Petrography, magnetic susceptibility and geochemistry of the Rio Branco Granite, Carajás Province, southeast of Pará, Brazil

Petrografia, suscetibilidade magnética e geoquímica do Granito Rio Branco, Província Carajás, sudeste do Pará, Brazil

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ABSTRACT: The Paleoproterozoic *Rio Branco* stock intrudes the Archean *Cruzadão* biotite monzogranite. It occurs west of the *Canaã dos Carajás* city, close to the *Sossego* copper mine in the *Carajás* Province. It is constituted by undeformed and isotropic, hololeucocratic syenogranites, showing equigranular texture. The granite is formed essentially by perthitic alkali feldspar, quartz, and plagioclase, with additional variable amounts of chloritized biotite. Fluorite, allanite, and zircon are common accessory minerals, whereas pyrite and chalcopyrite are scarces. Albitization and subordinate greisenization are the main alteration processes that affected the granite. The secondary mineralogy is represented by albite, fluorite, topaz, chlorite, muscovite, siderophyllite, and iron oxides. Magnetic susceptibility values are systematically low and vary between 1.3×10^{-5} a 6.9×10^{-4} (SI). The *Rio Branco* Granite is metaluminous to peraluminous and shows high $\text{FeO}^t/(\text{FeO}^t + \text{MgO})$. It has geochemical affinities with ferroan, reduced A2-subtype granites. The rare earth element (REE) patterns are flat with little heavy REE fractionation and show accentuated negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.08 - 0.13$). These characteristics are typical of evolved granites, derived from volatile-enriched liquids responsible by the intense subsolidus hydrothermal alteration. The dating of the *Rio Branco* granite did not give conclusive results, but the obtained data, associated with geological evidence, suggest that it is of Paleoproterozoic age. The comparison between the *Rio Branco* granite and Paleoproterozoic A-type suites of the *Carajás* Province suggests that the *Rio Branco* granite has more affinity with the *Velho Guilherme* suite and, in lesser degree, with the *Serra dos Carajás* suite. On the other hand, is clearly different from oxidized A-type granites of the *Jamon* suite. Despite its similarities with tin-specialized granites, the *Rio Branco* Granite is not associated with tin mineralizations.

KEYWORDS: magnetic susceptibility; geochemistry; A-type granites; Rio Branco granite; Carajás Province.

RESUMO: Petrografia, suscetibilidade magnética e geoquímica do Granito Rio Branco, Província Carajás, sudeste do Pará, Brazil. O Granito Rio Branco é um stock paleoproterozoico intrusivo no biotita-monzogranito arqueano Cruzadão. Ocorre a oeste da cidade de Canaã dos Carajás, nas proximidades da mina de cobre do Sossego na Província Carajás. É constituído por sienogranitos não deformados e isotrópicos, hololeucocráticos, em geral de granulação média. A mineralogia é formada por feldspato alcalino perítico, quartzo e plagioclásio. A biotita, intensamente cloritizada, é a principal fase máfica, acompanhada por fluorita, allanite, zircão, pirita e calcopirita como minerais acessórios. Albitização e, com menor intensidade greisenização, afetaram o granito, sendo a mineralogia secundária albita, fluorita, topázio, clorita, muscovita, siderofilita e óxidos de ferro. O Granito Rio Branco apresenta valores sistematicamente baixos de suscetibilidade magnética (SM) variando de $1,3 \times 10^{-5}$ a $6,96 \times 10^{-4}$ (SI). Geoquimicamente, é metaluminoso a peraluminoso, possui altas razões $\text{FeO}^t/(\text{FeO}^t + \text{MgO})$ e mostra afinidades com granitos ferrosos, tipo-A do subtipo A2. Os padrões dos ETR revelam um ligeiro enriquecimento de ETR leves em relação ao ETR pesados e anomalia negativa acentuada de Eu ($\text{Eu}/\text{Eu}^* = 0,08 - 0,13$), resultando feição em "gaivota", característica de granitos evoluídos. O conjunto de dados obtidos demonstra o caráter evoluído do Granito Rio Branco e sua derivação a partir de líquidos reduzidos e enriquecidos em voláteis, causadores das transformações hidrotermais tardias. O estudo comparativo deste corpo com aqueles das suítes anorogênicas da Província Carajás sugere que o Granito Rio Branco possui maior afinidade com os granitos das suítes Velho Guilherme e, em menor grau, Serra dos Carajás. Por outro lado, é claramente distinto da Suíte Jamon. Embora apresente características similares às dos granitos especializados em estanho, não há mineralizações desta natureza associadas ao corpo.

PALAVRAS-CHAVE: suscetibilidade magnética; geoquímica; granitos tipo A; Granito Rio Branco; Província Carajás.

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INTRODUCTION

A-type granites were initially described by Loiselle & Wones (1979) as alkaline rocks formed in a rift-related or anorogenic environment, with low concentrations of Al_2O_3 and CaO, high concentrations of elements with high ionic charges such as Zr, Y, Nb and similar, a high $\text{FeOt}/(\text{FeOt} + \text{MgO})$ ratios, formed under a low oxygen fugacity, and with low water content. Oxidized A-type granites, however, were later described (Anderson & Smith 1995, Anderson & Morrison 2005, Dall'Agnol *et al.* 1997, 1999, Dall'Agnol & Oliveira 2007). In the Carajás Province (CP) Paleoproterozoic A-type granites were subdivided into three suites — Jamon, Serra dos Carajás and Velho Guilherme — according to their petrographic and geochemical characteristics, metallogenetic potential, and the oxygen fugacities during their crystallization (Dall'Agnol *et al.* 2005). The Jamon Suite occurs in the region of the Rio Maria granite-greenstone terrane, the Velho Guilherme Suite occurs in the Xingu region, and the Serra dos Carajás Suite is distributed within various domains of the homonymous hill region, which also hosts the Rio Branco granite.

This granite occurs in the southeastern part of Pará State, west of Canaã dos Carajás town, and near the Sossego copper mine. It has characteristics similar to those of the A-type granites described by Dall'Agnol *et al.* (2005). Before the present study this stock was poorly described, lacking studies of petrography, geochemistry, geochronology and magnetic susceptibility. The results of these studies, reported here, allow the definition of its main characteristics, as well as an evaluation of its affinities with the three suites already mentioned. The study represents a contribution to understanding the Paleoproterozoic A-type granites of the CP.

REGIONAL GEOLOGY

The CP is located in the south-eastern part of the Amazon Craton which is composed of Archaean and Proterozoic terranes. Tassinari & Macambira (2004) and Santos *et al.* (2000) believe that the Amazon Craton is divided into geochronological provinces which formed around an Archaean nucleus, elongated NW-SE and originally called the Central Amazon Province (Teixeira *et al.* 1989). The surrounding terranes were formed by reworking and crustal accretion in mobile belts. Souza *et al.* (1996) subdivided the CP into two different blocks, Rio Maria and Carajás, and this proposal has subsequently been fortified (Dall'Agnol *et al.* 2006). Various Paleoproterozoic

A-type granites intrude both Archaean blocks (Fig. 1B) (Dall'Agnol *et al.* 2005). These granites were attributed to three suites — Jamon, Serra dos Carajás and Velho Guilherme — according to their petrographic and geochemical characteristics as well as the oxidation state of their magmas (Dall'Agnol *et al.* 2005). The oxidized A-type granites intruded into Archaean rocks of the Rio Maria domain were grouped in the Jamon Suite, represented by the Jamon, Musa, Marajoara, Manda Saia, Redenção and Bannach intrusions. The moderately reduced A-type granites which intrude Archaean rocks of the Carajás Basin and the Transitional Subdomain were included in the Serra dos Carajás Suite. The Seringa granite was recently added (Paiva Jr. *et al.* 2011) to the Serra dos Carajás, Pojuca and Cigano granites which formed the original group. In the Xingu region the tin-bearing granites of the Velho Guilherme Suite cut the Xingu complex and intermediate to felsic volcanic rocks of the Uatumã Supergroup (Teixeira 1999, Teixeira *et al.* 2002). Mafic and felsic dykes, which may be related to the event which generated the Proterozoic granites, cut Archaean units and the Paleoproterozoic granites (Gastal 1987, Huhn *et al.* 1988, Souza *et al.* 1990, Silva Jr. *et al.* 1999, Ferreira 2009).

GEOLOGY AND PETROGRAPHY OF THE RIO BRANCO GRANITE

The Rio Branco granite is exposed in a small hill, and forms a semi-circular body with an approximate area of 31 km². Its major, N-S axis measures 7 km, and its minor axis is 4.5 km. The countryside is formed by gently-sloping hills covered by dense vegetation, and has been transformed into an ecological reserve. Its contacts with country rocks are well defined in radar images (Fig. 1C), but they were not found in the field. The contrast between the geomorphological features of the granite and its surrounding rocks, and the systematic sampling undertaken contributed to the delimitation of its domains. The granite hills stand out from the local relief, and reach heights of up to 600 m. The local relief is dominated by peneplanes or low hills. The country rocks are foliated biotite monzogranite which is wide-spread in the region (Soares 2002, Sardinha 2005, Feio *et al.* 2012), and has been called the Cruzadão granite (Feio *et al.* 2012). The Rio Branco granite is composed of isotropic granite, and crops out as pavements or metre-size blocks formed by pink rocks which are locally bleached or reddened due to albitization or greisenization, respectively. The rocks generally have homogeneous textures which are medium-grained equigranular, locally coarse — or medium to fine-grained. They are

hololeucocratic with low modal proportions (< 5.5%) of biotite which is usually altered.

Modal composition

Table 1 presents the modal compositions in volume % obtained for samples from the granite. The QAP and Q - (A + P) - M' diagrams (Fig. 2) show that all the analysed rocks are hololeucocratic syenogranite with low mafic

mineral contents up to about 4.7%. In this diagram the compositions of the more evolved rocks of the three A-type suites are shown for comparison.

Samples from the SW border of the Rio Branco granite have somewhat higher mafic mineral contents due to incipient greisenization, while samples from the northern part have higher contents of subsolidus albite, allowing them to be classified in some cases as partially albitized granites.

Table 1. Modal compositions of Rio Branco Granite

Mineralogy	Rio Branco Granite										
	ARC 123 ¹	ARC 125 ¹	ARC 130 ¹	ARC 137 ²	ARC 133 ¹	ARC 82 ¹	ARC 91	ARC 135 ^{1,2}	ARC 136 ¹	ARC 138 ³	ARC 139 ³
Rock	SGM	SGM	SGM	SGM	SGMF	Albitized SGM	Albitized SGM	Albitized SGM	Albitized SGM	Greisenized SGM	Greisenized SGM
Grain size											
Albite + perthite	46.6	46	46.9	42	45.8	49.8	58.6	48.1	61.9	53.1	48.4
Quartz	34.9	39.6	32.2	38.8	37	33	28.8	30	25	23.6	35.9
Plagioclase	17	11.8	17	16.6	14.7	14.6	12.4	19.6	12.1	18.8	10
Biotite+ chlorite	0.1	1.8	2.7	2.3	1.8	1	-	2.1	0.1	3	4.7
Fluorite	0.6	0.6	1	0.2	0.4	0.8	-	-	-	0.8	0.8
Allanite	0.4	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
Zircon	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
Iron oxide/hydroxide	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr	Tr
Muscovite	Tr	Tr	Tr	0.1	0.3	Tr	Tr	0.2	Tr	Tr	Tr
Σ Mafic = M'	0.5	1.8	2.7	2.4	2.1	1	Tr	2.3	0.1	3	4.7

SGM: Medium-grained syenogranite; SGMF: Medium to fine-grained syenogranite; ¹Completely oxidized and chloritized biotite; ²Granite with topaz and albite; ³Granite with topaz, siderophyllite, chlorite and fluorite

Figure 1. (A) Map of Pará State with emphasis on the tectonic of Carajás and the Rio Maria domains within the Carajás Province (after Vasquez *et al.* 2008); (B) simplified geological map of the Carajás Province, showing the anorogenic suites and the Rio Branco Granite (after Dall'Agnoll *et al.* 2005); (C) radar image of the Rio Branco granite.

Syenogranite

This is the dominant variety, and has a medium-grained, equigranular hypidiomorphic texture with variation to coarse — or fine-grained. It is essentially composed of perthitic alkali feldspar, quartz and plagioclase (Fig. 3A). Chloritized biotite is the main mafic mineral, and the accessory minerals include fluorite¹, allanite, zircon and opaque minerals. The alkali feldspar has modified exsolution textures (Smith & Brown 1988), mainly represented by vein perthite. Granophyric intergrowths of alkali feldspar and quartz are also common (Fig. 3B).

Greisenized syenogranite

The rocks are massive, pink with reddish tones which reflect the effects of the hydrothermal alteration. Textures are fundamentally similar to those of the dominant syenogranite. The post magmatic transformations, results of the greisenization, are shown by the presence of secondary minerals such as topaz (Figs. 3C and D), fluorite², muscovite and siderophyllite. Most of these minerals occur as anhedral to subhedral crystals which substitute plagioclase. Siderophyllite, and in some cases fluorite², may also be found in mafic aggregates.

Analyses by scanning electron microscopy identified Ce-fluorcerite, xenotime, and rare earth element minerals, all very fine-grained and of local occurrence.

Albitized syenogranite

This rock is bleached but its textures are similar to those of other petrographic varieties. It lacks mafic minerals and has important modal proportions of albite. This occurs in a number of forms, the most common of which is as exsolution lamellae inside alkali feldspar which are then modified

to form vein perthite (Smith & Brown 1988). In more intensely albitized rocks intergranular albite is present in textural varieties containing inverted coronas and as fingers (Fig. 3F; Ramberg 1962, Smith 1974, Dall'Agnol *et al.* 1993), as well as chess board albite (Fig. 3E; Smith 1974). These types represent products of substitution of alkali feldspar, and the alteration is stronger in the NE part of the body.

MAGNETIC PETROLOGY

Iron-titanium oxide minerals

The iron-titanium minerals identified in the Rio Branco granite are mainly hematite with very rare crystals of magnetite (Figs. 3G and H). Hematite normally occurs as inclusions in, or associated with chloritized biotite, or as thin films interstitial to feldspars. In the former occurrence hematite occurs as fine-grained, elongated crystals along the cleavage planes of chlorite (Fig. 3G). This type is common where the primary biotite was intensely chloritized and oxidized. Magnetite was found in a single sample (ARC-137) which has the highest magnetic susceptibility (MS) found in the granite. It occurs as rare, small subhedral to euhedral crystals which show signs of oxidation (Fig. 3H). The partial replacement of magnetite by martite (hematite) is evident. Martite occurs in irregular masses at the borders of the host magnetite.

Magnetic susceptibility

The Rio Branco granite has MS values in the range between 1.3×10^{-5} and 6.96×10^{-4} SI, with a mean value of 1.55×10^{-4} SI. Data and statistics are given in Tab. 2. Log SI values are between -4.88 and -3.15 with a concentration between -4.69 and -3.81. The statistical analysis is not very robust due to relatively small number of samples. The frequency histogram seems to be bimodal, but it is not possible to exclude a single mode. A normal probability graph, not shown here, was also drawn, and also suggested a single mode, but its interpretation was inconclusive.

The MS values are systematically very low, and this fact, allied to the information obtained from the studies of the Fe-Ti minerals, show that the rocks found at the present erosion level must have formed under reducing conditions. The alternative explanation that the rocks were formed under oxidizing conditions, but that subsolidus reactions destabilized magnetite, finds no support from textural features. In the only sample in which magnetite was found it is only slightly altered (Fig. 8H).

Figure 2. Q-A-P (fields according to Streckeisen 1976) and Q - (A + P) - M' modal diagrams for the studied rocks. A: potash feldspar + albite; M': Σ (biotite + zircon + iron hydroxide + allanite + chlorite). Data for the Jamon, Serra dos Carajás and Velho Guilherme suites after Dall'Agnol *et al.* (2005).

Figure 3. Textures of the Rio Branco granite. (A) Equigranular hypidiomorphic texture; (B) Granophyric embryos; (C and D) Hydrothermal association of topaz and muscovite substituting plagioclase; (E) Chess-board albite; (F) Albite fingers replacing perthite; (G) Hematite crystals along cleavage planes in chloritized biotite; (H) Subhedral crystal of magnetite undergoing incipient martitization. Abbreviations of mineral names follow Kretz (1983). Photomicrographs A to F were taken in transmitted light, A and F with crossed nicols. Photomicrographs G and H were obtained in reflected light with crossed nicols.

GEOCHEMISTRY

The chemical analyses for major elements and trace elements, including the REE (rare earth elements), were performed by ICP-ES and ICP-MS, respectively, at the ACME Analytical Laboratories Ltd. In Canada. The chemical compositions of the Rio Branco granite are given in Table 3 together with representative analyses of the most evolved facies of the anorogenic granites of the CP.

The granite is composed of silica-rich rocks ($73.84\% < \text{SiO}_2 < 77.71\%$), with low concentrations of TiO_2 , Al_2O_3 , CaO , MgO and P_2O_5 . The samples have low concentrations of Sr and Ba, moderate concentrations of Zr and Hf, and systematically high concentrations of Rb, Y, Th, U, Nb and Ga. In general the compositions of the samples are relatively uniform except for those samples which passed through post-magmatic transformations.

The dominant syenogranites are metaluminous to peraluminous (Fig. 5A), and show affinities with intraplate granite (Fig. 5B), and with rocks of the A2 subgroup of A-type granites (Figs. 5C and D). $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios are above 1.0 (Table 3), and $\text{FeOt}/(\text{FeOt} + \text{MgO})$ ratios are very high (> 0.95). In the $\text{FeOt}/(\text{FeOt} + \text{MgO})$ versus SiO_2 diagram (Fig. 5E, Frost *et al.* 2001) the compositions plot in the field of ferroan A-type granites, and the reduced character is revealed using the $\text{FeOt}/(\text{FeOt} + \text{MgO})$ vs. Al_2O_3 diagram (Fig. 5F; fields according to Dall'Agnol & Oliveira 2007).

Table 2. Magnetic susceptibility data and statistics for the Rio Branco Granite

Rio Branco Granite		
Sample	K(SI)	Log (K)SI
ARC-137	6.9×10^{-4}	-3.15697
ARC-138	5.7×10^{-4}	-3.24413
ARC-132A	1.5×10^{-4}	-3.81436
ARC-126	1.4×10^{-4}	-3.83367
ARC-139	1.0×10^{-4}	-3.98576
ARC-133	9.3×10^{-5}	-4.03152
ARC-140	8.6×10^{-5}	-4.06550
ARC-130	4.6×10^{-5}	-4.33724
ARC-136	4.3×10^{-5}	-4.36653
ARC-123	3.3×10^{-5}	-4.48149
ARC-135	2.0×10^{-5}	-4.69897
ARC-125	2.0×10^{-5}	-4.69897
ARC-91	1.3×10^{-5}	-4.88606
Statistics		
Mean	1.55×10^{-4}	-
Geometric mean	7.53×10^{-5}	-
Variance	4.77×10^{-8}	-
Standard deviation	2.18×10^{-4}	-
Minimum value	1.30×10^{-5}	-
Maximum value	6.96×10^{-4}	-

As far as the lithophile elements are concerned, as a result of the low concentrations of Sr and Ba, and the high concentration of Rb, ratios such as Rb/Sr and Rb/Ba are always large.

The geochemical characteristics and signatures of the Rio Branco granite samples are consistent with those found for the Paleoproterozoic anorogenic suites of the CP (Dall'Agnol *et al.* 2005).

In the albitized syenogranite, concentrations of TiO_2 , FeOt , CaO and K_2O are diminished, while Al_2O_3 is somewhat enriched, and Na_2O , more so in comparison with the unmodified rocks. Contents of Ba, Rb, Zr, Y and Nb are also reduced by albitization. The intensely albitized sample ARC-91 has extremely low $\text{K}_2\text{O}/\text{Na}_2\text{O}$, Rb/Sr and Rb/Ba ratios (Table 3), while sample ARC-135 which presents petrographic evidence for incipient albitization does not have an unusually low $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio or a diminished Rb concentration, but shows other geochemical evidences for albitization, such as lower concentrations of Zr, Nb and Y.

The geochemical composition of the greisenized granite is generally similar to that of the unmodified granites, and the greisenization was clearly incipient, insufficient to cause expressive mobilization of the chemical elements.

REE patterns show a very accentuated negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.045 - 0.229$, Tab. 3), and slight relative enrichment of the heavy REE ($\text{La}_N/\text{Lu}_N = 1.039 - 5.826$) resulting in the gull-wing patterns which are typical of highly evolved granites, and of F and Sn-bearing granitic magmas (Haapala 1997, Taylor & Fryer 1983, Dall'Agnol *et al.* 1993). The pattern of the strongly albitized (sample ARC-91) is similar but less-rich in REE, showing that the fluids which caused albitization were also capable of leaching REE, while the pattern of the slightly greisenized sample is very similar to those of the unaltered samples, showing that the incipient greisenization did not mobilize the REE.

Figure 4. Histogram of magnetic susceptibility data for samples from the Rio Branco granite.

Figure 5. (A) A/CNK vs A/NK (molecular proportions; Shand 1950) showing the metaluminous character of the Rio Branco granite, which becomes peraluminous when affected by albitization; (B) discrimination of tectonic environment (Pearce *et al.* 1984); (C) diagram identifying A-type granitoids (Whalen *et al.* 1987); (D) Nb – Y – Ce diagram (Eby 1992) showing the distribution of analyses of the Rio Branco granite; (E) FeOt/(FeOt + MgO) vs. SiO₂ after Frost *et al.* (2001) demonstrating that the Rio Branco granite samples are ferroan A-type; (F) FeOt/(FeOt + MgO) vs. Al₂O₃ diagram with fields defined by Dall'Agnol and Oliveira (2007), demonstrating the reduced nature of the Rio Branco granite.

Table 3. Chemical composition of the Rio Branco Granite and representative samples of evolved facies of the anorogenic suite of the Carajás province (data from Dall'Agnol *et al.* 2005)

Granite	Rio Branco Granite						Jamon suite		Serra dos Carajás suite		Velho Guilherme suite	
Suite							Redenção		Serra dos Carajás		Antônio Vicente	Velho Guilherme
Facies	BSG	BSG	BSG	BSGA	BSGA	BSGG	BMzG	LMzG	BSG	BSG	BSG	BSG
Samples	ARC-130	ARC-123	ARC-137	ARC-135	ARC-91	ARC-139	JCR-01D	DCR-07	CJ-29B	CJ-32B	SL-3A	NN-VG32
SiO ₂ (wt.%)	73.84	74.29	74.34	77.50	77.71	73.90	74.20	76.00	73.89	74.50	74.40	75.67
TiO ₂	0.09	0.05	0.08	0.02	0.02	0.05	0.30	0.12	0.16	0.20	0.17	0.05
Al ₂ O ₃	12.93	13.25	12.47	12.43	13.47	12.87	13.30	13.10	12.68	11.85	12.42	12.29
Fe ₂ O ₃	1.67	0.66	2.38	0.77	0.16	1.54	1.31	0.65	1.10	1.03	2.25*	1.39*
FeO	1.50	0.59	2.14	0.69	0.14	1.38	0.62	0.31	1.34	1.92	nd	nd
MnO	0.02	0.02	0.01	< 0.01	< 0.01	0.01	0.05	0.03	nd	0.01	0.02	0.01
MgO	0.06	0.03	< 0.01	< 0.01	< 0.01	< 0.01	0.22	< 0.10	0.03	0.04	0.14	0.02
CaO	1.21	1.21	0.85	0.26	0.23	1.03	1.10	0.55	0.68	1.11	1.02	0.58
Na ₂ O	3.46	3.54	3.48	3.65	7.36	3.43	3.50	3.10	2.74	2.82	3.29	3.79
K ₂ O	5.37	5.72	4.85	4.50	0.18	5.68	5.10	5.40	6.03	5.57	5.22	4.57
P ₂ O ₅	< 0.01	0.01	0.03	0.01	0.02	0.03	0.05	0.01	0.13	0.14	0.12	0.01
LOI	1.2	1.0	1.3	0.8	0.8	1.3	0.31	0.17	0.55	0.22	0.86	0.71
Total	98.65	98.78	98.99	99.14	99.15	98.54	100.1	99.44	99.33	99.41	99.91	99.09
Ba (ppm)	227	443	90	145	37	103	909	32	nd	nd	386	20
Rb	278	226	443	358	11	352	204	396	243	253	339	533
Sr	27.1	52.6	10.9	8.9	33.5	11.8	196	27	69	62	51	9
Zr	163	174	301	58	107	137	258	126	244	301	163	106
Hf	9.4	11.5	17	4.6	9.6	8.8	nd	nd	nd	nd	nd	nd
Nb	94	129	182	46	55	123	21	21	28	75	34	37
Y	244	220	308	68	91	315	71	30	115	78	63	114
Ga	31	24	36	34	31	31	23	27	nd	nd	< 5	29
Th	103	74	150	38	49	91	< 5	< 5	nd	nd	56	48
U	32	16	34	18	25	29	< 10	< 10	nd	nd	30	12
Sn	2	< 1	6	2	< 1	2	nd	nd	nd	nd	nd	nd
Cu	16.2	14.7	3.9	41.7	4.8	7.7	nd	nd	nd	nd	9	nd
Zn	16	17	19	7	7	12	nd	nd	nd	nd	24	27
La	45.5	172.8	110.9	44.1	20.2	61.0	71.8	11.9	268	160	80.90	26.38
Ce	104.9	183.0	261.3	176.9	16.9	138.6	139.7	31.9	259	331	157.80	61.58
Nd	61.4	178.7	115.0	38.1	20.4	85.6	51.7	9.2	168	107	49.4	32.31
Sm	18.35	43.15	28.36	9.50	6.30	25.84	9.3	1.8	27	16.5	10.7	9.13
Eu	0.66	3.22	0.43	0.16	0.59	0.49	1.4	0.2	2.33	1.24	0.7	0.10
Gd	23.37	43.32	30.81	8.32	8.46	31.93	7.6	1.3	18.9	11.1	8.7	10.49
Dy	29.45	40.50	37.70	13.60	14.42	39.42	5.0	0.8	17.2	8.91	9.8	14.35
Er	20.09	23.26	26.45	11.36	11.52	27.05	3.6	0.4	9.78	4.82	6.3	10.69
Yb	20.78	21.24	26.14	17.09	12.69	26.59	2.8	0.4	8.44	4.05	7.6	11.56
Lu	3.10	2.87	3.80	2.56	1.88	3.86	0.4	0.1	1.06	0.56	1.0	1.79
FeOt/(FeOt + MgO)	0.96	0.95	0.99	0.98	0.93	0.99	0.90	0.92	0.98	0.98	0.94	0.98
K ₂ O/Na ₂ O	1.55	1.61	1.39	1.23	0.024	1.65	1.46	1.74	2.20	1.98	1.59	1.22
Eu/Eu*	0.10	0.23	0.04	0.05	0.25	0.05	0.49	0.29	0.30	0.26	0.21	0.03
(La/Lu)N	5.82	1.04	1.67	1.42	10.33	2.82	18.63	12.37	25.90	28.57	8.09	1.47

LOI: loss on ignition; nd: not determined; Fe₂O₃ is total; A: Albitized; G: Greisenized; B: Biotite; MzG: Monzogranite; SG: Syenogranite; L: Leuco.

Figure 6. Rare earth element patterns normalised to chondrite (Evensen *et al.* 1978) for representative samples of the Rio Branco granite, compared to patterns for different facies of the Jamon, Serra dos Carajás and Velho Guilherme Suites (Dall'Agnol *et al.* 2005).

GEOCHRONOLOGY

The isotopic analyses of the Rio Branco granite were performed at the Geochronology Laboratory (Pará-Iso) of the Federal University of Pará (GI-UFPA). The Pb-evaporation method on zircon by thermo-ionization was used. The procedures developed by Kober (1986, 1987) were adapted for use at Pará-Iso by por Gaudette *et al.* (1998).

Zircon concentrates were extracted from ca. 10 kg rock samples using conventional gravimetric methods of heavy mineral separation and magnetic (Frantz isodynamic separator) techniques. The analyses were made using a Finnigan MAT-262 mass spectrometer. The Pb is extracted by heating in three evaporation steps at 1450, 1500, and 1550°C and loaded on an ionization filament.

Ages were determined for each of these stages. The age accepted for each sample was taken to be the mean of the most coherent ages obtained at the higher temperatures. Corrections for the presence of common Pb (^{204}Pb) used the model proposed by Stacey and Kramers (1975).

The biotite syenogranite (sample ARC-137) contained two morphological types of zircon: (1) euhedral to subhedral brown crystals; and (2) light caramel-colored subhedral, sometimes rounded crystals. In general the crystals are fractured with sieve structures, and contain dark (in transmitted light) inclusions which, using a scanning electron microscope (see later), yield very bright back scattered electron images. Semi-quantitative energy dispersive spectrometric analysis shows that these inclusions contain about 29% Th, suggesting that they are composed of thorinite (Figs. 7A and B). Some of the crystals are short prisms with abraded edges and internal zoning (Fig. 7C).

24 grains selected for analysis and only 7 produced sufficiently stable Pb beams (Tab. 4). Of these, the results for grains 1, 3, 4 and 9 were discarded from the age calculation because they yielded high common Pb ($^{204}\text{Pb}/^{206}\text{Pb} > 0.0004$). Grain nº 7 yielded an age of 1697 Ma, but with a very large error of 183 Ma, and was also excluded from the age calculation. This left grains 2 and 5 with ages of 1909 ± 7 Ma, and 1894 ± 16 Ma for

Figure 7. Zircon crystals from the Rio Branco granite. (A and B) strongly metamict crystals; (C) Zoned prismatic crystal. Back scattered electron images obtained with a scanning electron microscope.

a single evaporation stage. These ages are not necessarily trustworthy since they could be older ages revealed only at the highest temperatures.

These attempts at dating the granite were inconclusive, probably due to the metamict character of the zircon crystals in the chosen sample. An earlier attempt at dating a different granite sample (ARF-27) encountered the same difficulties, according to unpublished data of A. S. Sardinha. The problem seems to be general, and related to the fact that the granites are very evolved and subject to strong post magmatic modifications. The same is true of very evolved anorogenic granites, and this makes the determination of a precise age, difficult, although in some cases this is possible (cf. Teixeira *et al.* 2002).

On the other hand, the two ages obtained for grains 2 and 5 of sample ARC-137 are quite close to those obtained (1.88 Ga) for anorogenic granites of Eastern Amazônia (Dall'Agnol *et al.* 2005). The Paleoproterozoic age together with the other lines of evidence, allow the correlation of the Rio Branco granite with the anorogenic suites of the CP.

ZR/HF RATIOS IN ZIRCON FROM THE RIO BRANCO GRANITE

Zr and Hf are elements with similar ionic radii and electrical charges. Most of their abundance in granites is contained in zircon, and the Zr/Hf ratio found in this mineral is regarded as being close to that of the original magma (Owen 1987). Zircon is, therefore, a geochemical tracer mineral. The abundance of Hf in zircon is useful in the identification of the source rocks, the environment of crystallization and the processes of magmatic fractionation, as well as being useful in provenance studies of detrital zircon in sedimentary rocks (Heaman *et al.* 1990, Uher *et al.* 1998, Hoskin & Ireland 2000, Pupin 2000, Wang *et al.* 2000, Belousova *et al.* 2002). Specialized granites contain zircon significantly enriched in Hf, Y, Th, U

Table 4. Analytical results of Pb-evaporation on zircon of the syenogranite (ARC-137) of the Rio Branco Granite

Rio Branco Granite										
Zircon	T(°C)	Ratios	$^{204}\text{Pb}/^{206}\text{Pb}$	2 σ	$(^{208}\text{Pb}/^{206}\text{Pb})^c$	2 σ	$(^{207}\text{Pb}/^{206}\text{Pb})^c$	2 σ	Age	2 σ
ARC137/1	1450 [#]	0/36	0.002306	0.000348	0.44521	0.00687	0.06661	0.00579	825.7	181.5
ARC137/2	1500	4/22	0.000000	0.000000	0.14381	0.00279	0.11684	0.00045	1908.7	7.0
	1550*	0/6	0.000339	0.000400	0.11054	0.01364	0.10462	0.00555	1708.0	97.4
ARC137/3	1450 [#]	0/8	0.001107	0.000026	0.24742	0.00235	0.06331	0.00043	718.8	14.4
ARC137/4	1450 [#]	0/16	0.000800	0.000020	0.66911	0.00399	0.09177	0.00225	1463.1	46.7
	1500*	0/16	0.000167	0.000044	0.19629	0.00168	0.11343	0.00082	1855.3	13.0
ARC137/5	1500	16/16	0.000028	0.000005	0.17136	0.00137	0.11586	0.00102	1893.6	15.8
ARC137/7	1500*	0/6	0.000000	0.000000	0.18900	0.02858	0.10387	0.01032	1694.7	183.1
ARC137/9	1500 [#]	0/32	0.001538	0.000679	0.37123	0.01791	0.06998	0.01138	928.1	333.8

^cratios $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ corrected for common Pb. *Evaporation stage subjectively rejected.

and Ca, with low Zr/Hf ratios, and this fact can be useful as a guide during the initial evaluation of the metallogenic potential of bodies which could be mineralized in Sn, W, Mo, Ta and Li (Wang *et al.* 2000, Kempe *et al.* 2004, Lamarão *et al.* 2007, 2010).

The zircon crystals of the Rio Branco granite were analyzed for Hf at the Scanning Electron Microscope Laboratory (LABMEV) of the GI-UFPA using energy dispersive spectrometry (SEM/EDS). The crystals are heavily corroded and altered, having Hf enrichment at the borders. 187 point determinations of border and nuclei revealed variation of Hf concentrations between 1.8 and 4.8% with a mean of 3.5%, while Zr/Hf ratios vary between 8.6 and 30.5 with a mean of 15.5.

COMPARISONS BETWEEN THE RIO BRANCO GRANITE AND PALEOPROTEROZOIC A-TYPE GRANITES OF THE CARAJÁS PROVINCE

The data presented here allow a comparison between the Rio Branco granite and the anorogenic suites of the CP (Dall'Agnol *et al.* 2005). In common with these suites this granite is isotropic with hypidiomorphic equigranular texture, with no evidence for expressive deformation, and is clearly discordant with the country rocks of Archaean and possibly Paleoproterozoic age. Porphyritic and rapakivi textures are not seen in this granite, but these are not consistent features of the anorogenic suites. The granite has many textural and compositional features found in the more evolved anorogenic suites. In petrographic terms it is similar to the more evolved rocks of the Jamon and Serra dos Carajás Suites, and to the dominant facies of the Velho Guilherme Suite (Fig. 2). It contains biotite, allanite and zircon as primary mafic phases, while post magmatic phases are represented by albite, topaz, fluorite, siderophyllite and sericite — muscovite. In the Jamon Suite the primary accessory minerals are zircon, apatite, magnetite, ilmenite, allanite and titanite (Dall'Agnol *et al.* 1999, Oliveira *et al.* 2008, 2009). Fluorite occurs only in the most evolved rocks. Subsidiary processes generally are limited to alteration of plagioclase and mafic minerals. In the Serra dos Carajás Suite the accessory mineral assemblage is similar to that of the Jamon Suite, except that titanite is rare or absent and fluorite is commoner. Tourmaline is occasionally present (Barros *et al.* 1995, Javier Rios *et al.* 1995, Ely *et al.* 2001). In the Velho Guilherme Suite the syenogranitic facies lacks titanite, fluorite is relatively more common, and monazite and xenotime occur sporadically. Siderophyllite may be present on the greisenized topaz.

The MS data and the petrography of opaque minerals for the Rio Branco granite show that it is typical of reduced granites, and this is corroborated by the geochemical data (Fig. 5F). Magalhães *et al.* (1994) and Dall'Agnol *et al.* (2005) found relatively high MS values (1.0×10^{-3} to 54.7×10^{-3} SI) with a single mode for Jamon Suite granites. The higher values were found in granodiorite and monzogranite with amphibole, while the lower values occur in biotite leucogranite. SM values for the Serra dos Carajás Suite are moderate (1.0×10^{-3} to 5.0×10^{-3} SI), while the Velho Guilherme Suite has values in part overlapping the range found for the Serra dos Carajás Suite, but with predominance of lower values of $< 1.0 \times 10^{-3}$, principally in syenogranite and alkali-feldspar granite. The frequency polygon and the comparative table of opaque minerals shown in Fig. 8 demonstrate that the Rio Branco granite has a greater affinity with the Velho Guilherme Suite.

Representative data for some of the more evolved granites of the Jamon, Serra dos Carajás and Velho Guilherme Suites (Tab. 3; Fig. 5) show that they are metaluminous to peraluminous (Fig. 5A), are geochemically similar to Phanerozoic intraplate granites (Pearce *et al.* 1984; Fig. 5B), and have A-type characteristics (Whalen *et al.* 1987; Fig. 5C) of the A2 subtype (Eby 1992; Fig. 5D). They are ferroan granites with $\text{FeOt}/(\text{FeOt} + \text{MgO}) > 0.8$ (Fig. 5E), and are either reduced (Serra dos Carajás and Velho Guilherme Suites) or oxidized (Jamon Suite). Silica concentrations are $> 65\%$ (Tab. 3), and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios usually plot between 1.0 and 2.0, with a progressive increase in the sequence Jamon – Velho Guilherme and Serra dos Carajás (Dall'Agnol *et al.* 2005).

REE patterns have low (La_N/Lu_N) ratios, and moderate to large negative Eu anomalies (Tab. 3), in general becoming more prominent from the less to the more evolved facies. According to Dall'Agnol *et al.* (2005), the more prominent negative Eu anomalies are found in specialized syenogranites of the Velho Guilherme Suite and in leucogranites of the Serra dos Carajás Suite. Although the general form of the geochemical characteristics of the Rio Branco granite are similar to those found for the anorogenic granites, its affinity with reduced A-type granites (Fig. 5F; Dall'Agnol & Oliveira 2007) and its gull-wing REE pattern (Fig. 6) places it closer to the Velho Guilherme Suite.

Zircon compositions also contribute to the comparisons through the Hf concentrations and the Zr/Hf ratios (Lamarão *et al.* submetido). The mean concentration of Hf (3.5%) and the mean Zr/Hf ratio (15.5) found for the Rio Branco granite are higher and lower, respectively than the means encountered if the oxidized Jamon and moderately reduced Serra dos Carajás Suites (Hf = 2.1 and 3.1%, and 25.0 and 19.0, respectively). The Rio Branco zircons

Figure 8. Frequency polygon and comparative table of opaque minerals in the Rio Branco granite and anorogenic suites of the Carajás Province. Data for the latter are based on Magalhães *et al.* (1994) and Dall'Agnol *et al.* (2005). Tmt: titanomagnetite; BSG: biotite syenogranite; ABMG: amphibole-biotite monzogranite; ABMP: porphyritic amphibole-biotite monzogranite; MT: modified monzogranite; Ilmenite types: I – individual; C – composite; T – trellis; S – sandwich.

are slightly richer in Hf than those from the stanniferous granites of the Velho Guilherme Suite (mean Hf concentration = 3.3%, mean Zr/Hf ratio = 16.6), although syenogranites of the Bom Jardim granite, one of the members of this suite, has Hf concentrations up to 5.4%, and associated greisens have Hf concentrations of 5.9%, resulting in Zr/Hf ratios of 8.2 and 7.0 (Lamarão *et al.* submetido).

The characteristics of the Rio Branco granite show that it has potential for tin mineralizations, although so far none have been discovered. It may be that, although it shows favorable characteristics, some at present unknown factor, perhaps the lack of a source rock sufficiently rich in tin which would have allowed its concentration during the magmatic evolution, impeded the formation of mineralizations.

CONCLUSIONS

- The Rio Branco Granite, a Paleoproterozoic stock intrusive on Archean Cruzadão Granite, was partially affected by albitization and greisenization.
- SM data, together with mineralogy (absence of magnetite and titanite) and geochemistry — high FeOt/(FeOt + MgO) — show that Rio Branco granite was formed in low oxygen fugacity, below to FMQ tampon. The data suggest similarities with granites of the Velho Guilherme suite or, subordinately, Serra dos Carajás suite. On the other hand, differ from Jamon suite.

Figure 9. Histogram of Zr/Hf ratios in zircon from the Rio Branco Granite compared to those found for zircon in the anorogenic suites. Total numbers of analyses are given in brackets.

- The Rio Branco show geochemistry signature of anorogenic, intraplate and A-type granites.
- The geochronology data indicate a Paleoproterozoic age for crystallization of Rio Branco Granite as those of anorogenic suites of Carajás Province.

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