UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE GEOCIÊNCIAS

**Geochronology and petrogenesis of the southern portion of Socorro Granitic Batholith
based on U-Pb dating and isotope geochemistry**

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À Maria
(*in memoriam*)

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“Viver – não é? – é muito perigoso. Porque ainda não se sabe. Porque aprender a viver é que é o viver mesmo”.

Guimarães Rosa.

RESUMO

O Batólito Socorro é uma das manifestações graníticas mais expressivas associadas à evolução Neoproterozóica no SE do Brasil, ocupando uma extensa área (~ 1.200 km²) na porção sul da Nappe Socorro-Guaxupé (NSG). Datações U-Pb em zircão por SHRIMP foram realizadas para determinar as idades dos principais componentes do batólito, e análises de geoquímica isotópica (Sr-Nd-Hf) para determinação das áreas-fonte. Biotita-hornblenda granitos porfiríticos com caráter cálcio-alcálico de alto-K e com teores de SiO₂ relativamente baixos (60 - 67 %) são os componentes mais volumosos deste e de outros batólitos sin-tectônicos na NSG (Água Limpa e Pinhal-Ipuiúna) e em outros corpos do Cinturão Ribeira, como os Domínios Apiaí e São Roque. Três amostras coletadas em diferentes localidades do Batólito Socorro apresentam idades de cristalização magmática semelhantes, 610.1 ± 7.0 Ma, 608.3 ± 6.6 Ma e 610.4 ± 6.8 Ma. Os valores de $\epsilon_{\text{Nd}}(t)$ para essas rochas variam de -12,3 a -12,9, com idades $T_{\text{DM}}(\text{Nd})$ entre 1.8-2.0 Ga, e razões iniciais $^{87}\text{Sr}/^{86}\text{Sr}(t)$ entre 0,7119-0,7131. Composições isotópicas de Hf em zircão ($\epsilon_{\text{Hf}}(t)$) destas amostras variam de -12 a -17. Dados semelhantes são observados em granitos cálcio-alcálicos de alto K do Domínio São Roque e do Batólito Cunhaporanga. Amostra de um corpo de granito mais fracionado (SiO₂ > 72%, Pluton Bairro da Pedreira) apresentou idade de 612.4 ± 4.6 Ma, sugerindo caráter contemporâneo aos granitos cálcio-alcálicos de alto-K. Por outro lado, um outro corpo de leucogranito (Pluton Bocaina) levemente peraluminoso, reportado na literatura como relacionado a um evento mais jovem (“magmatismo Socorro II”), forneceu idade claramente mais velha (624.4 ± 3.6 Ma), semelhante à de granitos anatóticos regionais. Ambas as ocorrências de granitos mais evoluídos apresentam $\epsilon_{\text{Nd}}(t)$ negativos, com valores de -16,16 e -16,19, idades $T_{\text{DM}}(\text{Nd})$ entre 1.9 e 2.0 Ga, razão $^{87}\text{Sr}/^{86}\text{Sr}(t)$ entre 0,7156-0,7171 e valores de $\epsilon_{\text{Hf}}(t)$ fortemente negativos, com uma média em ~ -16 em ambas amostras, indicando uma maior contribuição de fontes crustais antigas. Dados isotópicos similares são observados nos corpos tardi-orogênicos do Batólito Agudos Grandes, que são possivelmente produtos de anatexia da crosta média. Um leucogranito mais fracionado (Pluton Fazenda São Sebastião) apresenta química distinta, com alto teor de SiO₂ (75%), baixo teor de Th e $\epsilon_{\text{Nd}}(t) \sim -12$. Duas rochas charnockíticas que mostram contatos transicionais com granitos são um pouco mais antigas que esse magmatismo. O Charnockito Socorro apresenta $\epsilon_{\text{Nd}}(t) = -6,1$, $\epsilon_{\text{Hf}}(t) = -9,1$ (média), $^{86}\text{Sr}/^{87}\text{Sr}(t) = 0,7093$, e uma idade de 641.6 ± 4.1 Ma que se sobrepõe às idades de ortognaisses regionais (em parte com caráter charnockítico), que se considera associados com tectônica précolisional (relacionados com subducção?). O Charnockito Atibaia tem afinidade geoquímica distinta (mg# e teor de Sr mais baixos; Zr mais

alto), $\epsilon\text{Nd}(t) = -14,1$ $\epsilon\text{Hf}(t) = -8.9$ (média) e razão $^{86}\text{Sr}/^{87}\text{Sr}(t) = 0,7197$, e apresenta idade um pouco mais jovem (633.3 ± 6.2 Ma), e pode sinalizar uma configuração tectônica diferente, no final do período de consumo de placas, ainda carente de caracterização.

Palavras-chave: Datação U-Pb, Nappe Socorro Guaxupé, Granitos cálcio-alcalinos de alto-K

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CHAPTER 1 - INTRODUCTION

1.1 Organization of the dissertation

First, I present the research aims that justify this work and all the analytical methods used to reach the main objective (Chapter 2).

The presentation of the results is in the form of two scientific articles: one already published (Annex 1) and a second in the process of submission (Chapter 3). These articles contain all the results achieved by this work, being the Annex 1 composed of the article titled "SHRIMP U-Pb Geochronology of Socorro Batholith and implications for the Neoproterozoic evolution in SE Brazil", and chapter 3 composed of the rest of obtained results; the subsequent chapters are the discussion of the results and consequent conclusions.

1.2 Justification and research aims

Neoproterozoic granitic magmatism occupies about 30% of the exposed area of the crystalline basement in the state of São Paulo and is distributed throughout the geological domains that constitute it. The largest volume of granites occurs as large elongated batholiths, dominated by high-K calc-alkaline granites whose their origin is still a matter of large uncertainties, with some authors associating them to subduction-related (Heilbron et al., 2004a; Janasi and Ulbrich, 1991) and others to post-collisional settings (Meira et. al, 2015). Over the last decades, systematic works have been carried out on the most expressive batholiths: Socorro (Artur et al., 1993), Agudos Grandes (Janasi et al., 2001; Leite et al., 2007b), Pinhal-Ipuiuna (Haddad, 1995), Três Córregos (Prazeres Filho et al., 2003), Cunhaporanga (Guimarães, 2000) and Serra da Água Limpa (Vinagre et al., 2014), revealing a wide compositional variety, with a predominance of K-rich calc-alkaline hornblende-biotite megaporphyritic granites. Published U-Pb ages vary from 640 Ma to 600 Ma, with distinct isotopic signatures, but always indicative of important recycling of the continental crust.

The Socorro Batholith was the main focus of the initial studies, stimulated by systematic mapping at 1: 50,000 scale (Artur et al., 1993; Campos Neto et al., 1984; Wernick et al., 1984a; Wernick et al., 1984b); however, these studies occurred at a time when modern isotopic and geochronological analysis techniques were not available (e.g., whole-rock Sm-Nd isotope

geochemistry; in situ Pb-Pb isotope geochemistry on alkali feldspar), or not had been developed (e.g., in situ U-Pb dating by SHRIMP and LA-ICPMS; in situ Hf isotope geochemistry on zircon). Thus, although there is a good set of petrographic and geochemical data, generated from systematic field work, partly on the scale of 1:50,000 (cf. synthesis of (Artur, 2003), geochronological and isotope geochemistry data, which are necessary to better define the sources of the magmas and their tectonic meaning, are scarce for the Socorro batholith. The southern half of the batholith, which exposes a wide diversity of granite types, is the portion best covered by previous detailed field work (Artur et al., 1993), but even so, many inconsistencies exist between the different available mapping studies (e.g., Campos Neto et al., 1984; Oliveira et al., 1986).

The present study proposes to fill these gaps, providing U-Pb dating by SHRIMP of the different granite types of the Socorro Batholith, and a systematic elemental and isotope (Sr-Nd-Hf) geochemistry study concentrated on the main rock types occurring at its southern portion, which was subject of new field work to integrate previous maps and define geological relationships.

CHAPTER 2 – ANALYTICAL PROCEDURES

2.1 Whole-rock elemental and isotope geochemistry

2.1.1 Major, minor and trace elements determinations by FRX

The sample preparation steps prior to the FRX determination were based on Sertek et al (2014). Around 6 to 8 kg of granite rock were used, which were broken into pieces of about 3-5 cm using a hammer or hydraulic press. These were then crushed to sand size fragments in Mn-steel jaw crusher. The material is then quartered, yielding 100 to 150 g portions of representative fragments of the starting material. The first subsample was then submitted for 15 minutes to a Pulverisette planetary mill containing agate rings and cylinders.

The X-ray Fluorescence determinations were performed in a PANalytical model AXIOS MAX Advanced spectrometer with autosampler at the X-ray Fluorescence Laboratory of the Geonality Research Support Center (NAP-Geoanalitica), IGc-USP.

The analyses of major elements, was done in fused discs prepared with a mixture of 1 g of sample and 9 g of spectroscopic grade tetra and lithium metaborate, which was melted at a temperature of 1100-1200 ° C in a platinum-gold crucible using the Claisse model M4 melter. The material was then poured into a 40 mm mold, also made of platinum-gold, and cooled to obtain the glass.

The analyses of trace elements was done in powder pellets, obtained by mixing 7g of the rock powder, previously micronized in McCrone Micronizer model equipment, and then dried, mixed with wax and pressed in Herzog powder tungsten carbide platen pellet machine for 60 seconds at 30 kPa, producing a 40-mm diameter pellet.

Further details of XRF analyses are given in Mori et al. (1999).

2.1.2. Rare Earth elements and other trace-elements determinations by ICP-MS

The methodology used for these analyzes is described by Navarro et al (2008), with the determinations performed in an inductively coupled plasma mass spectrometer with quadrupole

analyzer, model iCap from Thermo-Fisher Co., available at the Chemistry and ICP-MS Laboratory from NAP-Geonalitica at IGc- USP.

Approximately 40 mg of <200 mesh particle size rock powder was placed in a Teflon capsule with addition of 2 mL nitric acid and 6 mL HF, both distilled below the boiling point). The Teflon capsule with the rock powder was inserted in a Parr bomb and heated at 200°C for 5 days. After cooling to room temperature, the solution was transferred to PFA beaker and heated on a hotplate to almost complete dryness with loss of SiF₄. Next, 3 ml of HNO₃ was added to the residue and again evaporated to almost complete dryness. This last procedure was repeated three times in sequence. After drying the material was dissolved and transferred to a plastic bottle, where the weight was adjusted to 80 g with 1% HNO₃.

2.1.3 Sm/Nd and Rb/Sr isotope geochemistry

Sr isotopic analyses of total rock samples were performed at the IGc-USP Geochronological Research Center (CPGeo), based on the methodology described by Sato et al (2008). The attack of the samples was similar to that used for ICP-MS, with differences related to digestion time (10 days at 160° C) in Parr pump. For the isotopic separation steps, AG-50W-X8 resin cation exchange columns (200-400 mesh) were employed, using deionized water and HCl also submitted to sub-boiling distillation at varying concentrations. Sr extraction was performed with 2.5 N HCl and the residue from this step was washed with 6.2 N HCl to extract the ETR. Separation of Sm and Nd was performed on the 6.2 N HCl aliquot from columns filled with Teflon powder and successive washes with 0.26 N HCl for separation of Nd and 0.55 N HCl for extraction of Sm.

Sr isotopic determinations were performed on Thermo Scientific model TRITON thermo-ionization mass spectrometer (TIMS) and Nd on Thermo Scientific Neptune coupled inductively coupled plasma mass spectrometer. Absolute Sm and Nd concentrations were determined by Q-ICPMS (quadrupole analyzer and coupled induced plasma mass spectrometer) and those of Sr and Rb by FRX, both at NAP Geoanalitica. The normalizing ratios are $^{86}\text{Sr}/^{87}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (De Paolo, 1981), with decay constants given in Steiger and Jäger (1978) and Michard et al (1985) for Sr and Nd, respectively. In the period of analysis, the Nd blank was 70 pg and the Sr blank 60 pg. Sr external reproducibility was tested by analysis of NIST-USA reference material NBS-987, which yielded a ratio of 0.710254 ± 0.000018 . External reproducibility of Nd was checked by reference material JNdi-1 (Tanaka, 2000) which

in the period of analysis yielded an average $^{143}\text{Nd}/^{144}\text{Nd}$ ratio was 0.512099 ± 0.000006 . For the calculation of Nd epsilon (ϵ) the values of ($^{143}\text{Nd}/^{144}\text{Nd}$) CHUR of 0.512638 and ($^{147}\text{Sm}/^{144}\text{Nd}$) CHUR of 0.1967 (Hamilton et al, 1983) were used.

2.1.4 Zircon Geochronology and Geochemistry

2.1.4.1 Zircon concentration, mounting and cathodoluminescence

The routine used at CPGeo for zircon separation and concentration is described by Sato et al (2014) and consists of the following steps: a) rock samples (0.5 to 3 kg for granites and ~ 20 kg for mafic rocks)-are crushed in a jaw crusher; b) crushed material is screened to separate a fraction of 100-250 mesh particle size, using a disk mill and a battery of sieves; c) the separated fraction is taken to a vibratory table to concentrate heavy minerals; d) magnetic minerals are removed with a hand magnet; e) minerals with different magnetic susceptibilities are concentrated in a Frantz-type magnetic separator, by varying the inclination and the intensity of the electromagnetic field; f) the least magnetic fractions are passed successively into bromoform ($d= 2.85 \text{ g/cm}^3$) and methylene iodide ($d= 3.2 \text{ g/cm}^3$) to further concentrate the heavy minerals of interest. Any remaining sulfides present in the concentrates are eliminated with HCl or HNO_3 . About 50-100 zircon grains are separated by hand picking with the aid of a magnifying microscope, and then mounted on double sided adhesive tape and embedded in epoxy-type resin. The mount is then polished to expose the fresh surface of the grain trapped in the resin.

A previous study of cathodoluminescence (CL) images of each of the samples was necessary to choose the proper position of the spot during the pointed analyses by SHRIMP. After a thin layer of gold cover (2-3nm) was added to the mounts, these images were obtained in a FEI Quanta 250 SEM spectrometer with a XMAX CL detector (Oxford Instruments). Operating conditions were: high voltage, 15 kV, distance, 16.9-17 mm, PMD detector, range of magnification, 95-250x.

2.4.1.2 Zircon U-Pb dating by SHRIMP

U-Pb zircon dating was performed in the SHRIMP IIe equipment installed at CPGeo, Instituto de Geociências, Universidade de São Paulo. The SHRIMP is a mass spectrometer coupled to a high resolution ion microprobe that uses a collimated and accelerated beam of

primary ions (O₂) to reach a target where secondary ions are generated from 30 m spots. The secondary ions are accelerated through the equipment and the isotopes generated by the sample, ²⁵⁴UO⁺, ²⁰⁶Pb⁺, ²⁰⁷Pb⁺, ²⁰⁸Pb⁺, ²³⁸U⁺ and ²⁵⁴ThO and ¹⁹⁶Zr₂O⁺, are measured successively. The corrections required by the technique are made by the analyses of unknown materials and reference materials with known isotopic ratios (matrix-matched) for determining specific calibration factors (Black et al, 2004). 12-16 spot analyses from each of the unknown zircon samples are performed according to the method described in Sato et. al. (2014). During the run every 5 determinations analyzed the Temora-2 reference material (estimated age 416.78 ± 0.33 Ma; Black et al, 2004) is used as ²⁰⁶Pb/²³⁸U age reference, for calculation of common Pb correction factors and fractionation factors. Common lead corrections usually use ²⁰⁴Pb according to Stacey and Kramer (1975). Reference material SL13 (238 ppm) is used as U composition reference. Data are reduced with SQUID 1.6 software (Ludwig, 2009) and ISOPLOT 4 (Ludwig, 2003) has been used for treatment of data to estimate ages and generate diagrams.

2.4.1.3 Hf isotope determinations by ICP-MS

Zircon Hf analyzes were performed using Thermo ICP-MS Neptune, a high resolution multicollector mass spectrometer for simultaneous measurements of isotopic ratios. The analyses were made in two rounds in different dates and show distinct references values.

A first round of analyses (done in 2016) was performed in samples BRP-08, BRP-12 and BRP-03 with operating conditions of 6 mJ, 8.55 J/cm² (100%), 7 Hz and a 47 µm spot. The ablated material was charged to the plasma, operated at 1000 W, through an air flow of 0.5 L / min, 0.25 L / min He and 1.2 L / min N₂. The measured ¹⁷⁶Hf/¹⁷⁷Hf ratios for reference material GJ-82C were 0.282040 ± 0.000026 (n = 4 2 sd), in line with the recommended value of 0.282000 ± 0.000004 (Morel et al., 2008). The obtained results were treated in Excel using the decay constant of ¹⁷⁶Lu = 1.867×10^{-11} (Soderlund et al, 2004), and for calculations of the ε_{Hf} the ratios ¹⁷⁶Hf/¹⁷⁷Hf = 0.282772 (CHUR) 0.283225 (DM); ¹⁷⁶Lu/¹⁷⁷Hf = 0.0332 (CHUR), 0.038512 (DM) and 0.015 for bulk Earth (Blichert-Toft; Albarede, 1997, Vervoort; Blichert-Toft, 1999).

The second round (done in 2019) is represented by samples ATB-13, ATB-08, BRP-31A and BRP-14A. The mean measured ¹⁷⁶Hf/¹⁷⁷Hf ratio values for reference material GJ-82C was ¹⁷⁶Hf/¹⁷⁷Hf = 0.282040 ± 0.000026 , in line with the recommended value of ¹⁷⁶Hf/¹⁷⁷Hf = 0.282015 ± 0.000025 (Y.S. Liu et al, 2010) . Each analysis was composed of 50 sequential

measurements (approx. 1s integration each) on the ICP-MS "Neptune" under the ablation of the "Analyte Excite" excimer laser; seven isotope signals are measured simultaneously, all in Faraday cups (for better intercalibration): 171, 173, 174, 175, 176, 177, 178 and 179. At the end of each measurement sequence, the mean instrumental blank value is immediately subtracted from each of the 7 isotope signals.

For all calculations, the abundances of the isotopes of Yb (171, 173, 174 and 176), Lu (175 and 176) and Hf (176, 177, 178 and 179) are those published by IUPAC (<https://www.ciaaw.org/pubs/TICE-2009.pdf>); 171, 173 signals and part of 174 signal are used to calculate Yb mass bias coefficient (β_{Yb}) by adopting an exponential law; 179, 178, 177 signals and part of 174 signal are used to calculate the fractional coefficient of Hf (β_{Hf}), also adopting an exponential law. Since it does not have enough isotopes to correct itself, the Lu fractionation coefficient was assumed as: $\beta_{Lu} = \beta_{Hf}$. The $^{176}Hf/^{177}Hf$ ratio is obtained after subtracting the interferences of the interfering ^{176}Yb (estimated via β_{Yb}) and ^{176}Lu (estimated via β_{Lu}) from the total 176 signal. ϵ_{Hf} and $t(DM)$ are calculated using the formulas of Yang et al. (2007).

2.4.1.4 Zircon trace-elements determinations by ICP-MS

Around 10-12 chemical analyses of trace-elements were performed in each of the seven samples that were subjected to U-Pb dating. The analyses were carried out at NAP-Geoanalitica, IGc-USP, using the New-Wave/ESI Laser Ablation model UP-213AF with the supercell model sample cell coupled to the iCAP Q – Thermo Scientific quadrupole mass spectrometer.

The synthetic NISTSRM610 of the National Institute of Standards (NIST) was used for external calibration, control of instrumental drift and fractionation, with reference values provided by NIST; these values are also available on the website of Georem at http://georem.mpch-mainz.gwdg.de/sample_query.asp. This standard was analyzed twice at the beginning and twice at the end of each analytical cycle, and once on the middle of analysis (after 5 or 6 samples). Stoichiometric ZrO_2 (67 wt%) was used as internal standard. The reference material zircon 91500, from Kuhel Lake (Ontario, Canada), described and monitored by Wiedenbeck et al (1995), was used for quality control, being analyzed as an unknown.

Thirty-four elements are analyzed; in the first 60 seconds of analysis, blank measurements are performed, which are readings of all the isotopes under normal conditions of

analysis, but without the activation of the laser. The next 60 seconds are used to acquire analytical data of the material removed by the laser by ablation of the sample.

The results obtained are treated using the Glitter ® software (Van Achterbergh et al, 2001), which performs corrections of instrumental drift through the use of internal standard of a previously chosen element and external reference material, in addition of the calculation of the contents of the elements under analysis.

CHAPTER 5 - CONCLUSIONS

Whole-rock elemental and Sr-Nd isotope geochemistry and zircon Hf isotope geochemistry by LA-ICP-MS reveal that the Ediacaran (~640-610 Ma) granite magmatism that formed the Socorro Batholith derived from varied crustal sources, possibly with some contribution from a mantle component, as suggested by the relatively primitive (<65 wt% SiO₂) composition of important volumes of these granites (e.g., Socorro Charnockite; Bragança Paulista-type granites) .

The HKCA magmatism, represented mostly by Bragança Paulista-type granites, is characterized by low SiO₂ (~ 65 wt%), K₂O ~ 4% and high Ba, Sr, U, mg#, TiO₂ and P₂O₅. Sr-Nd-Hf isotope data reveal a relative long crustal residence with contribution of a continental crust possibly reworked at 1.4 Ga.

More fractionated rocks (leucogranites) have significant geochemical and isotope differences, but all are dominantly products of crustal anatexis. The Bocaina Pluton shows a wide spread of ϵ_{Hf} , and a negative ϵ_{Nd} value (-16), indicating co-existence of multiple and isotopically distinct magma batches produced by partial melting of different crustal domains. This possibly includes a metasedimentary source, similar to Nazaré Paulista-type granites (Martins, 2009).

The Bairro da Pedreira Pluton has a Sr-Nd-Hf isotope signature similar to the Bocaina Pluton, but a ~12 Ma younger age and some differences in trace element composition (e.g., higher Th). The studied samples of the Fazenda São Sebastião Pluton have lower Ba, Sr and Th contents than the two other leucogranites, as well as positive Eu anomalies. These features are interpreted as indicative of feldspar accumulation and the participation of melts derived from distinct sources .

The geochemistry of the Socorro Charnockite is similar to Bragança Paulista-type granites but it is 30 Ma older (640 Ma), overlapping the ages of regional orthogneisses (Hackspacher, 2003). This is suggestive of a different tectonic environment, related to subduction processes. It has less negative Nd and Hf isotope signatures, reflecting sources with lower crustal age or a greater mantle component.

Compared to the Socorro Charnockite, the Atibaia Charnockite is characterized by elevated Rb/Sr, Zr, K₂O and lower Sr and mg# contents. The Nd isotope signature is similar to the Bragança Paulista-type granites ($\epsilon_{Nd} = -14$), suggesting sources of similar crustal age, but the high $^{87}\text{Sr}/^{86}\text{Sr}(t)$ requires a source with higher time-integrated Rb/Sr. Zircon grains from this rock show the more pronounced negative Eu anomaly, reflecting reducing crystallization conditions. These features are consistent with an origin by partial melting of a distinct granulite source, with high Rb/Sr ratio. These geochemical differences and a slightly younger age (633 Ma) than the other charnockite (Socorro) can also indicate differences tectonic environment, possibly reflecting the end of plate consumption.

The new geochronological data presented in this work confirms our previous studies (Toledo et. al., 2018) that suggested a wide time interval for the build up of Socorro Batholith. The batholith was formed over ~30 M.y., beginning with calc-alkaline charnockites (Socorro) at ~642 Ma and ending with voluminous high-K calc-alkaline metaluminous (biotite-hornblende) granites (Bragança Paulista-type) and contemporaneous leucogranites (Bairro da Pedreira Pluton) at 610 Ma. The peak of granite magmatism in the Socorro Batholith at ~610 Ma is comparable to batholiths of Ribeira Belt dominated by high-K calc-alkaline granites, although slightly younger plutons are present in the Agudos Grandes batholith and in the of the São Roque Domain (respectively, ~600 Ma and ~600-590 Ma; Leite et al., 2007; Janasi et al., 2016).

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