New U–Pb ages and lithochemical attributes of the Ediacaran Rio Doce magmatic arc, Araçuá confined orogen, southeastern Brazil

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ABSTRACT

The Araçuá orogen of southeastern Brazil, together with its counterpart located in Africa, the West Congo belt, formed through closure of a gulf connected to the Adamastor Ocean by the end of the Ediacaran and beginning of the Cambrian. Convergence of the margins of the gulf led to the development of the Rio Doce magmatic arc between 630 Ma and 580 Ma on a continental basement mostly composed of Rhyacian orthogneisses. The Rio Doce arc mainly consists of tonalite–granodiorite batholiths, generally crowded with mafic to dioritic enclaves, and minor gabbro–norite–enderbite–charnockite plutons, suggesting mixing processes involving crustal and mantle sources. We investigate the basement, magma sources and emplacement ages of the Rio Doce arc. Our data suggest the arc comprises three main granitic rock groups: i) Opx-bearing rocks mostly of enderbite to charnockite composition; ii) enclave-rich tonalite–granodiorite (ETG); and iii) enclave-poor granite–granodiorite with minor tonalite (GT). The Opx-bearing rocks are magnesian, calc-alkalic to alkali–calcic and metaluminous. Together, the ETG and GT rock groups range in composition from tonalite to granite, are metaluminous to slightly peraluminous, show a predominantly medium- to high-K, expanded calc-alkaline signature, and other geochemical and isotopic attributes typical of a pre-collisional volcanic arc formed on a continental margin setting. Mineralogical, chemical, and geochronological data suggest the involvement of HT-melting of granulitic (H₂O-depleted) sources of Rhyacian age for the generation of Opx-bearing granitic rocks, additionally to magma mixing and fractional crystallization processes. In conclusion, the studied rock groups of the Rio Doce arc were likely formed by interactions of mantle and crustal processes, in an active continental margin setting. These processes involved ascent of mantle magmas that induced partial melting on the continental basement represented by the Rhyacian gneisses.

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1. Introduction

The Araçuá orogen (SE Brazil) and its counterpart located in Africa, the West Congo belt, represent a branch of the Brasiliano – Pan-African orogenic network (Fig. 1) formed during the amalgamation of West Gondwanaland by the end of the Neoproterozoic (Trompette, 1994; Brito Neves et al., 1999). In contrast to typical plate margin orogens, the Araçuá – West Congo orogenic system developed inside an embayment of the São Francisco–Congo

palaeocontinent, i.e., a gulf-like basin, partially floored by ocean crust and connected to the Adamastor Ocean (Pedrosa-Soares et al., 1992, 1998, 2001, 2008; Cordani et al., 2003; Alkmim et al., 2006). Such a peculiar geotectonic scenario, together with the occurrence of ophiolites and a pre-collisional magmatic arc, inspired the concept of a confined orogen (Pedrosa-Soares et al., 2001), as an intermediate term between the typical continental margin or intercratonic orogens, and the wholly ensialic intracontinental orogens or inverted aulacogens (Rogers and Santosh, 2004).

Despite this confined environment, the Araçuá orogen shows a well-developed calc-alkaline magmatic arc, the Rio Doce arc, which occupies an area of over 20,000 km² (Figueiredo and Campos Neto, 1993; Nalini Jr. et al., 2005; Pedrosa-Soares and Wiedemann-Leonardos, 2000; De Campos et al., 2004; Martins et al., 2004; Gonçalves et al., 2010; Novo et al., 2010; Pedrosa-Soares et al., 2011).

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Fig. 1. The Araçuaí–West Congo Orogen and the adjacent São Francisco–Congo craton in the context of West Gondwana (after Alkmim et al., 2006; Noce et al., 2007). Simplified geological map of the central to southern Araçuaí orogen, showing the focused region (modified from Pedrosa-Soares et al., 2008). ACSZ = Abre Campo shear zone; SFC = São Francisco Craton.

Central to a systematic reconstruction of the Rio Doce arc is the determination of its chemical and isotopic variations that would lead to a much clearer understanding of the magmatic processes involved in the pre-collisional phase of the orogen, and of the nature of the sources involved in the formation of the granitoids. In this paper, we provide field/petrographic observations, major and trace element data, and zircon U–Pb ages to characterize the geochemical diversity of I-type rocks that comprise the Rio Doce

arc. We also combine the new geochemical and geochronological dataset with previously published data to discuss the magmatic processes and possible sources involved in the genesis of the arc granitoids.

The study area, located between Governador Valadares and Ipanema in eastern Minas Gerais State, Brazil, was selected based on the fact that it is well covered by systematic geological mapping, contains many of the best exposures of plutons forming the Rio

Doce arc and, consequently exposes a wide variety of magmatic rocks, representative of much of the arc. Geological maps, mostly from systematic mapping projects in the 1:100,000 scale, covering the study area have been published since the 1960's (Barbosa et al., 1964, 1966; Vieira, 1993, 2000; Féboli, 2000; Féboli and Paes, 2000; Ribeiro, 2000; Signorelli, 2000; Tuller, 2000; Oliveira, 2000). Our integrated map (Fig. 2) resulted from a thorough compilation of those maps, assisted by a large amount of carefully detailed descriptions from our own field-based work and petrographic studies, providing a consistent geological basis for the presented studies. The compiled geochemical and geochronological datasets were collected from many outcrops (tens of kilometers apart) and they are useful to outline regional geochemical features, concerning a general model for the petrogenesis of the Rio Doce arc.

2. Geological setting

The evolution of the Araçuaí orogen lasted from the Early Ediacaran up to the Cambrian-Ordovician boundary, and produced igneous rocks that are currently exposed from shallow to deep crustal levels over an area of 350,000 km² (Fig. 1). Based on field relationships, structural features, geochemical and geochronological data, granitic rocks from this orogen, including their Opx-bearing (charnockitic) equivalents and associated mafic rocks, have been grouped into five supersuites, the G1, G2, G3, G4 and G5 (Pedrosa-Soares et al., 2011).

The G1 Supersuite represents the plutonic component of the Rio Doce magmatic arc (Fig. 1). G1 plutons intruded the Rhyacian basement and are associated with metamorphosed pyroclastic and volcanoclastic rocks of dacitic and rhyolitic composition of the Rio Doce Group, forming a roughly NS-trending and 55 km wide belt that extends for over 300 km along the eastern part of the orogen (Nalini Jr. et al., 2000; Pedrosa-Soares et al., 2001, 2011; Vieira, 2007; Gonçalves et al., 2010). It mainly consists of medium- to high-K, calc-alkaline, tonalitic to granitic bodies, and their Opx-bearing equivalents, generally crowded with mafic to dioritic facies and enclaves (Nalini Jr. et al., 2000; Gonçalves et al., 2010; Pedrosa-Soares et al., 2011), and a few mafic to intermediate plutons rich in gabbro to enderbitic facies (Novo et al., 2010; Tedeschi, 2013). The zircon U–Pb crystallization ages of the G1 Supersuite range predominantly from 630 Ma to 580 Ma, predating the ages of emplacement of syn-collisional, S-type granites (G2 Supersuite) between 582 and 560 Ma (Nalini Jr. et al., 2000; Pedrosa-Soares et al., 2008, 2011; Silva et al., 2005, 2011). All these features, together with the pre-collisional, volcanic arc signature of G1 rocks, led several authors to interpret this supersuite as forming a continental magmatic arc (e.g., Nalini Jr. et al., 2000, 2005; Pedrosa-Soares and Wiedemann-Leonardos, 2000; Pedrosa-Soares et al., 2001, 2008, 2011; Martins et al., 2004; Gonçalves et al., 2010; Novo et al., 2010; Tedeschi, 2013), named Rio Doce arc by Figueiredo and Campos-Neto (1993). This arc seems to have been formed in response to subduction of oceanic lithosphere from west to east (present day geography), between 630 Ma and 580 Ma, i.e., before the collisional event that led to the full development of the Araçuaí-West Congo orogen at around 575–560 Ma (Pedrosa-Soares et al., 1998, 2001, 2008; Alkmim et al., 2006).

The basement of the Rio Doce arc mainly comprises the Rhyacian orthogneisses of the Juiz de Fora Complex, cropping out along the southern and southwestern portions of the arc, and the Pocrane Complex, exposed in the central-southern and northwestern arc sectors (Fig. 1).

The Juiz de Fora Complex consists essentially of green-grayish, banded, granulitic gneisses of enderbite to charnockite composition with intercalations of mafic granulites, representing a calc-alkaline suite with minor tholeiitic rocks. Although the Opx-

bearing rocks are generally free or poor in biotite, this mineral can replace pyroxenes and hornblende along shear zones. Opx-Grd-bearing granitic leucosomes and small plutons (the so-called garnet charnockite) occur as product of partial melting of the Juiz de Fora enderbite gneisses, during the Brasiliano orogeny. Zircon U–Pb age determinations on the Juiz de Fora gneisses constrain its crystallization age between 2.2 Ga and 2.0 Ga (Table 1). Positive to close to zero epsilon Nd values, and the absence of inherited zircon grains characterize the Juiz de Fora Complex as part of a juvenile magmatic arc (Figueiredo and Teixeira, 1996; Machado et al., 1996; Duarte et al., 1997, 2000; Costa, 1998; Fischel et al., 1998; Noce et al., 2007, 2012; Heilbron et al., 2010; Novo et al., 2010). The Rhyacian (2.2–2.08 Ga) Pocrane Complex consists of poorly to non-migmatized, banded to laminated, biotite-hornblende orthogneisses of dioritic to granitic composition, representing a calc-alkaline series metamorphosed in the amphibolite facies (Féboli and Paes, 2000; Pereira and Zuchetti, 2000; Tuller, 2000; Novo, 2013). The Pocrane Complex also lacks in inherited zircon grains and shows positive epsilon Nd values, representing a less metamorphic (upper crustal level) correlative of the juvenile Juiz de Fora Complex (Novo, 2013).

3. Analytical methods

Whole rock geochemical analyses were conducted on 25 samples of the least deformed plutonic rocks of the G1 Supersuite granitoids. All the samples were crushed and milled at the Departamento de Geologia of the Universidade Federal de Ouro Preto (Brazil). Major and trace element concentrations were determined using Inductively Coupled Plasma Atomic Emission (ICP-AES) and Mass (ICP-MS) Spectrometry, respectively, at the ACME Analytical Laboratory LTDA, Vancouver, Canada. Detection limits are 0.01% for oxides and 0.1 ppm for most trace elements, reaching values up to 0.01 ppm for Heavy Rare Earth Elements, such as Tb, Tm and Lu. The 25 samples from this study (Table 2) were combined with 144 published rock compositions from the G1 Supersuite, exposed between the towns of Teófilo Otoni and Juiz de Fora. These 144 samples were grouped according to the three groups individualized in this study, presented in detailed in the following section. The dataset of samples from the literature is presented as Supplementary Data – Item 1. The compiled dataset covers the outcrop map area of the Rio Doce magmatic arc and represents approximately 30% of the recognized magmatism in the Araçuaí orogen (Fig. 1).

U–Pb zircon LA-ICP-MS analyses were carried out at the Isotope Geochemistry Laboratory of the Departamento de Geologia of the Universidade Federal de Ouro Preto (Brazil), and the results are presented as Supplementary Data – Item 2. Zircon grains were hand-picked and mounted on adhesive tape, enclosed in epoxy resin and then polished and photographed in transmitted light. Extensive use of cathodoluminescence (CL) imaging was made in order to identify internal structures and choose potential target sites for U–Pb analyses. The mounts were then cleaned and the U–Pb isotopic compositions of zircon were analyzed by using an Agilent 7700 ICP-MS and 213 nm laser ablation system of the Departamento de Geologia of the Universidade Federal de Ouro Preto (Brazil). Spot laser ablation was adopted in this study with a beam size of 40 µm and laser pulse frequency of 10 Hz. For details on the LA-ICP-MS methods and running conditions refer to Appendix I.

4. Sampling, petrography and field relationships

Based on our field, petrographic and geochemical data, as well as on compiled information from the literature, the rocks forming

Fig. 2. Geological map of the study area showing the sample sites for geochemical and geochronological analyses. Modified from Gonçalves et al., 2010.

Table 1

Main features and crystallization ages of plutons belonging to the G1 Supersuite and basement rocks.

Local name	Petrography	Structure	Age (Ma)	Technique	References
Derribadinha	Biotite-bearing tonalitic-granitic gneiss	Strongly foliated to banded	561 ± 8 (anatectic overgrowth) ~2100 (inherited grains)	Zircon U–Pb SHRIMP	Silva et al. (2011)
Derribadinha	Tonalite with associated granitic veins	Isotropic to slightly foliated	580 ± 8 ~2100 (inherited grains)	Zircon U–Pb LA-ICP-MS	Petitgirard et al. (2009) Mondou et al. (2012)
Divino Suite	Charnockite of monzodioritic composition	Slightly to strongly foliated	592 ± 7 and 595 ± 4	Zircon U–Pb LA-ICP-MS	Novo (2009)
Galiléia	Tonalites, granodiorites and granites with associated mafic enclaves	Foliated to isotropic	594 ± 6 ~2100 (inherited grains)	Zircon U–Pb TIMS	Nalini Jr. (1997)
Manhuaçu	Biotite-hornblende tonalite with mafic and dioritic enclaves	Isotropic to slightly foliated	597 ± 3	Zircon U–Pb	Pedrosa-Soares et al. (2011)
Muniz Freire	Tonalite	Foliated	588 ± 4	LA-ICP-MS	
Muriaé Batholith	Porphyritic granite to tonalite	Isotropic to foliated	593 ± 4	Zircon U–Pb LA-ICP-MS	Figueiredo (2009)
Chapada do Bueno	Tonalite	Foliated to banded	625 ± 11	Single zircon Pb–Pb evaporation	Paes (1999)
Derribadinha sample 242	Tonalite	Foliated	597 ± 4 ~2100 (inherited grains)	Zircon U–Pb LA-ICP-MS	This study
Galiléia sample 3	Quartz diorite enclave	Foliated	581 ± 3 2117 ± 9 (inherited grains)	Zircon U–Pb LA-ICP-MS	This study
Frei Inocêncio gneiss	Biotite-hornblende orthogneiss with associated mafic enclaves and leucocratic veins	Migmatized, foliated to banded	2122 ± 11 565 ± 7 (overgrowth)	Zircon U–Pb SHRIMP	Silva et al. (2011)
Juiz de Fora complex	Charnockite gneiss	Slightly foliated	2134	Zircon U–Pb TIMS	Machado et al. (1996)
Juiz de Fora complex	Enderbitic gneiss with charnockite veins	Migmatized, banded	2084 ± 13	Zircon U–Pb SHRIMP	Noce et al. (2007)
Juiz de Fora complex sample 247	Enderbite	Isotropic to slightly foliated	2116 ± 13	Zircon U–Pb LA-ICP-MS	This study
Pocrane complex sample 17	Tonalitic gneiss	Banded rock	2102 ± 8 2099 ± 9	Zircon U–Pb LA-ICP-MS	This study

the G1 Supersuite in the study area can be subdivided into three rock groups, namely (Fig. 2): i) Opx-bearing rocks, ii) enclave-rich tonalite-granodiorite (ETG), and iii) enclave-poor granite to tonalite (GT). These rock groups form batholithic masses, and do not represent necessarily individual plutons (in fact, detailed studies of individual plutons are still rare in the Rio Doce arc, and an example can be found in Tedeschi, 2013). All these rock groups include variable amounts of mafic to intermediate enclaves and facies. Similar rock groups have been recognized elsewhere in the Rio Doce arc, e.g., the Divino Suite composed of Opx-bearing rocks from gabbro to charnockite composition (Novo et al., 2010), the Manhuaçu Tonalite rich in mafic to dioritic enclaves (Noce et al., 2006; Pedrosa-Soares et al., 2011), and those recently studied by Tedeschi (2013), the Chaves Enderbite rich in gabbro to tonalite facies and enclaves, the Brasilândia Tonalite rich in mafic enclaves, and the enclave-poor Guarataia Granodiorite.

In the study area, the zone with Opx-bearing rocks occurs along the western sector, forming a NS-elongated thrust slice sandwiched between Rhyacian orthogneisses of distinct metamorphic facies: to the west, the granulitic Juiz de Fora Complex and, to the east, the amphibolite facies Pocrane Complex (Fig. 2). The dominant rock unit occurring along this zone is the Derribadinha Tonalite, a gneissic rock with common migmatitic and mylonitic structures, ranging in composition from tonalite to granite (Féboli, 2000; Féboli and Paes, 2000; Pereira and Zucchetti, 2000; Ribeiro, 2000; Signorelli, 2000; Gonçalves, 2009; Silva et al., 2011). The Derribadinha batholith contains a large number of small bodies of Opx-bearing rocks which are predominantly greenish, fine- to medium-grained enderbites, and minor diorites and gabbros. The studied Opx-bearing rocks consist in average of quartz (~30%), plagioclase (~25%), microcline (~15%), and up to 30% of total mafic minerals (orthopyroxene, clinopyroxene, hornblende and biotite). Titanite, zircon, allanite, garnet, pyrrhotite, chalcopryrite, pyrite, pentlandite are common accessories. Although Opx-bearing rocks locally show preserved igneous

features, in most cases they display a solid-state metamorphic foliation marked by the alignment of hornblende and/or biotite. The brown-reddish biotite is, occasionally, a product of hornblende breakdown. Hornblende defines the rock foliation, but also occurs without shape preferred orientation. Igneous orthopyroxene is commonly replaced by hornblende and/or biotite (Fig. 3a and b). Feldspar grains, mostly plagioclase, show undulose extinctions, mechanical twinning and recrystallized grains. Quartz shows evidence of solid-state deformation, such as elongated grains, undulose extinctions, deformation bands, recrystallized grains, ribbons and subgrains in chessboard pattern.

The main field characteristic of the enclave-rich tonalite-granodiorite rock group (ETG) is the outstanding presence of cm- to m-long melanocratic to mesocratic enclaves (Fig. 4a), with compositions ranging from gabbro to tonalite. These ETG rocks are exposed as large elongated bodies in the central and eastern parts of the study area, and they are the most common rock-assemblage within the Rio Doce arc (the so-called Galiléia, São Vitor and similar tonalitic batholiths; Féboli, 2000; Vieira, 2000; Féboli and Paes, 2000; Oliveira, 2000; Tuller, 2000). The studied rocks are light to dark gray, medium to coarse-grained, and composed in average of plagioclase (~40%), quartz (~35%), biotite (~12%), orthoclase (~5%), microcline (~5%) and hornblende (~3%). Garnet, titanite, allanite, apatite, rutile, ilmenite, magnetite, pyrrhotite and chalcopryrite are common accessory minerals. Muscovite and clinozoisite are secondary products of plagioclase breakdown, whilst chlorite forms as replacement of biotite. Quartz shows elongated grains, undulose extinction, subgrains or recrystallized grains, as well as triple grain junctions. Feldspars show mechanical twinning, undulose extinction, or recrystallized grains, although plagioclase grains with concentric zoning, possibly with calcium-rich core, are visualized indicating preserved igneous features.

The enclaves and their host granitoids have similar mineral compositions, but different mineral proportions. The enclaves, that locally exhibit chilled margins, consist of biotite, hornblende, zoned

Table 2

Selected major and trace element data for the analyzed rock groups of the G1 Supersuite in the study area.

	Opx-bearing group							Enclave-rich tonalite and granodiorite (ETG group)										Enclave-poor granite to tonalite (GT group)								
Sample	L243	L072	L222	L242	L036	L020	L246	L108	L160	L005	L040	L008	L003	L049	L307	L001	L294	L185	L317	L326	L190	L197	L311	L188	L119	
Major element (wt.%)																										
SiO ₂	56.44	59.89	61.31	61.82	61.93	62.48	66.61	63.98	66.06	66.56	67.94	67.90	67.86	68.50	69.79	71.79	72.80	62.69	66.11	67.31	70.65	71.94	72.15	75.48	76.18	
TiO ₂	0.77	0.95	1.01	0.97	0.78	1.06	0.43	0.69	0.53	0.57	0.43	0.62	0.51	0.47	0.37	0.26	0.30	0.87	0.59	0.57	0.33	0.31	0.24	0.14	0.12	
Al ₂ O ₃	16.08	18.87	16.67	14.23	17.32	16.56	15.80	16.74	16.87	16.16	16.50	15.19	15.49	15.42	15.58	14.55	13.76	16.76	16.72	15.70	14.99	14.20	15.07	13.15	12.58	
Fe ₂ O ₃	9.64	5.67	8.14	9.64	6.65	5.82	4.73	6.21	5.14	5.32	4.18	5.56	5.11	4.31	3.81	3.06	3.61	6.60	4.58	4.91	3.31	2.77	1.80	1.56	2.47	
tot																										
MgO	4.40	2.18	2.77	2.81	2.02	2.06	2.09	1.82	1.08	1.40	0.82	1.53	1.30	1.23	0.61	0.68	0.62	1.82	1.20	1.33	0.70	0.63	0.59	0.27	0.07	
MnO	0.15	0.05	0.15	0.19	0.08	0.10	0.07	0.09	0.06	0.07	0.06	0.06	0.08	0.08	0.05	0.04	0.05	0.12	0.06	0.09	0.06	0.02	0.02	0.04	0.04	
CaO	6.82	5.51	3.02	5.16	6.52	3.88	4.83	5.20	4.63	4.51	5.55	3.63	4.13	4.54	4.16	3.03	2.97	4.88	4.54	4.03	2.94	1.15	1.21	1.54	1.84	
Na ₂ O	3.75	3.93	2.36	4.09	3.06	3.67	3.50	2.77	3.60	2.81	3.40	3.05	2.71	2.81	3.50	2.84	2.74	3.16	3.44	3.11	3.52	2.50	3.67	2.89	3.38	
K ₂ O	1.68	2.48	4.39	0.86	1.45	3.90	1.83	2.32	1.87	2.45	1.01	2.19	2.68	2.49	2.03	3.63	3.06	2.85	2.58	2.79	3.37	6.25	5.15	4.89	3.29	
P ₂ O ₅	0.28	0.47	0.18	0.22	0.19	0.47	0.11	0.17	0.16	0.14	0.11	0.27	0.13	0.14	0.09	0.13	0.09	0.24	0.18	0.16	0.13	0.23	0.09	0.04	0.03	
L.O.I	0.40	1.00	0.50	0.90	0.30	0.40	0.60	0.40	0.40	0.10	0.70	0.50	0.40	0.40	1.00	0.80	0.40	0.50	0.80	0.20	0.30	0.30	0.60	0.00	0.20	
Major element (molar %)																										
A/CNK	0.80	1.01	1.20	0.85	0.95	0.99	0.96	1.03	1.04	1.06	0.99	1.11	1.05	1.00	1.01	1.04	1.05	0.99	1.01	1.03	1.03	1.12	1.10	1.03	1.01	
Mg#	0.47	0.43	0.40	0.37	0.38	0.41	0.47	0.37	0.29	0.34	0.28	0.35	0.33	0.36	0.24	0.30	0.25	0.35	0.34	0.35	0.30	0.31	0.40	0.26	0.05	
Trace element (ppm)																										
Ni	14.00	10.60	31.20	21.60	4.80	7.10	27.70	7.80	3.60	11.80	2.90	8.80	12.30	8.10	1.90	32.20	3.20	4.00	2.60	2.20	1.40	3.30	8.60	1.20	1.50	
v	168.00	92.00	114.00	145.00	105.00	97.00	69.00	83.00	44.00	67.00	44.00	73.00	61.00	58.00	29.00	19.00	28.00	94.00	53.00	65.00	30.00	13.00	11.00	12.00	8.00	
Ta	0.5	0.7	0.7	0.8	0.3	1.2	0.3	0.7	0.5	0.8	0.3	1.3	0.6	1.0	0.3	0.7	0.5	0.9	0.3	0.8	0.5	0.6	0.3	0.4	0.5	
Sr	546.3	374.3	641.8	189.0	349.8	315.2	499.8	216.8	337.0	215.3	346.4	209.9	189.6	195.3	293.1	205.6	175.9	334.0	436.3	355.0	265.9	159.0	199.2	203.6	189.9	
Th	0.9	0.6	14.3	1.2	1.4	3.3	0.8	7.6	11.6	12.6	8.1	6.4	11.2	8.0	10.1	10.3	11.6	9.2	8.3	8.5	6.8	20.9	12.2	6.0	10.6	
Rb	51.0	102.0	133.6	9.9	45.1	217.2	58.7	81.3	85.1	88.3	25.6	91.3	92.4	76.5	52.7	112.8	76.1	89.4	61.8	75.6	87.0	226.2	157.8	109.3	57.3	
Ba	603	673	1765	113	770	1069	296	579	438	599	528	609	576	488	1207	766	963	1248	2037	730	1317	924	395	1089	2283	
Nb	10.8	15.0	14.1	14.9	9.9	26.8	8.3	11.4	12.6	12.2	8.5	18.1	11.5	9.8	8.7	8.2	10.8	14.9	10.0	8.7	8.1	9.7	6.8	6.7	8.5	
U	0.2	1.0	1.3	0.5	0.6	3.3	0.2	1.1	0.9	1.3	0.6	1.7	1.4	3.1	0.8	2.0	1.7	1.1	0.9	1.9	1.1	3.9	1.5	1.3	1.4	
Zr	136.5	224.4	364.3	194.4	238.3	298.2	91.9	206.1	213.1	179.7	334.6	285.2	201.4	169.0	211.6	154.2	171.3	328.6	274.3	125.5	151.0	227.1	108.1	88.3	187.0	
v	23.7	15.5	26.6	41.0	26.7	26.2	7.8	25.6	10.4	19.6	22.2	10.3	21.4	29.2	18.0	15.5	16.0	28.2	13.2	16.5	16.4	27.1	3.9	9.5	27.8	
La	30.8	21.3	56.6	24.8	22.3	20.0	27.4	32.8	50.0	47.4	63.9	17.0	39.4	22.2	55.4	29.7	43.8	47.9	61.6	36.0	27.4	51.3	10.5	18.3	49.6	
Ce	73.8	48.3	113.9	57.0	53.3	52.6	48.6	69.8	105.8	99.8	128.8	43.7	85.2	46.8	117.1	62.2	94.0	99.6	121.1	75.7	54.0	118.8	43.9	38.9	103.6	
Pr	9.31	6.35	12.60	7.17	7.08	7.49	4.90	8.26	12.00	11.74	14.48	4.40	9.87	5.69	13.25	7.12	10.80	11.20	12.60	8.59	6.07	14.71	2.53	4.64	13.29	
Nd	37.7	27.5	46.5	30.2	30.4	31.1	17.7	33.8	45.8	44.6	54.9	17.0	37.6	22.5	50.7	26.4	41.8	43.5	44.1	32.6	20.7	57.2	9.5	17.6	55.0	
Sm	7.06	5.87	7.17	7.03	6.12	6.79	2.58	6.07	6.95	7.33	8.17	3.15	6.62	4.69	8.02	4.55	6.85	7.62	6.04	5.72	3.59	10.54	2.01	3.16	10.18	
Eu	1.69	1.57	1.89	1.28	1.58	1.83	1.22	1.46	1.65	1.46	1.91	0.99	1.30	1.12	2.05	1.21	1.57	1.84	1.97	1.41	1.23	1.24	0.62	0.98	2.36	
Gd	5.57	5.24	5.37	7.21	5.76	6.02	1.98	5.46	4.78	5.55	6.38	2.66	5.18	4.53	5.89	3.37	5.01	6.51	4.15	4.24	3.00	8.20	1.45	2.36	8.46	
Tb	0.86	0.73	0.87	1.30	0.92	0.98	0.29	0.90	0.62	0.79	0.92	0.44	0.78	0.81	0.81	0.50	0.68	1.05	0.57	0.63	0.52	1.23	0.20	0.35	1.24	
Dy	4.46	3.31	4.83	7.48	5.10	5.09	1.53	4.79	2.65	3.78	4.57	2.10	3.87	4.63	4.06	2.71	3.40	5.55	2.81	3.28	2.81	6.05	0.95	1.78	6.19	
Ho	0.88	0.56	0.97	1.53	0.99	0.89	0.30	0.94	0.40	0.67	0.85	0.37	0.74	0.94	0.77	0.55	0.64	1.08	0.53	0.62	0.58	1.01	0.13	0.34	1.15	
Er	2.38	1.40	2.86	4.49	2.80	2.35	0.76	2.61	0.84	1.93	2.16	0.98	2.04	2.87	2.00	1.65	1.70	2.81	1.39	1.69	1.59	2.35	0.38	0.89	2.95	
Tm	0.38	0.16	0.46	0.69	0.39	0.33	0.12	0.41	0.12	0.29	0.32	0.15	0.31	0.47	0.30	0.28	0.27	0.43	0.21	0.27	0.25	0.31	0.05	0.15	0.42	
Yb	2.36	0.91	3.02	4.18	2.40	1.75	0.78	2.32	0.72	1.62	1.67	0.90	1.91	2.97	1.71	1.69	1.71	2.61	1.37	1.69	1.67	1.54	0.38	0.92	2.49	
Lu	0.34	0.13	0.45	0.62	0.34	0.24	0.12	0.33	0.11	0.24	0.25	0.14	0.28	0.46	0.25	0.27	0.26	0.38	0.21	0.25	0.27	0.21	0.05	0.14	0.34	
La/Yb	8.87	15.90	12.73	4.03	6.31	7.76	23.86	9.60	47.18	19.88	25.99	12.83	14.01	5.08	22.01	11.94	17.40	12.47	30.55	14.47	11.14	22.63	18.77	13.51	13.53	
Eu/Eu*	0.82	0.86	0.93	0.55	0.81	0.87	1.65	0.77	0.87	0.70	0.81	1.04	0.68	0.74	0.91	0.94	0.82	0.80	1.20	0.87	1.14	0.41	1.11	1.09	0.78

Fig. 3. Photomicrographs of an Opx-bearing rock (sample 36) showing: (a) subhedral orthopyroxene (Opx) crystal partially replaced on the rim by hornblende (Hbl) and biotite (Bt), and (b) a cross-polarized micrograph showing in detail orthopyroxene (Opx) partially replaced by hornblende (Hbl) and biotite (Bt). Symbols refer to Plagioclase (Pl), Quartz (Qtz) and K-feldspar (Ksp). See Fig. 2 for sample locality.

plagioclase (An₃₅₋₈₈), orthoclase, microcline, quartz, orthopyroxene and clinopyroxene (Nalini Jr., 1997). The accessory minerals are titanite, garnet, apatite (locally acicular), allanite, rutile, zircon, pyrrhotite, chalcopyrite, ilmenite, magnetite, pyrite and pentlandite.

The enclave-poor granite to tonalite rock group (GT) occurs mainly in the central and southeastern portions of the study area (Fig. 2). The studied rocks are light gray, medium to coarse-grained, and consist in average of quartz (~45%), plagioclase (up to 25%), K-feldspar (microcline and orthoclase, up to 20%), biotite (~7%), and hornblende (~3%). Most biotite crystals are primary, but occasionally it is a product of hornblende breakdown. Quartz shows undulose extinction, subgrains or minor recrystallized grains. Feldspars sometimes show polygonal, straight and long boundaries. Zircon, allanite, titanite and occasionally garnet are common accessory minerals. Although many parts of GT plutons are free of solid-state foliation and show preserved igneous features (Fig. 4b), this rock group also includes highly deformed portions. It is common to find euhedral feldspar grains with straight boundaries (Fig. 4c), suggesting an igneous origin, as well as quartz grains with weak undulose extinction and straight boundaries that form dihedral contact at 120°. The GT rock unit shows variable amounts of melanocratic to mesocratic enclaves. Extensive bodies free of mafic enclaves also occur. The lack of enclaves may be explained by one or more of the following reasons: i) exposures of plutons cut in different erosional levels (like in eroded batholiths composed of incestuous plutons; Pitcher, 1997); ii) upper crustal level, allochthonous plutons emplaced far from magma mixing zones; iii) plutons or part of them composed of more evolved melts formed from fractional crystallization; iv) plutons or part of them composed by more differentiated melts formed by partial melting of other granitic plutons of the arc itself and/or from basement sources of adequate composition.

5. Geochemistry of the G1 Supersuite

The analyzed samples include 8 tonalites/enderbites (ETG, GT and Opx-bearing groups), 11 granodiorites (ETG and GT groups), 4 monzogranites (GT group), 1 gabbro (Opx-bearing group), and 1 diorite (Opx-bearing group) (Table 2).

The analyzed rocks forming the G1 Supersuite in the study area vary from diorite to alkali-granite, with granodiorite and tonalite representing by far the most representative rocks of the supersuite (Fig. 5). The composition of the intermediate and acid rocks of the G1 Supersuite is strongly variable, they are both magnesian and ferroan (Fig. 6a), metaluminous and peraluminous and from calcic

to alkali-calcic (Fig. 6b and c). The Opx-bearing rocks are essentially magnesian, while the ETG and GT rocks range from magnesian to ferroan compositions (Fig. 6a). The ETG rocks are calcic, whilst the GT and Opx-bearing rocks cover from calcic to alkali-calcic compositions (Fig. 6b). The Opx-bearing rocks are dominantly metaluminous, with one exception (sample L222), which is peraluminous ($A/CNK = 1.20$), whilst the GT and ETG rocks plot into the transition field between metaluminous and peraluminous rocks (Fig. 6c). All together, the analyzed rocks show similarity to an expanded calc-alkaline series (Fig. 6d).

When compiled the geochemical dataset of the G1 granitoids, the diagrams show that the great majority of the rocks are magnesian (~80%), metaluminous to slightly peraluminous (~84%) and between calcic and calc-alkalic (~83%) (Fig. 6a–c). The gabbroic rocks plot mostly on the calc-alkaline field (Fig. 6d).

The Opx-bearing rocks have SiO₂ content ranging from 56.44 wt.% to 66.61 wt.%, whilst for the ETG and GT rocks the SiO₂ content varies from 63.98 wt.% to 72.80 wt.%, and from 62.69 wt.% to 76.18 wt.%, respectively (Fig. 7, and Table 2). The K₂O content is between 0.86 wt.% and 4.39 wt.% for the Opx-bearing rocks, between 1.01 wt.% and 3.63 wt.% for the ETG rocks, and between 2.58 wt.% and 6.25 wt.% for the GT rocks (Table 2). The highest CaO content of 6.82 wt.% was observed in the Opx-bearing rock group (sample L243), while the lowest value of 1.15 wt.% (sample L197) was obtained in the GT rock group. A slightly positive correlation between SiO₂ and K₂O is displayed by all rock groups (Fig. 7a). A clear negative correlation between CaO and SiO₂, as well as between V and SiO₂ could be observed (Fig. 7b and c). On the other hand, a slightly negative correlation between Ni and SiO₂, and Sr and SiO₂ could be observed for all rock groups (Fig. 7c, d and f). The highest V (168 ppm), and Ni (31.2 ppm) contents were obtained in the rocks of the Opx-bearing group, samples L243 and L222, respectively (Table 2). The highest Sr (641.8 ppm), and the lowest Sr (159 ppm) contents were obtained in the rocks of the Opx-bearing group (sample L222), and of the GT group (sample L197), respectively (Table 2). No clear correlation could be observed between SiO₂ and Rb, although a general positive correlation could be inferred (Fig. 7e).

When compared with literature data on the Rio Doce arc, the geochemical dataset shows that the Opx-bearing rocks record the greatest chemical variability, with SiO₂ ranging from 53.8 wt.% to 74.6 wt.%, maficity (Fe + Mg) from 0.02 to 0.24 (Fig. 6c) and K₂O from 0.9 wt.% to 7.3 wt.% (Fig. 7a). A significant percentage (~40%) of the Opx-bearing rocks plots in the field of alkali-calcic rocks (Fig. 6b). They show Mg# ranging from 0.22 to 0.58, and are particularly enriched in V and Ni with respect to the other

Fig. 4. Field pictures and microphotographs of the G1 Supersuite. a) Metric-scale diorite enclave hosted in granodiorite; b) Granite sample with biotite defining the foliation; c) Granite sample with well preserved euhedral feldspar grain; d) Massive granite pluton with (e) vertically zoned quartzite exposed close to its boundary with the country rock.

Fig. 5. Plot of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ versus SiO_2 (wt. %) content showing the great variability of the rocks forming the G1 Supersuite, which range mostly from diorites to alkali-granites. Note that the compositions of the enclaves, which are hosted in the ETG rocks, and gabbroic rocks are also plotted (after Wilson, 1989). Symbols: square – Opx-bearing rocks; circle – ETG rocks; triangle – GT rocks. Samples from this study are highlighted. See the text for further discussion.

described lithologies (Fig. 7c and d). The GT and ETG rocks have SiO_2 content varying from 59.4 wt.% to 76.2 wt.%. At similar SiO_2 contents, GT rocks have higher K_2O and lower CaO than ETG rocks (Fig. 7a and b), thus the former have higher MALI ($\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$), with ~28% and ~39% of samples plotting in the calc-alkalic and alkali-calcic fields, respectively (Fig. 6b). The GT and ETG rocks show $\text{Mg\#}$ values that range between 0.05 and 0.55, which are similar to values found for Opx-bearing rocks.

The GT, ETG and Opx-bearing rocks display similar REE patterns characterized by enrichment in LREE over HREE with $(\text{La}/\text{Yb})_N$ ratios ranging mainly between ~4 and ~47. Fig. 8a–c shows the fractionation patterns for the three groups of rocks. The GT rocks are slightly enriched in LREE than the other groups. The Opx-bearing rocks display both positive and negative Eu anomalies (Fig. 8a), while GT and ETG rocks show mostly negative anomalies (Fig. 8b and c) with average Eu/Eu^* of 0.93 and 0.83, respectively.

6. U–Pb geochronology

Previous U–Pb zircon geochronological studies in the area between the towns of Governador Valadares and Ipanema (Fig. 2) have been limited to a small number of samples: one from the G5 Supersuite (Petitgirard et al., 2009), one from the G2 Supersuite

Fig. 6. A) $\text{FeO}^{\text{tot}}/(\text{FeO}^{\text{tot}} + \text{MgO})$ versus weight per cent SiO_2 diagram showing the predominant magnesian character of the rocks forming the G1 Supersuite. Continuous line marks the boundary between ferroan and magnesian plutons, and was built based on analyses of 486 A-type granites and 538 Mesozoic batholiths from North America. Fit to the Fe^* line is $\text{FeO}^{\text{tot}}/(\text{FeO}^{\text{tot}} + \text{MgO}) = 0.486 + 0.0046 \times \text{wt. \% SiO}_2$. For sources of data for A-type granites as well as for Cordilleran type rocks see Frost et al. (2001) and references therein. B) Plot of $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO}$ (MALI) versus SiO_2 (wt. %) showing the spread distribution of the G1 rocks. For comparison enclaves and gabbroic rocks are also shown. Fits to the boundaries are alkalic to alkali-calcic: $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO} = -41.86 + 1.112 \times \text{wt. \% SiO}_2 - 0.00572 \times (\text{wt. \% SiO}_2)^2$; alkali-calcic to calc-alkalic: $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO} = -44.72 + 1.094 \times \text{wt. \% SiO}_2 - 0.00527 \times (\text{wt. \% SiO}_2)^2$; calc-alkalic to calcic: $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO} = -45.36 + 1.0043 \times \text{wt. \% SiO}_2 - 0.00427 \times (\text{wt. \% SiO}_2)^2$ (after Frost et al., 2001). C) Variation of the Aluminium Saturation Index ($\text{A/CNK} = \text{mol. Al}_2\text{O}_3/\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$) for granitoids, enclaves and gabbroic rocks of the G1 Supersuite. D) AFM diagram showing the distribution of the G1 rocks, which is similar to a typical calc-alkaline series (after Rickwood, 1989). Symbols as in Fig. 5. See the text for further discussion.

Fig. 7. A–B) Plot of weight per cent SiO₂ versus other oxides (Harker diagrams) for granitoids, enclaves and gabbroic rocks of the G1 Supersuite (after Bhatia, 1983). C–F) Plot of weight per cent SiO₂ versus other trace elements. Symbols as in Fig. 5. See the text for further discussion.

(Nalini Jr. 1997), two from the G1 Supersuite (Nalini Jr. 1997; Petitgirard et al., 2009), and two from the meta-volcanics of the Rio Doce Group (Vieira, 2007) (Fig. 2). In this study we have focused on the age of the surrounding basement which may have contributed to the G1 magmatism. We analyzed five rock samples: three samples from the basement rocks, as well as one from the Opx-bearing rocks and one from the mafic enclaves within the ETG group.

6.1. Basement rocks (samples 247, 17A and 17B)

Sample 247 (UTM 807430/7842740) was collected in the southwestern region of the study area from an enderbite that

belong to the Juiz de Fora Complex. The enderbite is greenish fine- to medium-grained and shows an isotropic aspect (Fig. 9a and b). Samples 17A and 17B (UTM 266028/7857896) were collected close to each other from a fine- to medium-grained banded orthogneiss that belongs to the Pocrane complex, in the central eastern region of the study area (Fig. 2). The orthogneiss is characterized by alternating leucocratic and melanocratic bands ranging from cm- to metric wide (Fig. 9c). The leucocratic band consists predominantly of quartz and feldspar, whilst the melanocratic band is made up of hornblende and biotite, which define the rock foliation. The accessory assemblage is composed of zircon, apatite, titanite, epidote and occasionally garnet.

Fig. 8. Rare Earth Elements diagrams normalized by Chondrite, according to values of Nakamura (1974). The diagrams show the pattern of the three rock groups (a) Opx-bearing rocks; (b) ETG rocks and (c) GT rocks, which are similar to arc-related magmatic rocks. Shadow area delimits the REE concentration for data from this study. See the text for further discussion.

The zircon grains extracted from these samples (samples 247, 17A and 17B) are very similar and comprise long-prismatic and large elongate grains (up to 400 μm), with length/width ratios predominantly of 3:1, although higher ratios up to 4:1 are observed. They are light-gray and most zircon grains display magmatic oscillatory zoning with no inherited cores on CL images (Fig. 10a). However, some of the grains show roundish or embayment cores with visible truncation with the surrounding oscillatory rims. Several attempts to date these cores have failed and no coherent age data could be obtained. Most grains have Th/U ratios ranging from 0.20 to 0.76, which are indicative of a magmatic origin. Sometimes, these grains show corroded boundaries, however no metamorphic overgrowth was observed.

Twenty spots obtained in the same number of zircon grains of the sample 247 yielded upper intercept at 2116 ± 13 Ma and lower intercept at 638 ± 38 Ma (MSWD = 2.1) (Fig. 11a). The upper intercept age is interpreted as the best approximation of the magmatic crystallization age of this sample. Fifty spots obtained from cores and rims of 25 zircon crystals for the sample 17A yielded upper intercept at 2102 ± 8 Ma and lower intercept at 420 ± 120 Ma (MSWD = 3.9) (Fig. 11b). The upper intercept is interpreted to be the crystallization age of this sample. Forty two spots obtained in the same number of zircon grains for the sample 17B plot along a Pb-loss Discordia with intercept ages of 2102 ± 5 Ma and 332 ± 130 Ma (MSWD = 1.13). The upper intercept age is similar (within error) of a concordia age of 2099 ± 9 Ma (MSWD = 1.7) given by eight concordant (<1% disc.) spots (Fig. 11c). We interpret the concordia age as the crystallization age of this sample. Assuming these results as the best estimate for orthogneisses and enderbite crystallization ages for the basement of the Rio Doce arc, they are in accordance to data available in the literature (Machado et al., 1996; Noce et al., 2007; Heilbron et al., 2010).

6.2. Granitoids and enclaves (samples 242 and 3, respectively)

Sample 242 (UTM 807645/7835314) was collected in the southwestern extremity of the study area (Fig. 2). This sample is a gray fine- to medium-grained tonalite and consists of hornblende, biotite, plagioclase, quartz and microcline. Accessory mineral assemblage and secondary minerals are made up of titanite, zircon, allanite, garnet, ilmenite, magnetite, pyrrhotite, $\pm$ chalcophyrite, $\pm$ pyrite, clinozoisite, muscovite and chlorite. The microstructural aspect of this sample is very similar to that earlier described for the enderbite (sample 247) of the Juiz de Fora complex, except that hypersthene was not observed on thin sections for the tonalite. Locally, mm- to cm-wide quartz veins are observed (Fig. 9d). Zircon grains extracted from this sample consist of short-prismatic, elongate or even zircon grains with rounded boundaries. They have length/width ratios mainly of 2.5:1, although higher values up to 3:1 were obtained. The axes of zircon grains range from 130 μm to 300 μm . Most grains are dark-gray and display magmatic oscillatory zoning with inherited cores on CL images (Fig. 10b). Attempts to obtain ages from these cores were unsuccessful due to the high level of discordance, however apparent ages are suggestive of a heritage from basement rocks of 2100 Ma. Although rounded boundary is a typical feature, no metamorphic overgrowth was observed. Nineteen spots from 19 grains of the sample 242 yielded a mean $^{206}\text{Pb}/^{238}\text{U}$ age of 597 ± 4 Ma (MSWD = 1.3) (Fig. 11d). This age is interpreted as the best approximation of the crystallization age of this sample.

Sample 3 (UTM 239888/7880586) was collected from an abandoned quarry in the northeastern portion of the study area, in the vicinity of Conselheiro Pena (Fig. 2). The outcrop consists of a granodiorite with an enormous volume of enclaves. This

Fig. 9. A) Macroscopic view of the enderbite sample from the Juiz de Fora complex showing its roughly banded structure – sample 247. B) Microscopic distribution of the main mineral assemblage showing hornblende (Hbl) crystals as likely product of retrograde metamorphism of orthopyroxene (Opx) (transmitted light; polarized light image in the upper right corner). C) Macroscopic aspect of a typical banded orthogneiss from the Pocrane complex, detail of the banding in the middle of the photo. D) Macroscopic aspect of the Tonalite from the Opx-bearing rock of the G1 Supersuite – sample 242. E) General view of the outcrop close to Conselheiro Pena town – sample 3. F) Detailed image of an enclave showing chilled margins, in the right side and millimetric garnet crystals – sample 3 (see Fig. 2 for samples locality).

granodiorite yielded magmatic crystallization ages of 579 ± 8 Ma (Gonçalves, 2009), while a granodiorite nearby yielded magmatic crystallization age of 594 ± 6 Ma (Fig. 2; Nalini Jr., 1997). The enclaves range in composition from tonalite/diorite to gabbro (Fig. 5); particularly in the sampled place it is a diorite. They have external

rounded shape or are strongly elongated and foliated parallel to the regional pervasive foliation of country rocks (Fig. 9e and f). Zircon grains of this sample comprise two distinct populations. The first is made up of short-prismatic, elongate or even zircon grains with rounded boundaries, similar to the previous sample (sample 242).

Fig. 10. CL images showing the external characteristics and internal structures of zircon crystals extracted from: A) basement rocks (sample 247 – Juiz de Fora complex, and samples 17A and 17B – Pocrane complex). B) G1 Supersuite (sample 242 – tonalite from the Opx-bearing rocks, and sample 3 – quartz-dioritic enclave hosted in granodiorite from the enclave-rich tonalite-granodiorite group).

They have length/width ratios mainly of 2.5:1, although higher values up to 3:1 were obtained. The second population consists of long-prismatic and large elongate grains, which are similar to zircon grains from basement rocks (samples 247, 17A and 17B). Most grains are dark-gray and display magmatic oscillatory zoning with inherited cores on CL images (Fig. 10b). Although rounded boundary is a typical feature, no metamorphic overgrowth was observed. Twenty seven concordant to near-concordant (<2% of discordance) spot analyses from the same number of zircon grains yielded a mean $^{206}\text{Pb}/^{238}\text{U}$ age of 581 ± 3 Ma (MSWD = 0.21) for the sample 3 (Fig. 11e). We interpreted the 581 ± 3 Ma mean age as the crystallization age of this sample. Seven spots obtained in 7 zircon crystals for the same sample yielded a concordia age of 2117 ± 9 Ma

(MSWD = 1.8) (Fig. 11f) and it is interpreted as inherited zircon grains from the continental Rhyacian basement.

7. Discussion

The G1 Supersuite, as exposed between the towns of Governador Valadares and Ipanema in eastern Minas Gerais, consists of three distinct associations of granitic rocks: the Opx-bearing, enclave rich and enclave poor rock groups. The Opx-bearing group is composed of predominantly green-grayish tonalitic rocks, mostly poor in enclaves. The enclave-rich rocks (ETG group) consist of light to dark gray tonalites and granodiorites, crowded of centimetric to metric-sized melanocratic to mesocratic enclaves.

Fig. 11. U–Pb concordia diagrams of LA-ICP-MS analyses of zircon from basement rocks: Enderbite of the Juiz de Fora complex - sample 247 (A), Orthogneiss of the Pocrane complex samples 17A (B) and 17B (C); and from the G1 Supersuite: Tonalite from the Opx-bearing rocks - sample 242 (D); and Enclave (sample 3) hosted in granodiorite from the enclave-rich tonalite-granodiorite group and (E) with magmatic age of inherited zircon grains from the Rhyacian basement (F) (see Fig. 2 for sample locality).

The enclave-poor rocks (GT group) are made up of light gray granites to tonalites, with rare occurrence of enclaves.

The geochemical signature of 7 samples of the Opx-bearing group revealed that it is composed of magnesian (Figs. 5 and 6a), calcic to alkali-calcic (Fig. 6b), predominantly metaluminous tonalites (Fig. 6c). Similar to a calc-alkaline series (Fig. 6d), the rocks

of this group are less evolved, in terms of the SiO₂ content, than the components of ETG and GT groups (Fig. 7). The Opx-bearing rocks have SiO₂ content in average of 61.50 wt.%, whilst the ETG and GT have SiO₂ content in average of 68.32 wt.% and 70.31 wt.%, respectively (Table 2). The geochemical characteristics of the rocks belonging to the ETG group (10 samples) and GT group (8 samples)

largely overlap. These rocks are magnesian to ferroan (Fig. 6a), predominantly calcic (Fig. 6b) and ranging from metaluminous to peraluminous terms (Fig. 6c).

The geochemical data presented here show that these granitoids are mostly magnesian, calc-alkalic to alkali-calcic, metaluminous to slightly peraluminous, and have a typical calc-alkaline trend, thus compositionally similar to other Cordilleran-type granitoids worldwide (e.g., Frost et al., 2001; Frost and Frost, 2008, and references therein).

Even though the study area does not cover the whole arc, it is clear that the analyzed samples cover the entire geochemical diversity shown by the Rio Doce arc rocks (Figs. 5–7). In this sense, ~150 samples from the literature (from published and unpublished data, see [Supplementary Data Item 1](#) for reference details) are now grouped according to the three rock groups here defined, based on field, petrographic and mainly the geochemical criteria. Therefore the initial 25 analyzed samples translate to: 43 geochemical analyses of rocks belonging to the Opx-bearing group, 70 analyses of rocks of the ETG group, 20 analyses of rocks of the GT rock group, as well as 22 analyses of enclaves and 14 analyses of gabbroic rocks.

Our new zircon U–Pb data belonging to the Opx-bearing group (sample 242), an enclave within the ETG group (sample 3), and the Rhyacian basement rocks (samples 247 and 17A and 17B) are in good agreement with previous data available to the pre-collisional G1 magmatism (630–580 Ma), as well as to the basement (~2100 Ma) of the Rio Doce arc (Nalini Jr. et al., 2000; Silva et al., 2002, 2005; Pedrosa-Soares et al., 2011; Figueiredo, 2009; Gonçalves, 2009; Novo et al., 2010; Petitgirard et al., 2009; Mondou et al., 2012; Novo, 2013; Tedeschi, 2013).

The three main groups range from acidic to intermediate igneous rocks (Table 3), and display similar U–Pb zircon crystallization ages (ca. 580–600 Ma). The available data only allow us to discuss possible petrogenetic processes under a regional perspective, as the studied rock groups do not represent individual plutons but composite batholithic masses (Fig. 2). Determining the unequivocal origin and source rocks of the Rio Doce arc may not be possible, due to the large range in composition and age of the rocks (630–580 Ma) forming this arc (Figueiredo and Campos-Neto, 1993; Nalini Jr. et al., 2005; Pedrosa-Soares and Wiedemann-Leonardos, 2000; De Campos et al., 2004; Martins et al., 2004; Gonçalves et al., 2010; Novo et al., 2010; Pedrosa-Soares et al., 2011).

Regionally, the granitic rocks forming plutons of the G1 Supersuite range in composition from diorite to alkali-granite, and their Opx-bearing equivalents, being predominant tonalite to granodiorite rocks (Fig. 5). The individualized rock groups follow the positive correlation for K and Rb, and the negative tendency for Ca, V, Ni and Sr against SiO₂ content. Indeed, the occurrence of diorites and

gabbros suggest the involvement of mantle-derived magmas in the genesis of the G1 Supersuite (Nalini Jr. et al., 2000; Pedrosa-Soares et al., 2011). However, the large petrographic and chemical variability characterizing the G1 granitic rocks, together with their large emplacement age range, suggest that different processes are likely to have contributed to shape the chemical composition of the supersuite, with the relative importance of these processes varying substantially for distinct plutons and batholiths.

Among possible petrologic processes (e.g., Pitcher, 1997; Annen and Sparks, 2002; Chappel, 2004; Annen et al., 2006; Clemens et al., 2011; Clemens and Stevens, 2012; Farina et al., 2012), we focus on the following main possibilities: i) fractional crystallization of mantle-derived magmas of gabbroic composition with assimilation of host rock as these magmas rose through the crust and emplaced, the so-called MASH process (melting, assimilation, storage and homogenization of deep crustal hot zones near the crust–mantle boundary); ii) mixing between crust- and mantle-derived magmas, with mafic enclaves representing evidence to support this process; iii) partial melting of plutonic sources with intermediate to acidic composition, relatively rich in biotite and hornblende.

It is worth noting that these three models have a strong implication on the mechanisms of formation of continental crust. In fact, the amount of juvenile magmas involved in the three scenarios is drastically different. According to the first process the G1 Supersuite would represent a major event of net crustal growth, while following the last hypothesis the amount of juvenile crust formed is only minor and the supersuite would comprise recycling outcomes from older continental crust. The second hypothesis stands between these end-members and represents a combination of the MASH and crustal melting processes. Actually, these processes have been proposed to occur simultaneously, with heat and H₂O released from the crystallizing primary magmas acting as the trigger for the crustal melting (Annen and Sparks, 2002).

7.1. Evolution of mantle-derived magmas

The efficacy of MASH depends on the efficient co-functioning of fractional crystallization, assimilation and magma mixing. Although this model may be involved at some extent in the generation of the G1 Supersuite, there are three lines of evidence arguing against MASH to explain the chemical diversity of the G1 Supersuite.

Firstly, the Sr and Nd isotopic composition available for the G1 Supersuite is typically crustal in signature (Nalini Jr., 1997; Martins et al., 2004; Pedrosa-Soares et al., 2011), although this may be accepted for continental magmatic arcs. In particular, Novo et al. (2010) analyzed the Nd isotopic signature (epsilon Nd = –10; T_{DM} model age ~2 Ga) of two 600 Ma Opx-bearing rocks of intermediate composition (SiO₂ = 54–57%) and relatively low-K

Table 3
Main features of the rocks forming the G1 Supersuite.

Group	Mineralogy		Geochemistry	Field observations
	Main minerals	Accessory minerals		
Opx-bearing rocks	orthopyroxene, clinopyroxene, biotite, hornblende, plagioclase, quartz and microcline	Titanite, zircon, allanite, garnet, pyrrhotite, chalcopryrite, pyrite and pentlandite	Magnesian, calc-alkalic to alkali-calcic and metaluminous	Predominantly greenish, fine-to medium-grained charnockites to enderbites
Enclave-rich Tonalite and Granodiorite	biotite, hornblende, plagioclase, quartz, orthoclase and microcline	Garnet, titanite, allanite, apatite, rutile, ilmenite, magnetite, pyrrhotite and chalcopryrite	Metaluminous to slightly peraluminous, calc-alkaline, intermediate-silicic plutonic rocks	Light to dark gray, medium to coarse-grained Granodiorites and Tonalites, rich in cm- to m- long melanocratic enclaves
Enclave-poor Granite to Tonalite	biotite, hornblende, orthoclase, microcline, quartz and plagioclase	Zircon, allanite, titanite and garnet		Light gray, medium to coarse-grained Granites to Tonalites, mostly poor of enclaves

contents ($K_2O/Na_2O + CaO = 0.16\text{--}1.3$), concluding for an important involvement of the Rhyacian granulitic basement in the origin of the Divino Suite. However, this suite also includes abundant gabbroic and dioritic rocks, pointing to significant mantle contribution, and an expanded high-K calc-alkaline signature and correlations in Harker diagrams suggesting fractional crystallization (Novo et al., 2010).

Sr and Nd isotopic composition of eight samples from four tonalite-granodiorite samples of the G1 Supersuite exposed in the northern part of the arc have variable negative Nd values (-5.6 to -12.9) but relatively constant ($^{87}Sr/^{86}Sr$) values ($0.710\text{--}0.709$) (Martins et al., 2004). Sr and Nd data from five ETG samples from the Galiléia batholith (granodiorites, tonalites and enclaves sampled near the town of Conselheiro Pena) also record negative Nd values (-8.3 to -9.3) and relatively similar ($^{87}Sr/^{86}Sr$) values ($0.712\text{--}0.713$) (Nalini Jr., 1997). Although assimilation of crustal rocks by the primary magmas may drive the composition of mantle-derived magmas toward higher $^{87}Sr/^{86}Sr$ and lower $^{143}Nd/^{144}Nd$, the crustal signature described for the reported samples requires large volumes of assimilated crust. This is in contrast with the existence of thermal limitations on the incorporations of whole-rock material into basaltic magmas (Glazner, 2007). In fact, the energy consumed in this processes results in considerable cooling, crystallization and formation of hybrid magmas that are so highly crystallized to become immobile and incapable of undergoing further magmatic evolution (Clemens and Stevens, 2012). On the other hand, our samples were collected from tonalites and granodiorites rich in gabbroic to dioritic enclaves, which suggest contribution from mantelic magma.

Secondly, assuming that plagioclase and orthopyroxene are the main minerals to fractionate from the gabbroic primary magma, gabbros involved in fractional crystallization should be 3 or 4 times more voluminous than the co-genetic granitoids with production of significant volumes of cumulatic gabbros (Fig. 12). In fact, there is no record of such cumulatic rocks in the G1 Supersuite. However, we cannot exclude that these rocks have not been found due to the lack of detailed studies on individual plutons, or that they were delaminated, due to their high density, in the collisional to post-collisional stages of evolution of the Araçuaí orogen.

Finally, plagioclase (Pl) and orthopyroxene (Opx) fractionation do not account for the great chemical diversity shown by the G1

Supersuite (Fig. 12a and b). Assuming that the chemical composition of the primary magma of the G1 Supersuite could be that of a gabbroic rock (sample T1 from an outcrop in the southern portion of the arc; Novo, 2009; Novo et al., 2010), it would be necessary to fractionate large proportions of Pl and Opx or even Pl and olivine (Ol) to reach the end-acid members (Fig. 12a and b). Indeed, using CaO and maficity as fractionation markers, crystallization larger than $\sim 20\%$ Pl and $\sim 20\%$ Opx would not fit the G1 Supersuite trend for both markers (Fig. 12a and b). This proportion would be even lower considering the synchronous Pl and Ol crystallization, $\sim 5\%$ and $\sim 4\%$, respectively (Figs. 12a and b).

Fractional crystallization has been postulated as a first-order mechanism controlling the magmatic evolution of the G1 Galiléia batholith (Nalini Jr. et al., 2005). Although such process may play an important role for the evolution of single plutons (Nalini Jr. et al., 2005; Novo et al., 2010), there is no evidence, in a regional scale, to consider fractional crystallization as a first-order mechanism to explain the chemical diversity shown by the G1 Supersuite.

7.2. Magma mixing and mingling

The occurrence of mafic bodies such as synplutonic dykes, pillows and enclaves in intermediate to felsic host rocks is commonly considered a strong evidence supporting hybridization between highly felsic melts from the continental crust and mantle-derived magmas to produce granodiorite and tonalite in many different tectonic settings (e.g., Pitcher, 1991). The widespread occurrence of mafic enclaves within most G1 plutons, and the occurrence of gabbroic plutons in the rock record of the G1 Supersuite indicate the involvement of mantle-derived magmas in the genesis of the supersuite. However, the real conundrum is to establish how and to what extent these mantle-derived magmas influenced the composition of the volumetrically dominant granitoid magma in the G1 Supersuite.

The importance of this process may vary substantially from pluton to pluton (e.g., Nalini Jr. et al., 2005; Pedrosa-Soares et al., 2011). Therefore, an estimation of the role of mantle-derived magmas in the origin of the G1 Supersuite would imply detailed studies on selected areas and would strongly rely on isotopic data that are not available.

Fig. 12. Plots of weight per cent SiO₂ versus CaO (A) and maficity (Fe + Mg) (B). The arrows indicate the vectors of fractional crystallization for Plagioclase (Plag.), Orthopyroxene (Opx.), and Olivine (Oliv.). Chemical composition of minerals come from Novo (2009) (Opx.), Kracek and Neuvonen (1952) (Plag.), and Cooper (1976) (Oliv.). Opx. = ferrosilite from a gabbro of Divino Suite (G1 Supersuite), southern part of the arc, Brazil; Plag. = Anorthite from an olivine norite of Grass Valley, California, USA; Oliv. = forsterite from a serpentinite of Douglas Creek, South Island, New Zealand. Dotted line is the best fit of the magmatic evolution of the G1 Supersuite. Solid square represents a likely end-mantle member of the G1 Supersuite, whose chemical composition is from a gabbroic rock (sample T1 of Novo, 2009). Open circles illustrate the effect of synchronous plagioclase and orthopyroxene crystallization in the magmatic evolution of the G1 Supersuite, whilst filled circles illustrate the effect of synchronous plagioclase and olivine crystallization. See the text for additional explanation.

7.3. Recycling the basement rocks

The G1 rocks intrude the Rhyacian orthogneisses of the Juiz de Fora and Pocrane complexes. The ca. 2.1 Ga U–Pb ages from this study, as well as published ages (Machado et al., 1996; Silva et al., 2011; Noce et al., 2007; Heilbron et al., 2010) clearly pin point the Pocrane and Juiz de Fora complexes as part of the Rhyacian component of the basement of the Araçuaí orogen. The granitoids of the G1 Supersuite, as well as some mafic enclaves hosted within them, contain large amounts of ca. 2.1 Ga inherited zircon grains that are possibly related to the Juiz de Fora and Pocrane rocks (Table 1; Fig. 11f). Thus, U–Pb crystallization and inherited ages presented here and in previous studies indicate a close association between G1 granitic rocks and the Rhyacian orthogneisses that make up the continental basement of the Rio Doce arc.

The U–Pb information complements the isotope data suggesting that rocks of the Rhyacian basement contributed for the genesis of G1 granitoids. The occurrence of mafic enclaves within tonalite-to-granite plutons, as well as the occurrence of gabbroic plutons indicates the initial involvement of mantle-derived magmas. However, it is worth noting that the SiO₂ and maficity (Fe + Mg) content of ETG and GT largely overlaps, suggesting that the difference between the two groups is unlikely to be produced by different degrees of interaction with a mantle-derived end-member.

The rocks forming the ETG and GT groups show overall chemical characteristics of I-type granitoids (e.g., Farina et al., 2012): a decrease in ASI with increasing maficity (Fig. 6c) as well as a negative correlation between CaO content and SiO₂ (Fig. 7b). These characteristics have been recently interpreted by Clemens et al. (2011) as resulting from biotite and hornblende partial melting of immature sediments with andesitic/dacitic composition and entrainment of a peritectic assemblage mostly constituted of pyroxene and plagioclase. The main difference between the ETG and GT groups is their alkali content, with GT rocks being significantly more K₂O-rich than ETG rocks at similar SiO₂. Partial melting experiments on metapelites and metagreywackes show how the K and Na content in granitic magmas reflect the stoichiometry of the melting reactions and the chemistry of the source (Farina et al., 2012). In particular, the K:Na of partial melts is related to the variability of the biotite/plagioclase ratio in the melting reaction, (biotite is the main K-bearing phase) as well as plagioclase composition (plagioclase is the main Na-bearing phase) in the source.

We suggest that the difference between the K₂O content of ETG and GT may reflect: 1) the occurrence of two different fertile protoliths in the crust during the genesis of the magmatic arc; 2) different heating cycle between two areas broadly characterized by the same sources. This latter hypothesis is based on the evidence that fluid-absent melting of biotite typically begins at temperatures around 830 °C (at 0.5 GPa; Stevens et al., 1997) while temperatures as high as 900 °C are required for hornblende melting (Skjerlie and Patiño Douce, 1995). According to the first hypothesis, partial melting of a biotite-hornblende source with intermediate composition was involved in the magmatism of the ETG rocks, while GT rocks show the contribution of mostly biotite fluid-absent melting of a more mature source with little contribution from hornblende melting. Alternatively, the heating cycle below ETG rocks allow temperature as high as 900 °C to be achieved and maintained enhancing coupled biotite and hornblende melting, while lower temperatures were reached in the crust below GT rocks. This second interpretation is in agreement with the large amount of mafic enclaves in the ETG rocks, while GT rocks are poor or free in mafic enclaves. In fact, the mafic enclaves can witness underplating of

mantle-derived magmas producing higher and more persistent temperature anomalies.

The composition of GT rocks is much more variable than that of ETG granitoids with some of the GT rocks showing enrichment in K and Rb and others displaying extremely high Sr content (Fig. 7a, e and 7f). This second-order variability within the individual identified lithotypes suggests that different petrogenetic processes have contributed to shape the composition of the G1 rocks. Accordingly, although detailed calculations of crystal fractionation and assimilation-fractional crystallization processes for the G1 Supersuite is out of the scope of this work, we present a general hypothesis for the petrogenesis of the Rio Doce magmatic arc. In this approximation partial melting processes are favored, although we believe that an unequivocal origin for the magmas responsible for the evolution and development of the Rio Doce arc is a challenging work, still to be done.

7.4. The charnockites forming the G1 supersuite

The intermediate to felsic (charnockitic) Opx-bearing plutonic rocks of the G1 Supersuite exhibit strongly variable chemical composition ranging from magnesian to ferroan and from calcic to alkalic (Fig. 6a and b). However, most of the charnockites are magnesian, calc-alkalic to alkali-calcic and metaluminous, thus compositionally similar to Cordilleran batholiths (Frost and Frost, 2008). The overall arc-like major and trace element compositions of the Opx-bearing rocks of the G1 Supersuite suggest that these charnockites represent the roots of the Rio Doce magmatic arc. The capacity of granitic magmas to dissolve and react with orthopyroxene during ascent, causing early, anhydrous, ferromagnesian minerals to be supplanted by hornblende and biotite, is related to the increase in a_{H2O} and a_{K2O} taking place in the magma during crystallization. This observation lead Frost et al. (1989) to conclude that if pyroxenes are to survive in a granitoid, charnockites must represent cumulates that formed early in the crystallization of a pluton, and were isolated from later, more hydrous portions of the batholith. However, the composition of the Opx-rocks of the G1 Supersuite is significantly scattered, with poor or absent positive linear correlations within the elements hosted in the early crystallizing phases (i.e., orthopyroxene and plagioclase) favoring other processes rather than fractional crystallization for the genesis of these rocks. The crustal Sr and Nd isotopic signature displayed by the charnockites of the G1 Supersuite led us to suggest, following Young et al. (1997), that high-temperature partial melting of dry and largely restitic, granulitic crustal sources may have been contributed for its genesis.

8. Conclusions

Field and petrographic observations, geochemistry and geochronology of one of the best exposed segments of the Rio Doce arc, combined with geochemical/isotopic data from the literature, led us to the following conclusions:

1. The Ediacaran continental Rio Doce magmatic arc of the Araçuaí orogen comprises a great diversity of rocks. In the study area, the rocks range from diorites to alkali granites with tonalite and granodiorite representing by far the most representative rocks of the arc. Three rock groups could be distinguished, namely: Opx-bearing rocks, enclave-rich tonalite-granodiorite (ETG), and enclave-poor granite to tonalite (GT).
2. The Rio Doce magmatic arc consists mostly of granitoids chemically similar to a series of magnesian, calc-alkalic to alkali-calcic, metaluminous to slightly peraluminous, which are

- compositionally similar to Cordilleran-type granitoids worldwide.
- U–Pb zircon ages reveal that, in the study area, the rocks forming the Rio Doce arc crystallized between 597 and 581 Ma, with ages roughly around 2.1 Ga obtained from inherited cores of zircon proving that a Rhyacian continental crust may be involved in the G1 rocks production. These results are in good agreement with the current literature about the Araçuaí orogen, particularly regarding the early development stages responsible for the building of its magmatic arc, the continental Rio Doce magmatic arc.
 - Key chemical and mineralogical features suggest that different igneous processes may be involved in the development of the Rio Doce arc. These processes are: i) fractional crystallization of mantle-derived magmas of gabbroic composition with assimilation of host rock as these magmas rose through the crust and emplaced; ii) mixing between crust- and mantle-derived magmas, with mafic enclaves representing evidence to support this process; iii) partial melting of plutonic sources with intermediate to acidic composition, relatively rich in biotite and hornblende. In the light of the present knowledge it is impossible to evaluate the real contribution of each one of the mentioned process. Most likely, playing different roles in distinct portions of the crust they compete during the formation of the Rio Doce arc.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jsames.2014.02.008>.

Appendix I

LA-ICP-MS

The laser ablation-ICP-MS method (LA-ICPMS) has been developed to yield reliable U–Pb ages on zircon on a routine basis at the Departamento de Geologia, Universidade Federal de Ouro Preto, Brazil. The analyses were performed using an Agilent 7700 Q-ICP-MS and a 213 nm New Wave laser. Operating conditions were optimized to provide maximum sensitivity for the high masses (^{207}Pb and ^{238}U) while inhibiting oxide formation ($\text{ThO}^+/\text{Th}^+ < 1.0\%$). The standard and unknown zircons were ablated in small volume (tear-drop shape) sample cell, with an insert that holds one 25-mm-diameter sample mount and a 7-mm-diameter standard mount. Acquisitions consisted of a 20 s measurement of the gas blank, followed by 40 s measurement of U, Th and Pb signals during ablation, and 30 s washout. Samples, standards and sample holders were acid-washed before being analysed to remove possible surface Pb contamination. Laser ablations were performed at 40 μm spot size, $\sim 6\text{--}8\text{ J/cm}^2$ fluence and 10 Hz repetition rate. Ablations occurred in a He carrier gas, and the resulting aerosol was

mixed with Ar prior to introduction into the ICP-MS via 4 mm Tygontubing (pre-cleaned with 1% ultra-pure nitric acid). Integration times were 15 ms for ^{206}Pb ; 40 ms for ^{207}Pb and 10 ms for ^{208}Pb ; $^{204}\text{Pb} + \text{Hg}$; ^{232}Th , ^{238}U .

The relevant isotopic ratios ($^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{232}\text{Th}$, $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$, where ^{235}U was calculated from ^{238}U counts via the natural abundance ratio $^{235}\text{U} = ^{238}\text{U}/137.88$) have been calculated using the data reduction software Glitter (van Achterbergh et al., 2001). Individual isotopic ratios were displayed in time-resolved mode. For our laser system, isotopic ratios generated during the first 5 s of each analysis were discarded. The integration window for the remainder of each analysis was chosen so as to maximize concordance and to exclude signal segments that were related to zones of Pb loss (e.g., fractures), high common Pb (as recognized by $^{204}\text{Pb} + \text{Hg}$ counts markedly higher than the high background caused by ^{204}Hg contamination) or Pb inheritance. Instrumental drift was corrected against the zircon standard using linear interpolative fits. Calibrations were based on six or more analyses of the standard (6–8 analyses of unknowns bracketed between 2 and 3 analyses of standards). ^{204}Pb -based common Pb corrections were not applied.

Two secondary standards were used during runs: Plešovice zircon ($337 \pm 1\text{ Ma}$; Sláma et al., 2008) and M127 zircon ($524 \pm 1\text{ Ma}$; Klötzli et al., 2009). Twenty four analyses of Plešovice zircon std gave a Concordia age of $338 \pm 2\text{ Ma}$ (mean $^{207}\text{Pb}/^{206}\text{Pb}$ age = 344 ± 12 ; mean $^{206}\text{Pb}/^{238}\text{U}$ age = 338 ± 2 ; mean $^{207}\text{Pb}/^{235}\text{U}$ age = $338 \pm 2\text{ Ma}$). Nineteen analyses of the M127 zircon std gave a Concordia age of $522 \pm 3\text{ Ma}$ (mean $^{207}\text{Pb}/^{206}\text{Pb}$ age = 522 ± 13 ; mean $^{206}\text{Pb}/^{238}\text{U}$ age = 523 ± 3 ; mean $^{207}\text{Pb}/^{235}\text{U}$ age $522 \pm 3\text{ Ma}$). See Supplementary Data for detailed information about the individual analyses and “within run” ages obtained for these zircon standards.

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