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Contribution to the understanding of the Rondonia Tin Province granites (SW Amazonian Craton) origin using U-Pb and Lu-Hf in zircon by LA-ICP-MS: implications to A-type granite genesis

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Abstract

The study of granite rocks is important in order to understand chemical evolution of the continental crust. Their isotopic composition provides information on their magmatic sources, whether being mantle, crust or a mixture of both. In the SW border of the Amazonian Craton, suites of rapakivi granites related with tin-polymetallic mineralization are emplaced within heterogeneous Proterozoic crust. Zircons from eleven rocks from three granite intrusions, Massangana, São Carlos and Caritianas, representative of the Younger Granites of Rondônia have been studied by using laser ablation inductively coupled plasma source mass spectrometry (LA-ICP-MS) in order to obtain U-Pb ages and Hf isotopic compositions. The samples from Massangana massif, show greater range in age (between 1026 – 993 Ma) and initial $^{176}\text{Hf}/^{177}\text{Hf} = 0.2817\text{--}0.2823$. The ϵHf values are both negative and positive (-6.2 to +3.4) in some samples, and only negative in others (-14.1 to -1.6) which reflects the heterogeneity of sources. The TDM age varying between 2.40 to 1.61 Ga also indicates that different sources were involved in the formation of these rocks. The samples from São Carlos massif show U-Pb ages between 996 to 974 ± 10 Ma and initial ϵHf between -15 and +11, corresponding to a TDM age range between 2.65 and 1.08 Ga. The samples from Caritianas massif with U-Pb ages of 1001 and 999 Ma, show more initial ϵHf positive values (13 zircon grains) than negative (6 zircon grains), different from the other massifs. The range of initial ϵHf of the Caritianas massif is -1.5 to +8.2, and residence crustal ages between 1.76 and 1.25 Ga. The great variation in the ϵHf values indicates heterogeneity of sources; the Massangana and São Carlos massifs represent mainly crustal melts with a subordinate mantle contribution. The Caritianas massif, which shows more positive values of the ϵHf parameter, seems to have had more mantle contribution than the other massifs studied here. The characterization of the sources of the rapakivi rocks may play an important role in the genesis of cassiterite ore and could represent an important tool for mineral exploration.

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1. Introduction

Granite rocks are formed in different tectonic environments and are important to understanding of the evolution of the continental crust. Suites of rapakivi granites are described in almost all the cratonic provinces in the world (Rämö and Haapala 1995; Anderson and Bender 1989; Dall'Agnol et al. 1999; Bettencourt et al. 1999; Scandolara et al. 2013; Geraldès et al. 2014) and occur mainly in the Paleo and Mesoproterozoic eras. The origin of these granites is still controversial; however, there is a consensus in the literature that rapakivi granites are A-type granites with high SiO_2 concentrations, low LILE/HFSE ratios and are preferentially related to intraplate environment or

rift zone (Goodge and Vervoort 2006). They are metaluminous to peraluminous, with high concentrations of light REE (Bonin 2007) and present Sn mineralization and other minerals with economic value.

Rondonia Tin Province is an example of rapakivi granites related with tin ore deposits. It has been studied for at least 50 years; however, there are still gaps to be filled, such as the source of the magmas that resulted in the formation of these rocks and their relationship with mineralization.

In the present study, three intrusions were studied: Massangana, São Carlos and Caritianas massifs, all belonging to the Younger Granites of Rondonia suite, and they have been analyzed by laser ablation inductively coupled plasma source mass spectrometry (LA-



ICP-MS) yielding zircon U-Pb ages and Hf isotopic compositions. These intrusions are related with important tin deposits from Rondônia state besides other minerals of economic interest and commodities, such as Nb, Ta, W, beryl and topaz.

The isotopic composition of zircon is a good tool for defining sources and genesis of granitic rocks (Goodge and Vervoort 2006). Zircon provides a unique opportunity for determining both U-Pb age and Hf isotope compositions in individual crystals and the model ages are also easily calculated and provide useful qualitative data, but they are not true ages and should be interpreted carefully (Vervoort 2014).

In this paper, we use U-Pb and Lu-Hf in zircon grains to gain insights into the evolution of the Younger Granites from Rondônia state and their host rocks. This data allowed us to identify the U-Pb age and the Lu-Hf signature of the Massangana, São Carlos and Caritianas massifs contributing to understanding the magmatic evolution of these intrusions in the geologic context which they are inserted in and to delimit possible sources of the magmas involved in these rocks' formation. This study intends to fill a gap in the geochronological and isotopic data in this region, contributing significantly to improve the A-type magma process generation.

2. Regional Geology

The Amazonian Craton (AC) is one of the largest cratonic areas in the world (about 4.3×10^5 Km²) divided into two Pre-Cambrian shields, the Guaporé and Guiana Shields, separated by the Amazonas Sedimentary Basin (Tassinari and Macambira 1999). Studies of the tectonic compartmentalization were conducted in the Amazonian Craton during the last forty years including geophysical, geochronological, isotopic and geological data (Cordani et al. 1979; Teixeira et al. 1989; Tassinari et al. 1996; Tassinari and Macambira 1999; Tohver et al. 2006; Teixeira et al. 2010, 2015).

Tassinari and Macambira (1999) based on Rb-Sr, K-Ar ages, Sm-Nd (model ages), and zircon U-Pb methods, structural trends, lithology, and geophysical evidence subdivided the AC into six major geochronological provinces: The Central Amazonian Province, the continental crust older than 2.3 Ga, divided into two domains: Carajás-Iricoumé Block and the Roraima Block. The other five provinces: Maroni-Itacaiúnas (2.2 to 1.95 Ga); Ventuari-Tapajós (1.95 to 1.8 Ga); Rio Negro-Juruena (1.8 to 1.55 Ga); Rondoniana-San Ignacio (1.55 to 1.30 Ga) and Sunsás (1.30 to 1.0 Ga) were considered mobile belts formed by reworking the pre-existing crust with accretion of juvenile magma and the two younger are interpreted as orogenic events of ensialic nature.

New geochronological reports (i.e. zircon U-Pb TIMS and SHRIMP) add important information about geologic evolution of the AC coupled with Rb-Sr and Sm-Nd isotopes, Santos et al. (2000, 2008) suggested a new division for the AC in eight geotectonic provinces. The Carajás Province (3.0 to 2.5 Ga) was created through dismemberment of the Central Amazonian Province (Archean); the Transamazonian Province (2.26 to 2.01 Ga) replaced the Maroni-Itacaiúnas, modification of the Ventuari-Tapajós Province to Tapajós-Parima (2.03 to 1.88 Ga) and integration of part of its terrain to the Rio Negro Province, division of the Rio-Negro Juruena Province into Rio Negro and Rondônia-Juruena Provinces (1.82 to 1.54 Ga) and inclusion of the Rondonian-San Ignacio Province into Sunsás Province (1.45 to 1.10 Ga) (Tassinari et al. 1996).

The Massangana, São Carlos and Caritianas massifs, the focus of this study, belong to the youngest rapakivi granites of the

Rondônia Tin Province, which intruded the polymetamorphic rocks of the Jamari Complex and Serra da Providência Suite, located in the Southwest portion of the AC, Rio Negro-Juruena Geochronological Province (Tassinari 1996; Tassinari and Macambira 1999) (Figure 1).

The SW portion of the AC is marked by extensive areas of crustal weakness with preferential trends WNW-ESE that characterize an evolution of an intraplate strike-slip deformation belt (Okida 2001; Santos et al. 2007). Through remote sensing, gamma-spectrometry data, geochronological, petrologic and structural data, these authors identified three deformation phases in the SW portion of the AC with tectonic compressive regime during the Meso- to Neoproterozoic. These structural features present transtensive and transpressive characteristics that provide favorable conditions for the emplacement of granitic bodies of different ages through thinning crustal and formation of rhombus-chasms, releasing-bends, pull-apart structures and others. Also, they are related to Rio Negro Juruena (1.8 to 1.55 Ga), Rondoniana-San-Ignacio (1.55 to 1.30 Ga) and Sunsás orogenies (1.30 to 1.0 Ga), respectively. The last one is also correlated with the Grenville Orogeny and related, by the aforesaid authors, to the emplacement of the Massangana massif.

The Rondônia-Juruena Province, where the plutons here studied intruded, is divided in three tectonic units named Roosevelt and Jamari terrains and Nova Brasilândia belt, which separates both terrains. The Jamari Complex is the metamorphic part of the Jamari Terrain and represents the host rock of major part of rapakivi granites from Rondônia Tin Province. The Jamari Complex is composed by two rock suites: (1) alkaline to subalkaline orthogneisses with medium and high K, represented by quartz diorite, tonalite, granodiorite and quartz monzonite formed in continental margin magmatic arc (Scandolaro 2006) and (2) metasedimentary younger rocks which are interpreted as an immature depositional sequence deposited in back-arc basin (Santos et al. 2000).

Geochronological data from Payolla et al. (2002), Scandolaro (2006), Scandolaro et al. (2013), Santos et al. (2008) indicate that the igneous rocks from the Jamari Complex crystallized between 1.76 and 1.74 Ga, and the sedimentary rocks between 1.67 to 1.65 (Santos et al. 2008) or 1.7-1.68 Ga (Scandolaro 2006).

Other studies (Rizzotto and Quadros 2004; Quadros and Rizzotto 2007) restricted the term Jamari Complex just to the ortho derivative rocks (orthogneisses, tonalites and quartz diorites) with subordinated intercalations of enderbite lenses, calc-silicate gneisses and rare amphibolites, while the metasedimentary rocks, such as biotite-sillimanite-garnet gneisses, sillimanite-biotite schist and quartzites belonged to another lithostratigraphic unit called Quatro Cachoeiras Suite.

The rocks of the Jamari Complex occur in layers alternated by frontal and oblique push that evolved to transcurrent. The rapakivi granites of Rondônia have intruded this complex during several episodes, ranging from 1.60 to 0.97 Ga. Most rocks of Jamari complex and Serra da Providência Suite from central-north part of the Rondônia state were metamorphosed during 1.35-1.32 Ga due to the Candeias collision (Santos et al. 2008). The rocks of Jamari Complex show Paleoproterozoic metamorphism: 1.68-1.64 Ga (Scandolaro 2006).

The Serra da Providência Suite (SPS) is an elongated batholith with extension of 140 km and several satellite bodies intruding rocks of the Jamari Complex and Quatro Cachoeiras Suite. Rizzotto et al. (1995) recognized four main granite units: porphyritic monzogranites (with or without rapakivi texture) with subordinate viborgites, equigranular syenite and porphyritic granite. Later, Bettencourt et al. (1999) characterized SSP as an

AMCG association (anorthosite-mangerite-charnockite-granite). Two types of mafic rocks occur associated with SSP in the form of dykes and small stocks: gabbro-norites and hornblende gabbros (Scandolara et al. 2013)

Ages obtained by the U-Pb method (SHRIMP), indicated crystallization ages between 1554 ± 47 Ma and 1606 ± 24 Ma (Bettencourt et al. 1999). Sm-Nd isotopic features indicated heterogeneous sources, with both crustal and mantle contribution to SSP formation (Scandolara et al. 2013). Recently, Costa et al. (2016) described wiborgites/piterlites and granophyric syenogranites, leucosyenogranite facies and porphyritic rhyolites in Serra da Providência suite. Also, U-Pb LA-MC-ICP-MS zircon ages of 1574 ± 9 Ma and 1604 ± 3 Ma were obtained for these rocks.

3. Rapakivi granites: comparison between other locations and the Rondônia Tin Province

Rapakivi granites are A-type granites that occur in large to giant batholiths (the area can be greater than a hundred square kilometers) distributed along the geological history of our planet mainly at the end of Paleoproterozoic and beginning of Neoproterozoic (generally from 1.8 to 1.0 Ga), although there are also granites in Archean and Phanerozoic considered as rapakivi provinces (Larin 2009; Haapala and Rämö 1999). They occur in almost all the continental

platforms in the world but are not regularly distributed and appear more frequently in the Eastern Europe and North and South America (Geraldes et al. 2000).

The term rapakivi refers to a porphyritic texture in granite rocks where alkali feldspar phenocrysts are preferential ovoid, most (not all) are mantled by a rim of oligoclase-andesine and the alkali feldspar and quartz crystallizes in two generations (Vorma 1976). The study of classic rapakivi granite plutons in the Baltics and North America (Rämö and Haapala 1995; Frost and Frost 1997; Anderson and Bender 1989; Anderson and Morrison 2005; Goodge and Vervoort 2006) showed that the term rapakivi is better related to rocks with chemical and tectonic similarities than a texture itself. Other relevant point is that mostly granites defined as rapakivi do not have the typical rapakivi texture (viborgite and piterlite), thus the most appropriate and used definition of rapakivi granites is that "Rapakivi granites are A-type granites of large batholiths, which include varieties with the rapakivi texture" (Haapala and Rämö 1999).

The characteristics of A-type rapakivi granites include a post tectonic or anorogenic emplacement, bimodal magmatic association, specific mineral association and chemical content which includes high Fe content in ferromagnesian silicates and enrichment in incompatible elements such as Sn, F, Nb, Ta, Au, Fe, U and REE.

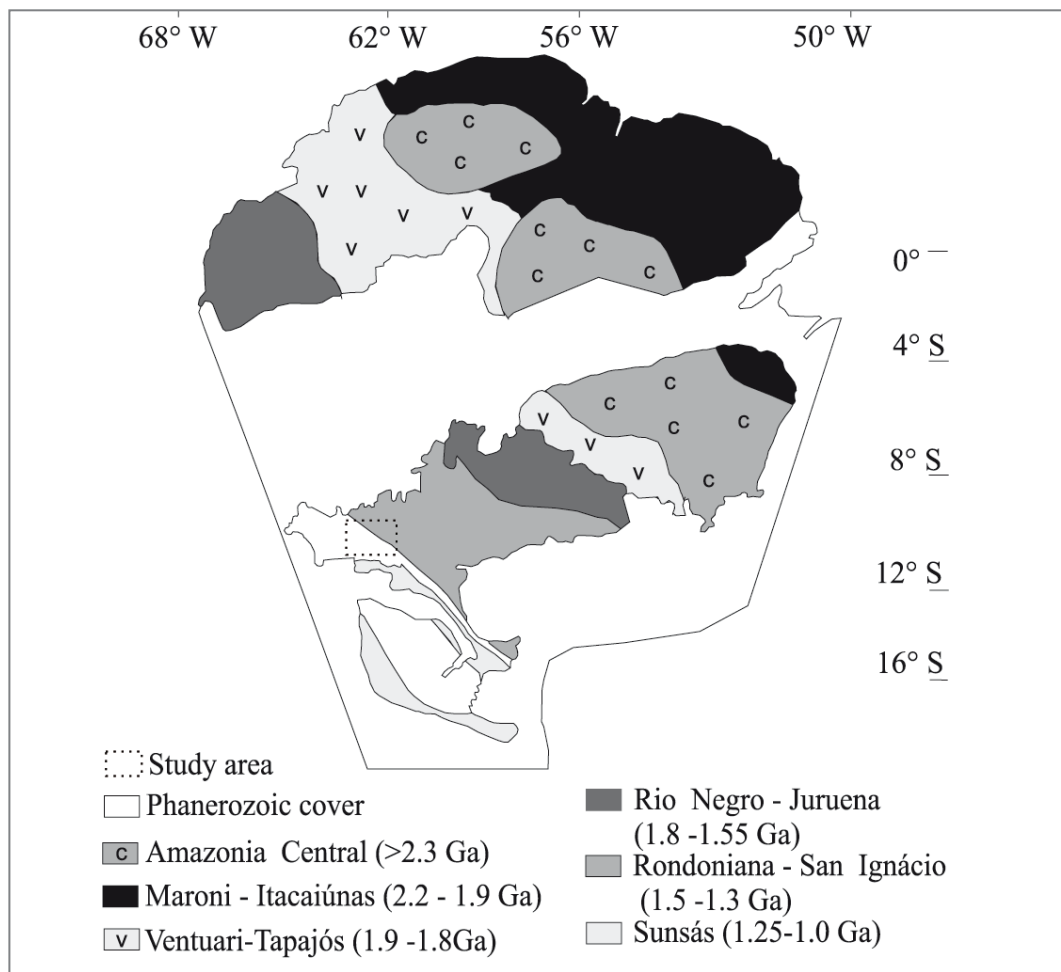


FIGURE 1 – Subdivisions of the Amazonian Craton according to Tassinari and Macambira (1999). The black-dotted rectangle shows the localization of the central portion of the Rondônia Tin Province

4. Local Geology

The rapakivi granites from Rondônia are related with cassiterite, Nb, Ta, W deposits, besides beryl and topaz. This region underwent intense rudimentary mining exploration in the 60s and 70s. Encouraged by the state and federal governments, private companies also started sending their geologists to study this promising new area. Kloosterman (1967) was one of the first geologists to describe several rapakivi granite bodies in the central part of Rondônia and compared them to the Younger granites of Nigeria, naming these granites as Younger Granites of Rondônia (YGR). The YRD show particular features like high fluorine concentrations instead of boron and the association to a volcanic-plutonic system, typical of subvolcanic environment as well as the presence of concentric ring structures aligned with the general direction NNE-SSW (Kloosterman 1967).

The evolution and comprehension of Rondônia Tin Province came with the advent of new geochronological and petrography data (Leal et al. 1976; Isotta et al. 1978; Bettencourt et al. 1999, 1995). In that time, other intrusive bodies with rapakivi textures, including the Serra da Providência batholith were described and the region of Rondônia was recognized as an example of anorogenic rapakivitic magmatism.

Bettencourt et al (1999) proposed the division of the Rondônia tin province into eight intrusive suites: (1) Serra da Providência (ca. 1.6 to 1.5 Ga) and (2) Rio Crespo (ca. 1.5 Ga) are composed of rapakivi granites, charnockite, mangerite and subordinate mafic rocks (Bettencourt et al. 1999; Payolla et al. 2002; Scandola 2006, Scandola et al. 2013); (3) Santo Antonio (1406 ± 32 Ma), (4) Teotônio (1387 ± 32 Ma), (5) Alto Candeias (1346 ± 5 Ma), (6) São Lourenço-Caripunas (1309 ± 24 Ma), (7) Santa Clara (1081 ± 50 Ma) and (8) Rondônia (998 ± 4 Ma) are characterized by syenogranites, monzogranites, microgranites and microsienites with subordinated alkali-feldspar granites and volcanic bodies with rhyolites and traquites in some suites. The Massangana, São Carlos and Caritianas massifs, studied here, belong to the youngest intrusive suite, which also includes the massifs of Palanqueta/Bom Futuro, Santa Bárbara, Ariquemes and Pedra Branca.

The Massangana massif is a large batholith (> 900 Km²) described by Romanini (1982) as a complex and not a massif because of its multiphase magmatism, and named the magmatic facies as Massangana, São Domingos, Bom Jardim and Taboca according to local names (Fig. 3). Romanini (1982) described the Massangana facies as the largest in area (about 80% of the total area of the complex) and identified the rocks as granites with porphyritic to pegmatitic, locally presenting coarse granulation, with microcline as the principal feldspar. Locally orthoclase is found as well. The São Domingos facies occurs arranged in a semi-parallel manner to the regional lineament of the Jamari Complex and occurring in contact with the Massangana facies. The São Domingos facies is composed of granular granites of fine to pegmatite granulation, very similar to those of Massangana facies.

The Bom Jardim facies constitutes an ellipsoidal "stock" with irregular contours and diameter of about 10 km, intruded in the Massangana facies through abrupt and interpenetrative contacts, with numerous enclaves of different lithotypes. It presents a wide textural variation, from microgranular to porphyritic granites, as well as microgranite dykes, mainly in the central part of the stock.

The Taboca facies is characterized by syenites, intruded in the Bom Jardim and São Domingos facies, but field relationships were not conclusive. The petrographic variations mainly include

syenite, quartz-syenites and quartz-monzonites. Romanini (1982) related the tin deposits of Massangana massif to Bom Jardim and São Domingos magmatic facies, being more notable in the latter. They occur in quartz and greisen veins and are more intense in the contacts with the host rocks, evidenced by strong greisenization. Quartz shafts with cassiterite, topaz and fluorite are described in the central part of São Domingos "stock".

The São Carlos massif with an area of about 290 km² is an elongated shape following the NNE regional trend showing abrupt contact with the host rocks in the northern and western portions and to the southeast, the contacts are apparently of tectonic nature (Payolla et al. 2002).

According to Okida (2001), at least three sub alkaline granitic units make up the São Carlos massif: biotite hornblende alkali-feldspar granite with medium to coarse granulation, biotite syenogranite porphyritic to equigranular and biotite syenogranite of fine to medium granulation that corresponds to the most expressive association in the area. Boiler collapse structures with about 10 km in diameter are partially preserved in the center of the massif. This structure is composed of a discontinuous ring-dyke of quartz-feldspar porphyry in the outer portion and subvolcanic alkaline rocks, amphibole-clinopyroxene melasyenite, clinopyroxene microsienites, microgranites, porphyry rhyolites and mega xenoliths of sub-alkaline granites besides gneisses in the portion which have a lower topography (Payolla et al. 2002).

In the Caritianas massif, Romanini (1982) identified two principal granite units: the first one consists of a medium granulation equigranular granite composed of biotite and alkali-feldspar with granodiorite enclaves and the second one is a biotite alkali-feldspar porphyritic granite. These granites have miarolitic cavities and are cross-cut by dykes of microgranites, aplite and pegmatites. There are also greisen and quartz veins distributed widely in the massif, mainly in the center-south portion where secondary tin deposits are found. According to Bettencourt et al. (1995) the Caritianas massif is one of the most productive in Sn, Nb and Ta, and therefore different from the São Carlos Massif.

5. Analytical procedures

Eleven samples were selected for U-Pb and Lu-Hf analysis, five from Massangana massif, four of São Carlos and two from Caritianas. Sample preparation was carried out in LGPA (Geological Laboratory Sample Processing) located at the State University of Rio de Janeiro (UERJ). Zircon grains were separated from crushed fresh samples by using gravimetric and magnetic separation method and hand picking under a binocular microscope. After collected, the zircon grains were mounted in epoxy resin disks and polished to expose the zircons to be analyzed.

Zircon U-Pb and Lu-Hf trace element analyses were conducted by laser ablation inductively coupled plasma spectrometry (LA-ICP-MS) housed at Multilab laboratory of State University of Rio de Janeiro, Brazil. The configurations of the multi collectors and faraday cups for the U-Pb and Lu-Hf methods are detailed in Tables 1, 2 and 3. The Neptune Plus is coupled to a laser ablation Photon Machines Inc, 193 mm with a high precision photographic camera and has the capacity to pulverize the material in many different spot sizes (4 µm - 110 µm). The isotopic ratios and ages of ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U. Tables 1-3 present multi collector configuration for U-Pb analyzes.

The Laser ablation spot diameter and frequency used in the analyses of this study was set to be 20 to 30 µm and 8 to 9 Hz

Table 1: ICP-MS multi collector configuration for U-Pb analysis

Collectors	IC-5	IC-4	IC-3A	IC3B	IC A	Central	H3	H4
Isotope	²⁰² Hg	²⁰⁴ Pb	²⁰⁵ Pb	²⁰⁷ Pb	²⁰⁸ Pb	Virtual	²³² Th	²³⁸ U
Interference		²⁰⁴ Hg				mass		

Table 2: ICP-MS faraday configuration for Lu-Hf analysis

Collectors	L4	L3	L2	L1	C	H1	H2	H3	H4
Isotope	¹⁷¹ Yb	¹⁷³ Yb	¹⁷⁴ Hf	¹⁷⁵ Lu	¹⁷⁶ Hf	¹⁷⁷ Hf	¹⁷⁸ Hf	¹⁷⁹ Hf	¹⁸¹ Ta
Interference		¹⁷⁴ Yb		¹⁷⁶ (Yb+Lu)		mass			

Table 3: LA-ICP-MS U-Pb and Lu-Hf analytic conditions during analysis performed for this study

Tune Conditions:	U-Pb	Lu-Hf
High Vacuum (pressure <):	2.15 to 2.4 x 10 ⁻⁷ L/min	1.92 to 2.17 x 10 ⁻⁷ L/min
Fore Vacuum (pressure <):	1.86 to 1.95 x 10 ⁻³ L/min	1,86 to 2.03 x 10 ⁻³ L/min
Sample gas:	0.789 a 0.830 L/min	0,811 a 0,981 L/min
Laser:		
Repetition :	8 a 9 Hz	10 Hz
Laser Energy:	30 %	65 and 70%
Spot size:	20 a 30 µm	50 µm

for U-Pb analyses and 50 µm and 10 Hz for Lu-Hf analyses and Helium gas flow of 0.550 L/min for MCF1 and 0.200 for MCF2. The external standard used was the Harvard zircon 91500 with a recommended ²⁰⁶Pb/²³⁸U age of 1065.4 ± 0.6 Ma (to correct mass bias and depth-dependent isotopic fractionation. The standard zircon GJ-1 (GEMOC, Macquarie University, Australia) was used to optimize the instrument. The value of the crustal ¹⁷⁶Hf/¹⁷⁷Hf ratio used to calculate the Hf-TDM model age was 0.015. The Lu decay constant used was (1.867 x 10⁻¹¹/yr) of Söderlund et al. (2004), the Chondritic values of ¹⁷⁶Hf/¹⁷⁷Hf = 0.0336 and ¹⁷⁶Lu/¹⁷⁷Hf = 0,282785 (Bouvier et al. 2008), the model depleted mantle with present day ¹⁷⁶Hf/¹⁷⁷Hf ratio of 0.28325 and ¹⁷⁶Lu/¹⁷⁷Hf ratio of 0.0388 (Griffin et al. 2000, updated by Andersen et al. 2008). Blank and isotope fractionation were corrected by offline spreadsheet.

The Lu-Hf isotopic system is today one of the most innovative and powerful tools in geochronology. This is due to the behavior of these elements in the zircon, mineral that has high concentrations of Hafnium (about 10,000 ppm), low Lutetium-Hafnium (Lu/Hf) ratio and resistance to subsequent isotopic perturbations. These characteristics have turned zircon into an ideal mineral for acquiring U-Pb and Lu-Hf isotopic data, especially if the analyzes are performed by a laser-coupled mass spectrometer (LA-ICP-MS). This tool is becoming popular in the scientific community due to the speed and practicality of combining in situ analyzes of Hf and U-Pb in a single zircon grain, which results in a higher resolution of the information acquired and greater consistency in interpretations (Vervoort 2014; Fisher et al. 2014; Spencer et al. 2016).

The average measured ¹⁷⁶Hf/¹⁷⁷Hf ratios at 2 standard deviations for the standard zircons were: 0.282016 ± 5 for GJ1 (n = 50), 0.282280 ± 80 for 91500 (n=30) and 0,282493 ± 51 for Mudtank (n=30), similar to the Hf values for these same zircons as quoted by Morel et al. (2008), Elhlou et al. (2006), Griffin et al.

(2006), Woodhead and Hergt (2005) and Hergt et al. (2005). In all tables and figures, εHf has been calculated using present-day CHUR values of ¹⁷⁶Hf/¹⁷⁷Hf = 0.282785 and ¹⁷⁶Lu/¹⁷⁷Hf = 0.0336 (Bouvier et al. 2008). For figures with depleted mantle evolution curves, present-day values for ¹⁷⁶Hf/¹⁷⁷Hf of the depleted mantle is 0.283214; and the corresponding value for ¹⁷⁶Lu/¹⁷⁷Hf is 0.0388. The Archean values were derived by averaging the values for early Archean gneisses reported in Goodge and Vervoort et al. (1996), whereas mantle values are from Goodge and Vervoort (2006). Tables information is based on Bertotti et al. (2014) and Bertotti and Chemale Junior (2015).

The data obtained by mass spectrometer were processed using an Excel spreadsheet, where off-line corrections were performed through the blanket procedure, following the sequence: blank, standard GJ1, the nine unknown analyzes, the standard 91500, the standard GJ1 and the blank again. The procedure works in order to correct the average of the final blank by the initial. In addition, GJ1 values are compared with true values (from the literature) in order to calculate a conversion factor that is applied to all nine unknown samples. Finally, the program ISOPLOT (version 4.1.5 of Ludwig 2003) is used to make the concordia diagrams.

6. U-Pb geochronology

We determined the U-Pb ages of 11 samples (Appendix A): five from Massangana massif (BD-MA-08, BD-MA-14, BD-MA-21, BD-MA-27 and BD-MA-32); four from São Carlos massif (BD-SC-45, BD-SC-46, CN-MG-10 and CN-MG-12) and two from Caritianas massif (BD-CT-02 and BD-CT-03). The sample BD-MA-08, collected in the southwest part of the Massangana massif, location that corresponds to the São Domingos magmatic facies of Romanini (1982). The other samples were collected in Massangana magmatic facies, which corresponds to about 80% of the massif extension (Romanini 1982).

The samples chosen for analysis are granites. The samples BD-MA-08, BD-MA-14 and BD-MA-32 of Massangana massif are biotite-granites with pinkish color and medium to coarse granulometry, composed by alkali-feldspar with perthitic texture, xenomorphic quartz and interstitial plagioclase. The biotite, unique mafic mineral, occurs in clusters or interstitial. The sample BD-MA-27 is a yellowish biotite-hornblende-granite with medium granulometry, containing orthoclase and microcline as main feldspar and interstitial plagioclase. Quartz occurs as xenomorphic big grains or interstitial. The accessory minerals are mainly zircon and titanite, and less frequently, in the biotite-granite facies, epidote, topaz, fluorite and apatite. Secondary minerals are sericite and chlorite.

Zircon grains in sample BD-MA-08 are colorless or light pink to brown. The subhedral to euhedral grains show near-spherical or near-prismatic morphology with lengths of ranging from 200 to 400 μm . The majority of the grains shows clear oscillatory zoning with some heterogeneous fracture zones, while the remaining grains show homogeneous composition (Fig. 4). A total of 12 spots from 12 zircons of this rock were used to build the Concordia diagram and the results show Th/U ratio varying from 0.30 to 0.71. The data define an upper intercept age of 993 ± 10 Ma (Fig. 4; MSWD = 0.50).

Zircon grains in sample BD-MA-14 are colorless or brownish and varies from elongated euhedral to short subhedral or broken prisms with lengths of 200-500 μm . Fourteen magmatic zircon grains were used to calculate the Concordia diagram and all of that show oscillatory zoning (Fig. 4). The results show Th/U ratio varying from 0.47 to 0.79 and yielded an upper intercept age of 1005 ± 10 Ma (Fig. 4; MSWD = 0.24).

Zircon grains in sample BD-MA-21 are light brown to brown. The euhedral to subhedral grains show near-prismatic morphology with lengths of 200-600 μm . Most grains show clear oscillatory zoning, mainly concentrated in the grains boundaries (Fig. 3). The results show Th/U ratio varying from 0.30 to 1.06. Fifteen magmatic zircon grains define a concordant cluster with an upper intercept yielding a U-Pb age of 1026 ± 16 Ma. (Fig. 4; MSWD = 0.013).

The zircon grains in sample BD-MA-27 are colorless, brownish and pinkish with fracture domains. The grains are euhedral to subhedral and show near-prismatic morphology with lengths varying from 200-500 μm . Some grains show oscillatory zoning in the whole grain, while others only on the boundaries. Twenty-four magmatic zircon grains from sample BD-MA-27 yielded an upper intercept age of 995.7 ± 9.5 Ma (Fig. 5 MSWD = 0.48) and a Th/U ratio varying from 0.24 to 0.76.

Zircon grains in sample BD-MA-32 are colorless, light brown or pinkish. The euhedral to subhedral grains show near-prismatic or near-spherical morphology with lengths varying from 150-500 μm . Some grains are homogeneous while others shown oscillatory zoning. Fifteen magmatic zircon grains define a concordant cluster with a Concordia age of 1010 ± 12 Ma. The data show Th/U ratio varying from 0.29 to 0.85 (Fig. 5; MSWD = 0.45).

In the São Carlos massif, the samples collected are alkali-granites (CN-MG-12 and BD-SC-45) and biotite-granites (CN-MG-10 and BD-SC-46). Both have alkali-feldspar (orthoclase and microcline) with mesoperthitic texture, besides quartz and interstitial plagioclase. The biotite in biotite-granites occurs are interstitials with brown color or reddish. Both show pleochroic halos because the occurrence of radioactive minerals inside it, like zircon. The secondary minerals are sericite, chlorite and muscovite and in samples from the alkali-granites goethite and titanium oxide also occur.

Zircon grains from São Carlos massif are pinkish to brownish or colorless and range from euhedral to subhedral grains with near-spherical or prismatic morphology with lengths of 100-500 μm . Some grains show intense oscillatory zoning while others do not or show the oscillatory zoning concentrate only on the boundaries. Seventeen magmatic zircon grains from the sample BD-SC-45 were used to calculate the Concordia diagram and the results show Th/U ratio varying from 0.54 to 1.03 and define a concordant cluster with Concordia age of 996 ± 8.2 Ma (Fig. 5; MSWD = 0.67). In sample BD-SC-46, twenty-four magmatic zircon grains are used to calculate the Concordia diagram and the results show Th/U ratio varying from 0.56 to 1.20. The data define an upper intercept age of 992.5 ± 7.7 Ma (Fig. 6; MSWD = 0.31).

Eleven magmatic zircon grains from sample CN-MG-10 define a Concordia cluster with age of 986 ± 12 Ma and the Th/U ratios varying from 0.45 to 1.25. (Fig. 6; MSWD = 0.55). In sample CN-MG-12, a total of sixteen magmatic zircon grains were used to calculate de Concordia diagram. The data show Th/U ratios varying from 0.3 to 1.2 and an upper intercept age of 974 ± 10 Ma. (Fig. 5; MSWD = 0.62).

In the Caritianas massif, the rocks are pink biotite-granites with medium granulometry and have alkali-feldspar with mesoperthitic texture, quartz, plagioclase and biotite as main mineralogy and zircon as the accessory mineral.

Zircon grains in sample BD-CT-02 are colorless to brownish. The grains are normally subhedral with near-spherical boundaries with lengths of 100-500 μm and show internal fracture zones. The oscillatory zonation occurs only in some grains. A total of sixteen magmatic zircon grains were analyzed and result in Th/U ratios varying from 0.45 to 1.06 and define a concordant cluster with a concordia age of 999 ± 12 Ma. (Fig. 6 MSWD = 0.45).

Zircon grains in sample BD-CT-03 are colorless to brownish. Some grains show prismatic morphology, but most are subhedral with near-spherical morphology and/or with the boundaries broken with lengths of 100-400 μm . Some grains show oscillatory zoning, but the majority do not show. Fifteen magmatic zircon grains define a concordant cluster with a Concordia age of 1001 ± 9.8 Ma (Fig. 6 MSWD = 0.65) and Th/U ratios varying from 0.40 to 1.02.

7. Lu-Hf isotopes

We determined Hf isotope compositions for 108 individual zircon crystals from eleven samples: five from the Massangana massif, four from São Carlos, and two from Caritianas. The Lu-Hf isotope compositions of the Rondônia Intrusive Suite granites analyzed in this study are shown in Appendix B, organized by massif and the sample locations of analyzed points are shown in Figure 5.

Most of the samples show both negative and positive values for the ϵHf parameter. The zircon grains from the samples BD-MA-21, BD-MA-27 and BD-MA-32 with U-Pb ages (this work) of 1026 ± 16 Ma, 995.7 ± 9.5 Ma and 1010 ± 12 Ma respectively show both negative and positive values, ranging from -3 to -0.2 and from +0.2 to +3.4. It corresponds to a variation in the TDM age from 2.0 to 1.52 Ga. These samples were collected in an area of the Massangana massif that corresponds to the Massangana magmatic facies, described for Romanini (1982). In sample BD-MA-14, collected in the central-south part of the massif and with crystallization age of 1005 ± 10 Ma, the ϵHf parameter shown only negative values ranging from -6 to -1.5. The depleted mantle age is between 1.73 to 1.57 Ga.

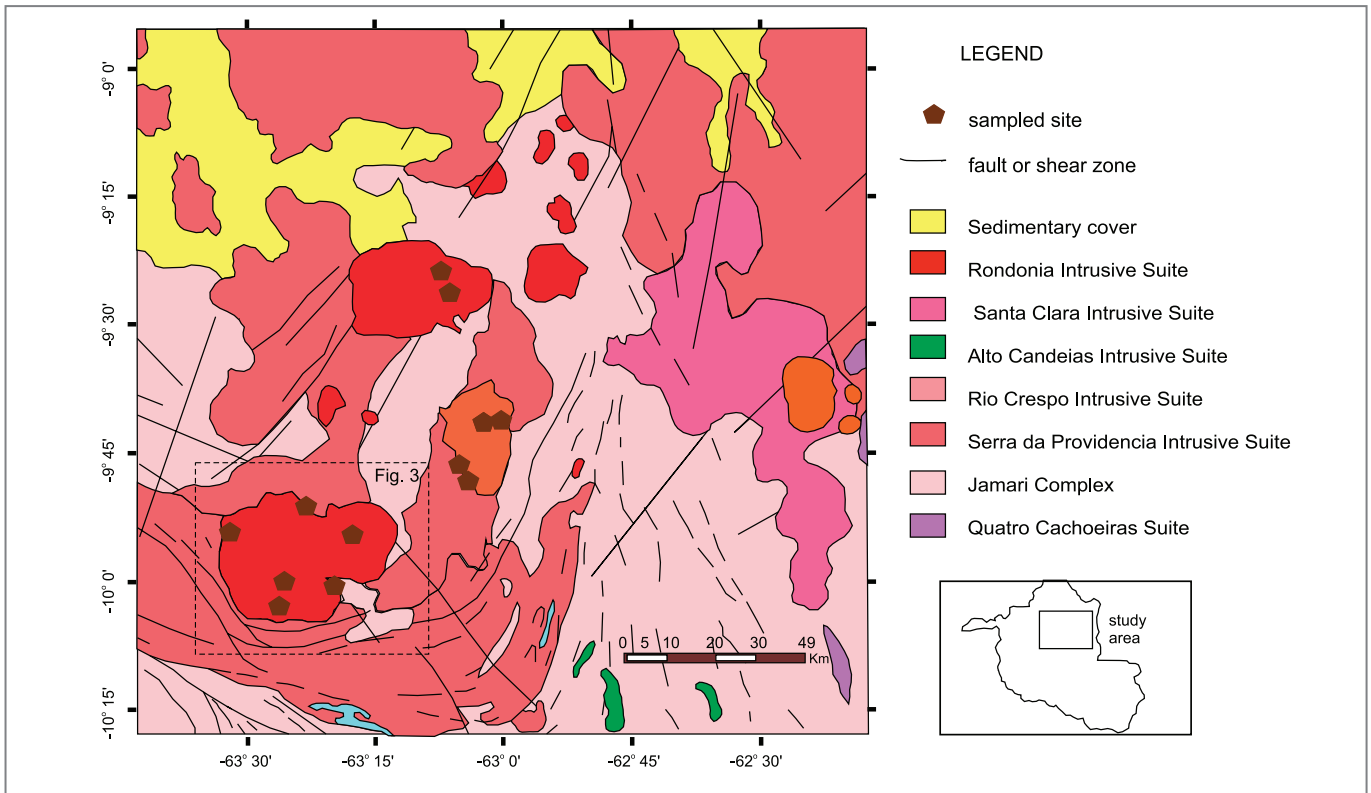


FIGURE 2 – Geologic map of the Rondônia Tin Province showing the points of U-Pb and Lu-Hf isotopic analysis (black stars). Massangana Massif: (A) Massangana magmatic phase, (B) São Domingos, (C) Bom Jardim and Taboca magmatic phases. Adapted and modified from < <http://geosgb.cprm.gov.br/>> and Romanini (1982). Analyzed samples: 1) BD-MA-14, 2) BD-MA-27, 3) BD-MA-08; 4) BD-MA-21; 5) BD-MA-32; 6) BD-SC-45; 7) BD-SC-46; 8) CN-MG-10; 9) CN-MG-12; 10) BD-CT-02 and 11) BD-CT-03

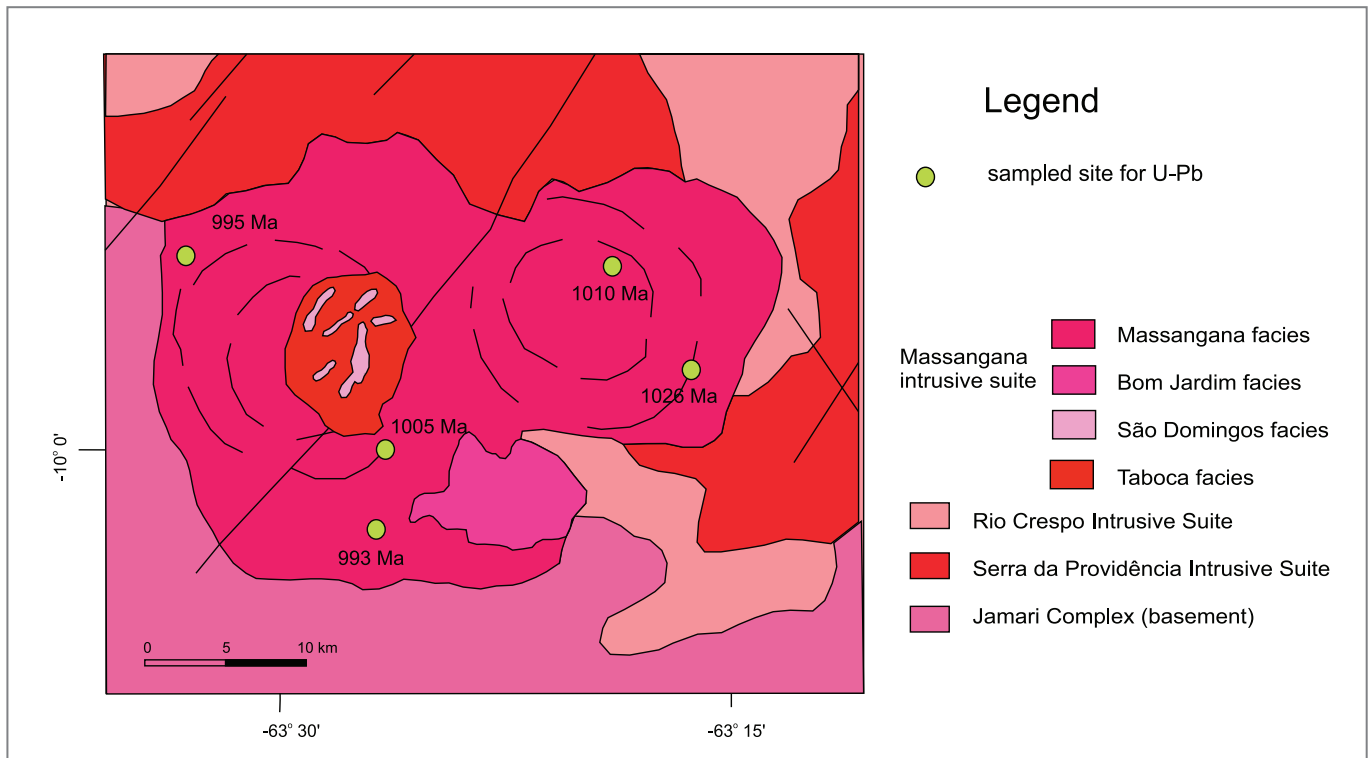


FIGURE 3 – Geologic map from Massangana massif adapted from Romanini (1982) and CPRM (2007) showing the distribution of the analytical points of U-Pb and Lu-Hf analysis.

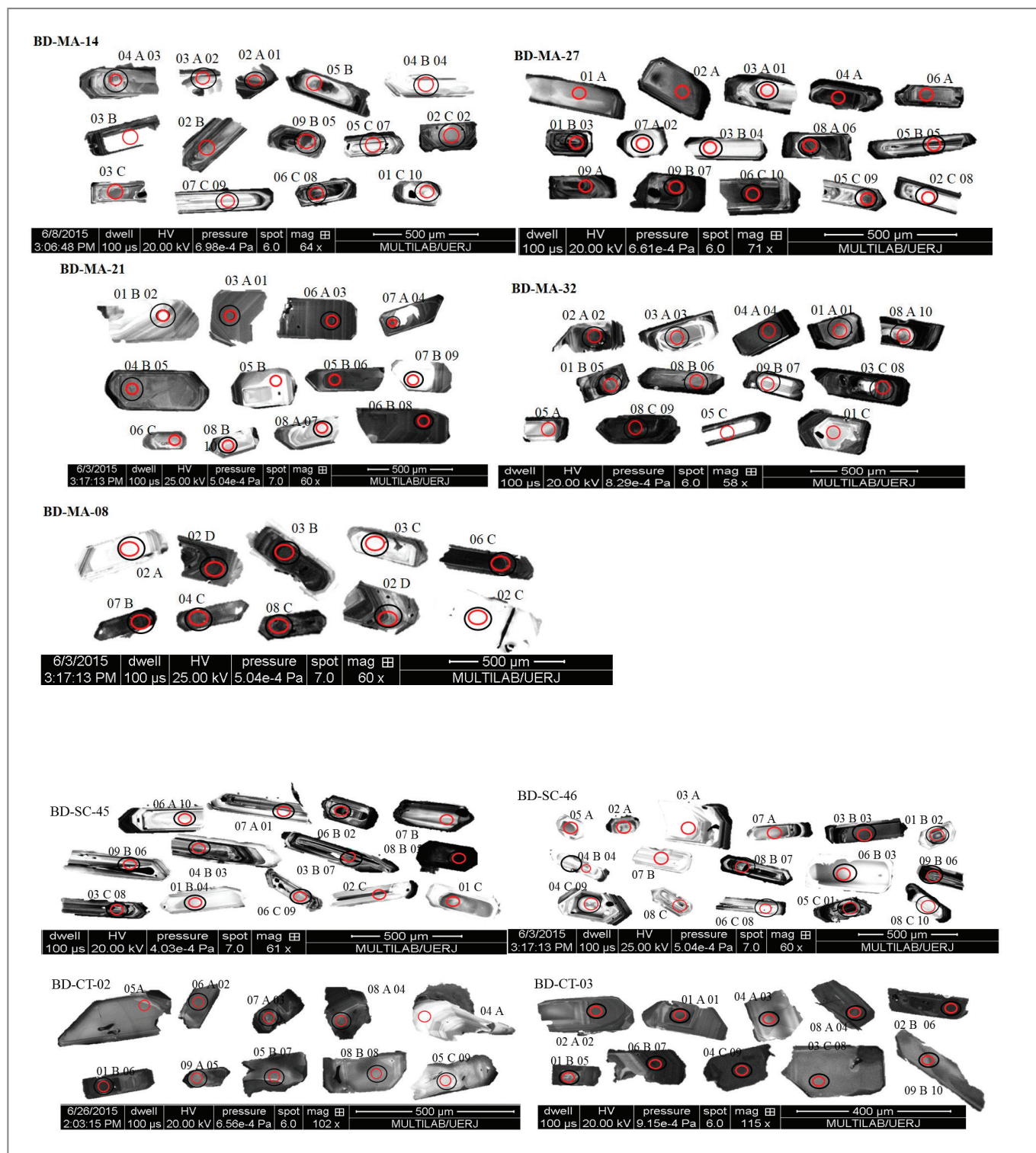


FIGURE 4 – Zircon grains from the Massangana, São Carlos and Caritinas massifs analyzed by LA-ICP-MS. The red circles correspond to the U-Pb analysis and the black ones to Lu-Hf. Note that both U-Pb and Lu-Hf analysis were shot in the same part of the zircon, what guarantees greater coherence in results and interpretations.

The sample BD-MA-08, were collected close from the limit with the São Domingos magmatic facies. This facies is described as the most tin deposits rich in Massangana massif and appears to have a different genetic signature from the rest of the Massangana massif (Romanini 1982). The U-Pb age of this sample reported herein, is 993 ± 10 Ma, and the ϵ_{Hf} values range from -14 to -11, except one zircon with positive value

to this parameter (+5.1). The TDM ages of this crystals were also different from the others, varying from 2.40 to 2.23 Ga, which suggests that an older different crust, not reported in the literature, are responsible for supply magmatic material to this rock, different from of the rest of the massif that has a derivation from 2.00 to 1.52 Ga. The ϵ_{Hf} values variation in the same sample may be due magma mixture/mingling, where the isotopic values

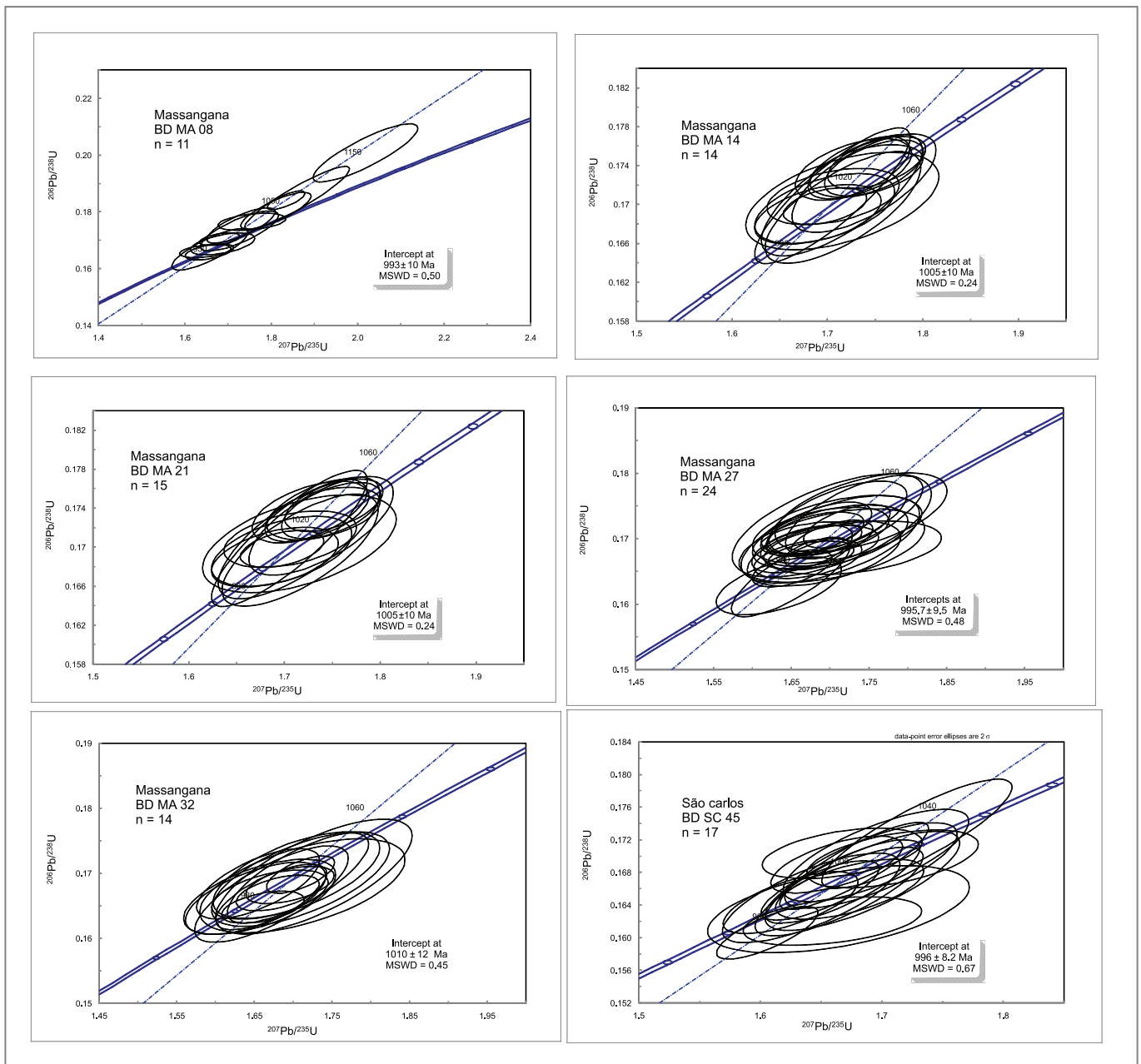


FIGURE 5 – Concordia diagrams showing U-Pb ages in zircon grains from Massangana and São Carlos massifs

from different magmas results in different reservoir within the zircon grain. In this way, an incomplete mixture may result ϵHf values respective to the source of the magmas.

The zircons from São Carlos massif show values to the TDM parameter that suggests an older source than the magmas that formed the Massangana massif. The samples BD-SC-45 and BD-SC-46 collected near the southwest boundary of the massif have present-day Hf isotopic compositions varying from 0.281616 to 0.281959, which correspond to a range in present-day of -19 to -7, a total range of 13 epsilon units. The depleted mantle ages vary from 2.65 to 2.03 Ga, which indicate an older source

The other two samples CN-MG-10 and CN-MG-12 were collected in the central part of the massif. The CN-MG-10 (zircon age: 986 ± 12 Ma) show present-day Hf isotopic compositions varying from 0.281953 to 0.2823458, values that correspond to a range in present-day ϵHf of -8 to +11. The TDM ages varying

from 1.05 to 1.82 Ga, and several zircons show values between 1.56 to 1.62 Ga. The sample CN-MG-12 (zircon age: 974 ± 10 Ma) show present-day Hf isotopic composition varying from 0.281908 to 0.282392, values that correspond to a range in present-day ϵHf of -3 to +7 (one value of -10, that corresponds to the older depleted mantle age of 2.16 Ga) the others show TDM ages varying from 1.30 to 1.81 Ga.

The samples from Caritianas massif showed more positive values to the ϵHf parameter than negative, different from the other massifs here studied. The ϵHf values range between -0.6 and +4.0. The data indicates that these magmas were probably mantle-derived but with important contribution from crustal rocks. The depleted mantle ages vary from 1.74 to 1.69 Ga to the negative and the positive values correspond to TDM ages varying between 1.68 to 1.46 Ga (one value is 1.25 Ga).

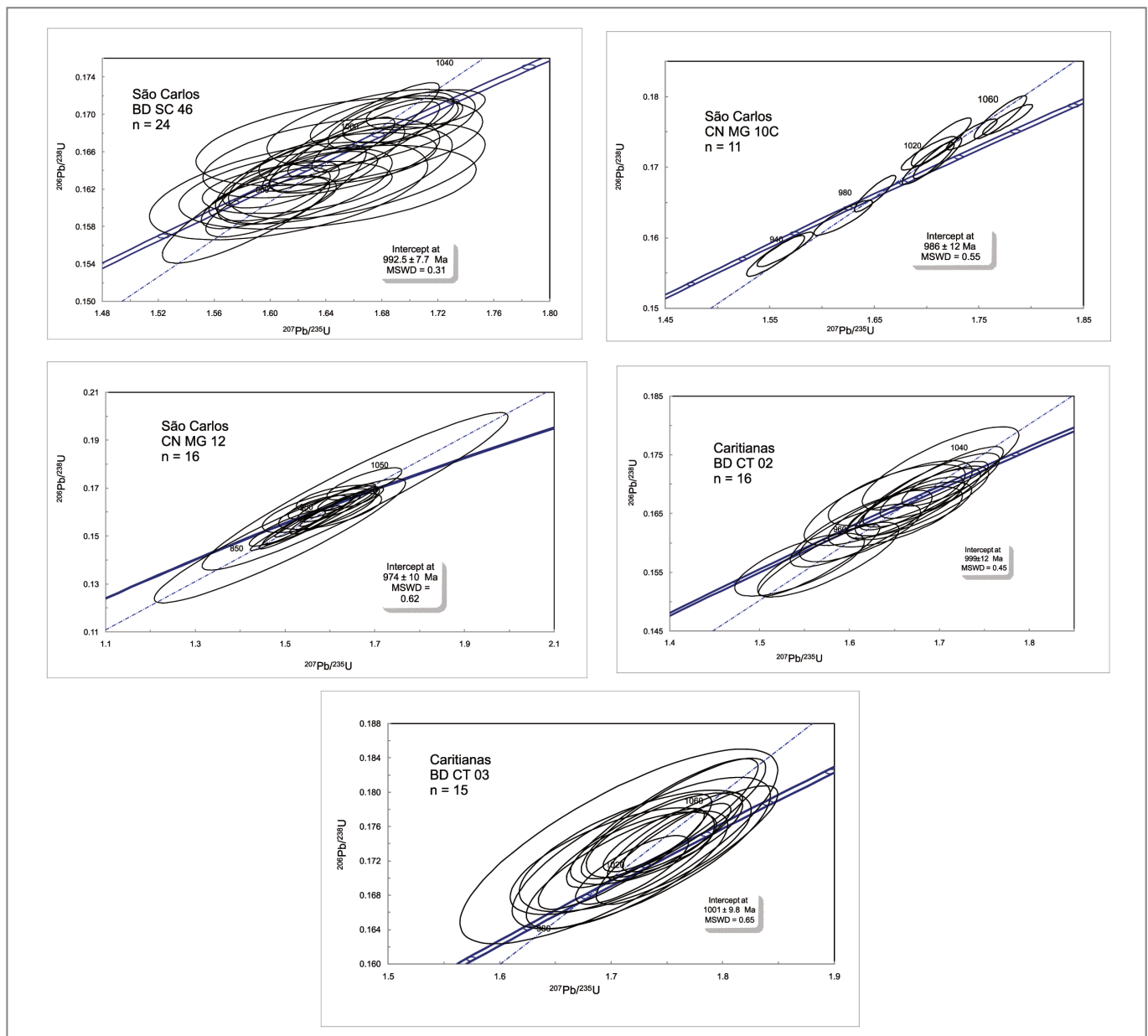


FIGURE 6 – Concordia diagram showing U-Pb ages in zircon grains from the Massangana, São Carlos and Caritianas massifs

8. Discussion

The Massangana, São Carlos e Caritianas massifs from the Younger Granites of Rondônia emplaced in heterogeneous terranes of the SW border of Amazonian Craton. They yield a wide range of Hf isotopic values and Hf-isotope depleted mantle ages reflected the different sources. The U-Pb ages shown that the Massangana massif has different ages (1026 ± 16 Ma, 1010 ± 12 Ma, 1005 ± 10 Ma, 995.7 ± 9.5 Ma and 993 ± 10 Ma) similar to those obtained by Amaral (1974) in K/Ar analysis (1058 ± 33 Ma, 996 ± 25 Ma and 934 ± 24 Ma) and with U-Pb zircon age- 991 ± 4 Ma from Bettencourt et al. (1999).

The older ages found are concentrated in the eastern border and SW portion of the massif and correspond to the Massangana magmatic facies, described by Romanini (1982) as the oldest facies. The sample collected in the area of São Domingos magmatic facies shown U-Pb age of 993 ± 10 Ma, younger than the others from Massangana facies, also suggested by Romanini (1982).

The variation in ϵHf values and TDM ages in the Massangana massif could be a reflection of its multiphasic magmatism and the heterogeneity of sources. The Massangana massif intruded at least three different suites and terrain, represented by the Serra da Providência and Rio Crespo Suites and the Jamari Complex (Fig. 2). This research did not allow us to suggest a specific crustal source (see Fig. 8), instead the mantle component could be confirmed in the ϵHf data from the BD-MA-21, BD-MA-27 and BD-MA-32 samples that show both negative and positive ϵHf values. The sample collected in the area that corresponds to the São Domingos facies has high negative ϵHf values (-14.1 to -11.8) corresponding to a TDM age between 2.40 to 2.23 Ga, one zircon is $+5.1$ with TDM age of 1.41 Ga. The sample BD-MA-14, similar with the data from the São Domingos area, shows only ϵHf negative values and TDM ages between 2.0 and 1.77 Ga.

The lack of records of an ancient crust may be related to the great depth at which this material is placed, so it does not crop in the region of study; or due to the scarcity of detailed

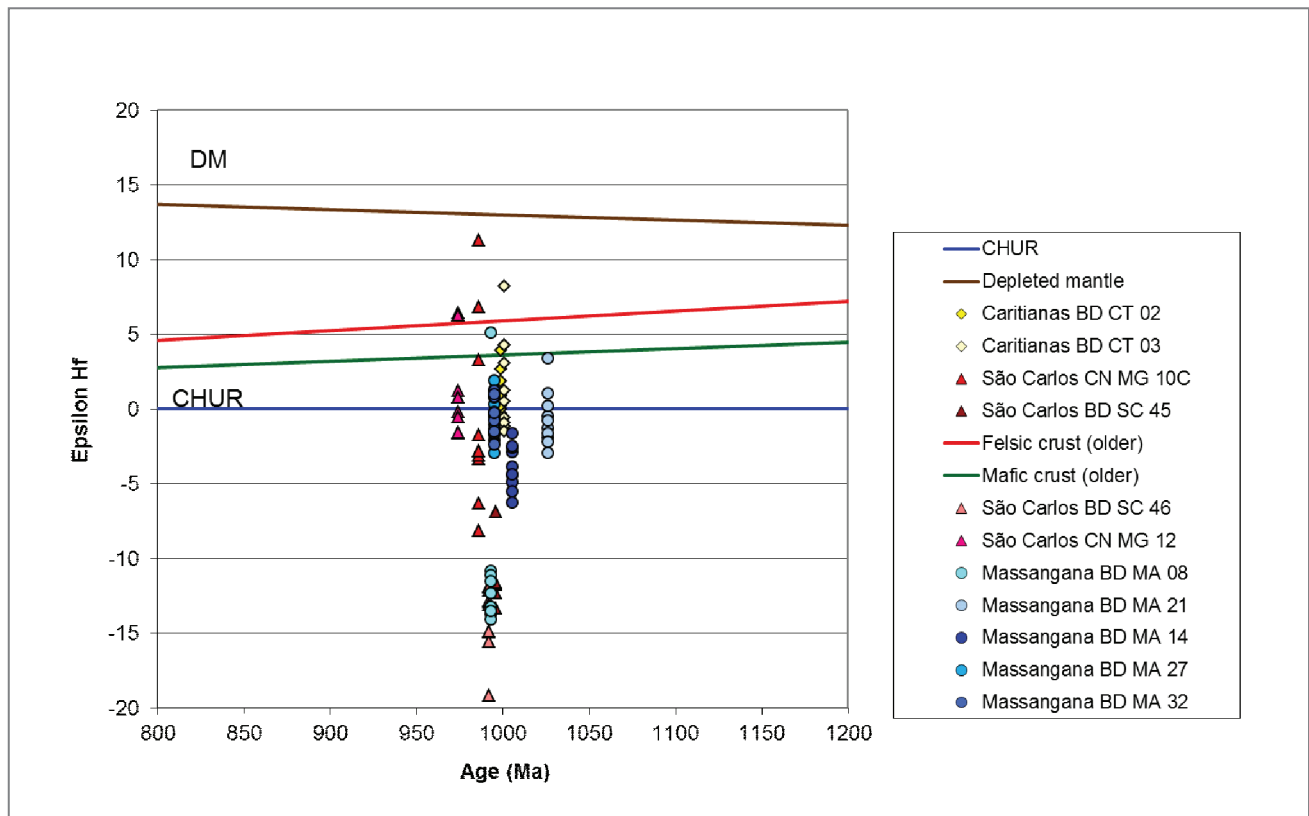


FIGURE 7 – Age vs. ϵ_{Hf} values for the Massangana, Caritianas and São Carlos massifs

geological mapping studies that identify these rocks; or because of the crustal reworking processes that may have consumed all this older crust. In the São Carlos massif, the samples collected in the southwest and central part of the massif shown strict petrographic and geochemical similarities, however they have differences in Hf isotopic compositions. The first group, represented by samples BD-SC-45 and BD-CS-46 with older U-Pb ages (996 ± 8.2 and 992.5 ± 7.7 Ma) presented TDM model ages with a range of 2.65 - 2.03 Ga. The central part of the massif (samples CN-MG-10 and CN-MG-12) shown U-Pb ages of 986 ± 12 and 977 ± 10 Ma and TDM model ages ranging from 2.09 to 1.08 Ga and may represent juvenile mantle sources (positive ϵ_{Hf} values in table 5) with contamination from an older crust (2.44 to 1.81 Ga).

The Caritianas massif shows ϵ_{Hf} negative values between -1.5 to -0.3 corresponding to a TDM model ages range of 1.76 - 1.69 Ga and positive ϵ_{Hf} values between +1.2 to +8.2 with a range of TDM model ages of 1.68 - 1.25 Ga which could be interpreted as product of juvenile mantle melts. However according to Goodge and Vervoort (2006), in this case, they would have ϵ_{Hf} values close to the depleted-mantle evolution curve (values about +10 to +12) and the results of Caritianas massif may indicate a mixture of mantle and crustal sources.

Another relevant aspect is that despite of these granites being defined as intraplate or no orogenic, some authors relate the rapakivi magmatism in Rondônia and other regions on world, like the Baltic Shield (Åhäll and Gower 1997), with the synchronous orogenic events that occurred in the region (Geraldes et al. 2001; Matos et al. 2004; Geraldes et al. 2008; Ruiz et al. 2004); Bettencourt et al. (1999) believe that the youngest granites of Rondônia Tin Province (including Santa

Clara and Rondônia Intrusive Suites) represent an inboard magmatism during a younger episode of reworking in the Rio Negro Juruena Province, during the final stages of the collisional Sunsás-Aguapeí orogeny (1.1 to 0.95 Ga).

Geraldes et al. (2004), comparing the idea proposed by Åhäll and Gower (1997) for the Baltic Shield case with the Amazonian Craton also suggested that an inboard bimodal rapakivi magmatism in Rondônia Tin Province could be related with the orogenic events that occurred in the southwest border of the Amazonian Craton. This way, the Serra da Providência suite was correlated to the Cachoeirinha orogeny (1.59-1.52 Ga); the Santo Antônio and Teotônio intrusive suites with the Santa Helena orogeny (1.44 - 1.42 Ga); the São Lourenço-Caripunas and Alto Candeias Intrusive Suites with the San Ignácio orogeny; and the Santa Clara and Rondônia Intrusive Suites with the Sunsás Orogeny which affected the northern region of Rondônia state between 1.07 and 0.97 Ga (Bettencourt et al. 1999). Anderson and Morrison (2005) and Goodge and Vervoort (2006) reported in Laurentia A-type granites with widespread low-grade heating in older country rocks do not constitute evidence for a widely distributed orogeny. Other relevant aspect is that, in Laurentia A-type granites, as in Massangana, São Carlos and Caritianas massifs in Rondônia, there is no evidence of arc-like geochemical and isotopic signature consistent with an active-margin origin.

A fundamental unresolved question is what process triggered the melting: Goodge and Vervoort (2006) suggested that the crustal thickening that occurs in collisional regimes must be the responsible for triggering the lower crustal melting rather than subduction of oceanic lithosphere and affirm that the regional characteristics observed in the Laurentia A-type province are better explained by a mechanism that involves melting within thickened crust.

9. Concluding remarks

The petrogenetic model that best accounts for the origin of Massangana, São Carlos and Caritianas massifs must consider the following isotopic and geologic relationships:

1) The five samples from Massangana massif yielded U-Pb ages from 1010 Ma to 993 Ma, ϵHf values range from -14 to +5 and TDM age from 1.52 to 2.40 Ga. The data indicate that these magmas were probably mantle-derived but with important contribution from crustal rocks.

2) The samples from São Carlos massif show U-Pb ages between 996 to 974 \pm 10 Ma and initial ϵHf between -15 and +11, corresponding to a TDM age range between 2.65 and 1.08 Ga. The Caritianas massif rocks yielded U-Pb ages of 1001 and 999 Ma, show more initial ϵHf positive values (13 zircon grains) than negative (6 zircon grains), different from the other massifs. The range of initial ϵHf of the Caritianas massif is between -1.5 to +8.2, corresponding to a magma source resided within (1.76 – 1.25 Ga);

3) The Massangana and São Carlos massifs rocks Hf isotopic signature represents dominantly crustal melts with a subordinate mantle contribution. Almost all the samples analyzed show negative and positive values to the ϵHf parameter.

4) The zircon grains from Massangana, São Carlos and Caritianas massifs show ranges of 30 ϵ units and up to 9 ϵ units for single samples. The excess of variation of Hf isotopes within a granitic intrusion indicates heterogeneity during periods of zircon saturation and is an evidence that these rocks were formed by mixing different sources including a mantelic one, especially in the Caritianas massif with more positive ϵHf values than negative, different from the other massifs studied here.

5) The two groups of TDM (Hf) ages identified in this investigation is still matter of debate, and may be correlated to crustal basement rocks formed during two stages of mantle

melting (orogenic cycles). The ϵHf values variation within the same sample may be due to magma mixture/mingling, where the isotopic values from different magmas results in different reservoir within the zircon grain. In this way, an incomplete mixture result ϵHf values respective to the source of the magmas and may play an important role for tin ore genesis.

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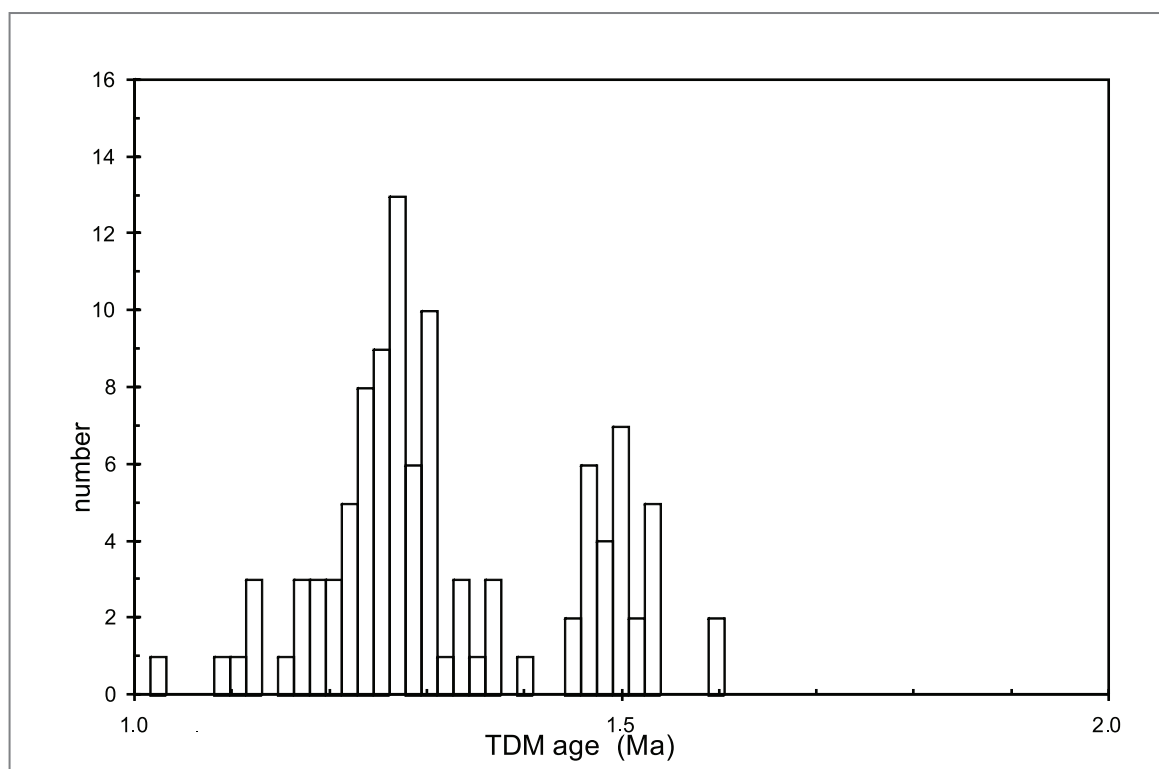


FIGURE 8 – Histogram with density plot of TDM Hf ages where two groups of ages may be observed

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