/Yb ratio granites define REE patterns that are similar, respectively, to those of the high, medium, and low La/Yb TTG groups of the tonalite-trondhjemite suites (Fig. 9). In both the leucogranodiorite-granite and tonalite-trondhjemite suites, the rocks of the three groups distinguished on the basis of REE behavior are not temporally or spatially distinct and thus could not be separated on geological maps. In the tonalite-trondhjemite suite, the high La/Yb group is dominant (Fig. 8a), whereas in the leucogranodiorite-granite suite, the medium La/Yb group is more abundant (Fig. 8e).

The $(K_2O/Na_2O) \times 5$ —CaO–Rb/20 triangular diagram (Fig. 10a) clearly shows the geochemical discrimination between the tonalite–trondhjemite and



FIG. 10. Triangular diagrams for samples of the late-Archean granitoids from the Rio Maria domain and late-Archean granitoids from the Pietersburg block and Limpopo mobile belt, South Africa (Laurent *et al.* 2014). (a) (K₂O/Na₂O)*5–CaO–Rb/20 diagram. (b) 3*CaO–Al₂O₃/(FeO_t + MgO)–5*K₂O/Na₂O diagram proposed by Laurent *et al.* (2014). (c and d) Na₂O/K₂O ratio–2*Al₂O₃/(CaO + Na₂O + K₂O)–2*(FeO_t + MgO)_{wt.%}*(Sr + Ba)_{wt.%} diagrams proposed by Laurent *et al.* (2014).

leucogranodiorite–granite suites of the Rio Maria domain. In this plot, the tonalite–trondhjemite samples fall dominantly on the right-hand side, displaying high CaO contents, whereas the leucogranodiorite–granite samples plot mostly on the left-hand side of the diagram, which means that the rocks from the latter group have higher K₂O/Na₂O values than the rocks from the first group. Additionally, all the leucogranodiorite–granite samples plot above the reference line corresponding to 59 ppm Rb, while more than half of the tonalite–trondhjemite samples plot below this line.

Classification of the studied Na-granitoids

Based on field, petrographic, and geochemical data for the Dharwar craton, Moyen *et al.* (2003) proposed four main types of late-Archean granitoids (TTG, sanukitoid, Closepet granites, and biotite-granite). They also admitted the presence of the two-mica leucogranites and A-type peralkaline granites in other cratons. However, Laurent *et al.* (2014) pointed out that a global descriptive classification of late-Archean granitoids is hindered because the granitoid groups of each craton show internal variability, owing to local conditions and to the potentially heterogeneous composition of available sources. Furthermore, the local terminologies and the frequent compositional overlap between the different groups make comparisons difficult. Thus, Laurent et al. (2014) proposed a "genetic" classification supported by late-Archean granitoids from the Pietersburg block and Limpopo mobile belt, South Africa. It discriminates late-Archean granitoids into four different groups: (1) Na-granitoids (TTGs) formed from partial melting of hydrous metabasalts at various depths; (2) sanukitoids sensu lato, whose magmas resulted from interactions between the mantle and a component rich in incompatible elements, and their differentiated products; (3) biotite- and two-mica granites derived by partial melting of pre-existing, felsic continental crust; (4) hybrid granitoids, generally granodiorites and granites, formed through interaction (e.g., metasomatism, mingling, mixing) between magmas or sources of any of the former three groups.

The Rio Maria tonalite–trondhjemite suites. These rocks exhibit petrographic and geochemical characteristics similar to the classical TTG series (Martin 1994). Most of their samples have high Al₂O₃ and low and medium HREE and for this reason are classified as TTG *sensu strictu* according to Moyen & Martin (2012), or high- and medium-pressure TTG (Moyen 2011). Using other classifications, Almeida *et al.* (2011) defined the Rio Maria TTGs as high Al-Sr (Champion & Smithies 2007), low-Sr sub-series (Moyen *et al.* 2007), and low-HREE TTGs (Käpyaho *et al.* 2006, Halla *et al.* 2009).

In this work, the Rio Maria tonalite-trondhjemite granitoids were compared with the TTGs of the Pietersburg block (Figs. 5 and 7). The Pietersburg block TTGs seem to be more leucocratic, being composed of biotite-trondhjemite and granodiorites, whereas in the Rio Maria TTGs, tonalites and trondhjemite are in roughly equal proportions and granodiorites are extremely rare. Hornblende is rare or absent in both cases. The Rio Maria tonalitetrondhjemite suites show higher Fe₂O₃ and CaO contents and lower Na₂O, Al₂O₃, and K₂O values compared to the Pietersburg-block TTGs (Fig. 5). Most samples from the Rio Maria and Pietersburgblock TTGs belong to the high- and medium-La/Yb groups (Almeida et al. 2011) and lack any significant Eu anomaly (Fig. 8a, b, g).

The Rio Maria leucogranodiorite-granite suite. The leucogranodiorite-granites have similar geochemical characteristics with the Transitional TTG of the Yilgarn craton (Almeida et al. 2010). In the genetic classification of Laurent et al. (2014), these rocks were included in the Hybrid granitoid group. The geochemical differences between the leucogranodiorite-granite suite and the hybrid granites from the Pietersburg block can be observed in several geochemical plots (Figs. 5, 7, 8). Laurent et al. (2014) point out that there is no typical geochemical signature for the hybrid granitoids, because the different components that are involved in their genesis differ from one craton to another. Almeida et al. (2010) showed that in the Rio Maria domain, the leucogranodiorite-granite suite is akin to both the granitic facies from sanukitoid suites (high Ba, Sr, and K₂O/Na₂O) and the trondhjemitic member from the TTG suites (high Al₂O₃ and Na₂O contents, low Yb and Y contents, and the behavior of the REE). In the case of the Pietersburg block, the hybrid granitoids share some features typical of the sanukitoid suites (high $FeO_t + MgO + MnO + TiO_2$, high REE and HFSE contents) and others observed in the biotite- and two-mica granites [low CaO/(Na₂O + K₂O), similar Rb, Ba, Th contents and K₂O/Na₂O; Laurent et al. 2014].

Petrogenesis

Petrogenetic models for the tonalite-trondhjemite and leucogranodiorite-granite suites from the Rio Maria domain were discussed in detail by Almeida *et al.* (2011) and Almeida *et al.* (2010, 2013), respectively.

The Rio Maria tonalite-trondhjemite suites. The overall geochemical characteristics of the TTGs from the Rio Maria domain give a strong indication that the high La/Yb group may have been derived from magmas generated at relatively high pressures (ca. 1.5 GPa), from sources able to leave garnet and possibly amphibole as residual phases. In contrast, the magmas that formed the low La/Yb group may have been generated at lower pressures (ca. 1.0 GPa) from an amphibolitic source with plagioclase as a residual phase. As for the medium La/Yb group, it may have been formed at intermediate pressure conditions, but still in the garnet stability field. Moreover, geochemical modelling (Leite 2001) indicates that the medium and subordinate high La/Yb groups may have originated from partial melting of garnet amphibolites derived from tholeiites similar in composition to Archean metabasalts (Martin 1987) or from metabasalts of the Identidade greenstone belt (Souza et al. 2001). The calculated residue comprised garnet, clinopyroxene, plagioclase, hornblende, orthopyroxene, and ilmenite. The degree of partial melting required would be 25-30% for the average Archean metabasalts and 10-15% for the metabasalts of the Identidade greenstone belt. On the other hand, the low La/Yb group may have formed from a liquid derived from a garnet-free and plagioclase-enriched source with a degree of partial melting around 10%.

The $Al_2O_3/(FeO_t + MgO) - 3*CaO - 5*(K_2O/Na_2O)$ ternary diagram (Fig. 10b) proposed by Laurent et al. (2014) also suggests that the metabasalts are potential sources of Rio Maria TTG magmas, where all samples plot in the field that represents the composition of melts derived from low-K mafic rock sources. Samples of the Pietersburg TTGs were plotted in this diagram for comparison. In the Na₂O/K₂O-2*A/CNK-2*FMSB classification diagram (Fig. 10c, d) for late-Archean granitoids (Laurent et al. 2014), the Rio Maria tonalite-trondhjemite suites, together with TTGs from other Archean cratons, plot towards the Na₂O/K₂O pole (Fig. 10c), hinting that these rocks can be produced through partial melting of the metaigneous mafic rocks with low to moderate K2O contents.

The Rio Maria leucogranodiorite–granite suite. Champion & Smithies (2007) and Almeida *et al.* (2010) discussed several hypotheses to explain the petrogenesis of Archean leucogranodiorites or 'transitional TTG' (*e.g.*, magmatic differentiation or partial melting of TTG, the restite model, and partial melting of mafic lithologies).

We think that these models are unable to explain the genetic processes and evolution of the Rio Maria leucogranodiorites-granites. Lopez et al. (2005) and Watkins et al. (2007) argued that there is a genetic link between late-Archean leucogranodiorites and mantlederived magmas (sanukitoids). According to Smithies et al. (2003), sanukitoids refer to a series of associated high-magnesium rocks (diorites to granodiorites) restricted to the late Archean (3.0-2.5 Ga) that have relatively high Mg numbers and high Cr, Ni, P, LILE (Sr and Ba), and LREE abundances for any given silica content. The geochemical characteristics of these rocks have been attributed to their origin by melting of an enriched mantle source (Stern et al. 1989, Stern & Hanson 1991, Stevenson et al. 1999, Smithies & Champion 2000, Moyen et al. 2001, Oliveira et al. 2011). These granitoids are normally present in small proportions (5 vol.%) in all Archean terranes. However, large domains of sanukitoid rocks have been identified in the Archean Rio Maria domain (Oliveira et al. 2009, 2010, 2011). Furthermore, granodiorites are the dominant rocks in this terrane, with subordinate monzogranites, quartz diorites, and quartz monzodiorites.

We suggest two alternative models (described below) to explain the origin of the Rio Maria leucogranodiorite–granites and both of them involve TTG and sanukitoid magmas. The dual geochemical character of this leucogranodiorite–granite suite is the reason why both models involve TTG and sanukitoid magmas, because these rocks share some characteristics that are typical of TTGs and others that are more commonly observed in sanukitoid suites.

Mixing between trondhjemite magmas and evolved liquids by fractional crystallization of sanukitoid magma. Almeida et al. (2010) proposed this model based on modeling and geochemical data. They concluded that the leucogranodiorite-granite suites may have been derived from mixing between Ba-Srenriched leucogranite and trondhjemite magmas. The granite magmas involved in the mixture were originated by fractional crystallization of 35% of a sanukitoid magma of granodioritic composition, leaving a residue consisting of plagioclase, hornblende, clinopyroxene, magnetite, ilmenite, and allanite. In this context, the heterogeneities observed in the leucogranodiorite-granite suite would be explained by mixing in different proportions between the granitic and trondhjemitic magmas.

Analogous petrogenetic models involving mixing between late-Archean granitoid magmas have been adopted to explain the origin of similar rocks. The major element data for the samples from the Rio Maria leucogranodiorite-granite and sanukitoid suites, as well as the hybrid and sanukitoid granitoids from the Pietersburg block and Limpopo belt, are plotted in a ternary diagram in Figure 10b. In this diagram, the fields for the Rio Maria and Pietersburg block sanukitoid rocks show considerable overlap, mainly plotting in the domain of melts derived from high-K mafic rocks. The granitic phases from the Pietersburg block sanukitoid suite show high K2O/Na2O ratios compared to monzogranitic facies from the Rio Maria sanukitoid suite. The leucogranodiorite-granite suite data are scattered and plot roughly between TTG and granitic sanukitoid rocks, suggesting that mixing of magmas of these two latter rocks could produce the leucogranodiorite-granite magmas. The monzogranitic phases produced through fractional crystallization of sanukitoid suites seem to be common in Archean terranes and their magmas can represent an important endmember in the genesis of hybrid granitoids (Laurent et al. 2014).

Furthermore, the samples from the Rio Maria leucogranodiorite–granite suite are concentrated in the central part of the ternary diagram in Figure 10d, together with the Pietersburg hybrid granitoids and other analogous rocks worldwide, suggesting a mixed origin for these rocks involving any of the magmas or sources related to other late-Archean granitoid groups (Laurent *et al.* 2014).

For the origin of the Rio Maria leucogranodiorite– granite, the mixing magmas hypothesis is weakened by the fact that there is no field evidence for this process. Moreover, TTG rocks coeval with the Guarantã suite were not found in the principal area of occurrence of the latter. In addition, petrographic features such as rapakivi-textured feldspars, quartz ocelli, sharply defined chemical zonation in solid solutions (*e.g.*, plagioclase and hornblende), distinct mineral cores, and resorbed cores were not observed in the studied rocks.

Interaction between LILE-enriched fluids derived from sanukitoid magmas and tonalitic crust. The dissolved water in intermediate magmas at mantle pressures can be transferred to the host rocks during the emplacement and crystallization processes of these magmas. This occurs because water can have a high solubility in intermediate magmas under these pressure conditions (Moore & Carmichael 1998, Carmichael 2002). When the water is released to the hosting crust, it decreases the melting temperature of crustal materials, causing the genesis of the late-Archean granites (Lopez *et al.* 2005).

According to Lopez *et al.* (2005), voluminous Archean granodioritic batholiths can be produced by the interaction between mantle-derived magmas (sanukitoid-like magmas) and tonalitic crust. In the case of the Rio Maria leucogranodiorite-granite suite, an alternative hypothesis to explain the origin of these rocks is to admit that fluids enriched in K, Sr, Ba, and H₂O, derived from the emplacement and crystallization of the LILE-rich sanukitoid magmas in a TTG crust, induced a gradual transfer of H₂O and LILE to the host tonalites. This produced a large-scale metasomatic process in the TTG crust, enriching these rocks in K₂O, Sr, and Ba, forming the leucogranodiorite-granites and still preserving some geochemical characteristics of the TTGs (e.g., high Al2O3 and Na₂O, low Yb and Y contents, and REE signature). This is favored by the fact that the Guarantã suite formed ca. 2.87 Ga and contains inherited zircon grains, possibly derived from the older TTGs (cf. Almeida et al. 2013).

Are the Rio Maria leucogranodioritic facies members of the TTG suites or independent lithologies?

There is general agreement that tonalite and trondhjemite complexes were generated by partial melting of hydrous metabasaltic rocks transformed into garnet-bearing amphibolites or eclogites under a variety of fluid conditions. These conclusions are supported by geochemical modeling (Martin 1994, Martin & Moyen 2002, Moyen et al. 2003) and experimental petrology (Beard & Lofgren 1991, Rushmer 1991, Winther & Newton 1991, Rapp 1994, Sen & Dunn 1994, Zamora 2000, Moyen & Stevens 2006), as well as by the study of modern analogues such as adakites (Drummond & Defant 1990, Martin 1999). The experimental work of Winther (1996) suggests that tonalitic melts are formed through partial melting of Archean tholeiite at high temperatures, low pressures, and high water content, whereas trondhjemitic melts are formed at lower temperatures, higher pressures, and low water content. However, although the K content increases with increasing pressure, the melts never achieve the composition of a granodiorite or granite.

The Neoarchean granodiorite–granite batholiths are normally intrusive in the tonalite–trondhjemite complex and some works have proposed that these bodies originated through fractional crystallization of tonalitic–trondhjemitic magmas (*e.g.*, Ridley *et al.* 1997). However, these models fail in giving a satisfactory explanation for the volume of granodiorites in relation to TTG complexes in Archean terranes.

In the Rio Maria domain, the rocks of the leucogranodiorite-granite suite, particularly the leucogranodiorite facies, were mistakenly inserted into the same units of the tonalite-trondhjemite suites for many years, as shown in previous geological maps (*e.g.*, Santos & Pena Filho 2000), resulting in overestimation of the Archean TTG/granites ratio. The reason for this is that the rocks of the leucogranodiorite–granite suite share some geochemical characteristics with the TTG suites, such as the relatively high Al_2O_3 and Na_2O , the low Yb and Y contents, and the behavior of the REE.

Over the past few decades, rocks with strong geochemical similarities to the leucogranodioritegranite suite have been described from the central Pilbara and Yilgarn cratons (Transitional TTG; Champion & Smithies 2001, 2003), Wyoming province (GG suite of Frost et al. 2006), Tanzania craton (Neoarchean granitoids; Opiyo-Akech et al. 1999), Dharwar craton (Arsikere-Banavara and Chitradurga-Jampalnaikankote-Hosdurga suites, Jayananda et al. 2006, and granitoids of the Hutti-Gurgunta area, Prabhakar et al. 2009), and Karelia terrane (Transitional TTG; Mikkola et al. 2011). These works have contributed to identifying this new group of Archean granitoids and to estimating the true volume of each plutonic component in the gray gneiss complexes (Moyen & Martin 2012).

Conclusions

Tonalite-trondhjemite-granodiorite suites are the most voluminous rock type in the Rio Maria domain and host leucogranodiorite-granite plutons. These rocks share common geochemical characteristics, such as relatively high Al_2O_3 and Na_2O contents, low Yb and Y contents, and the behavior of the REE. However, based on a comprehensive geochemical data set, it is possible to show that the leucogranodiorite-granites have higher K_2O , Ba, Sr, and Rb contents and lower CaO contents when compared to the tonalite-trondhjemites.

Simple plots like the $5*(K_2O/Na_2O)$ –CaO–Rb/20 triangular diagram (Fig. 10a) show that the leucogranodiorite–granites and TTGs fall in distinctive fields, and the analogous rocks from the Pietersburg block and Limpopo belt behave similarly.

The Rio Maria tonalite-trondhjemite suites probably originated from partial melting of garnet amphibolites derived from tholeiitic rocks or from the metabasalts of the Identidade greenstone belt at pressure conditions able to produce high, medium, and low La/Yb tonalite-trondhjemite groups. The ambiguous geochemical character of the Rio Maria leucogranodiorite-granites suite, which shares some characteristics that are typical of the tonalite-trondhjemite rocks and others more commonly observed in the sanukitoid suites, may be attributed to a complex evolution involving interaction between TTG and sanukitoid magmas. This work contributed to the discrimination of two types of late-Archean Na-granitoids in the Rio Maria domain, which were mistakenly inserted into the same units for many years. These rocks have been identified in Archean cratons worldwide and help to understand the dynamics of petrogenetic processes at the end of the Archean.

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