# APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE STUDY OF LOW-TITANIUM THOLEIITIC DYKES OF THE SERRA DO MAR SWARM (RJ)

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## ABSTRACT

The tholeiitic dykes of the Serra do Mar Swarm (SMS) outcrop along the coast of the São Paulo and Rio de Janeiro states (Southeastern Brazil), spreading over the Rio Paraiba Valley. Previous studies carried out in such dykes showed that they are related to the tectonic and magmatic processes that took place during the South Atlantic Ocean opening and gave rise to the Paraná Magmatic Province (PMP). The dykes are vertical to sub-vertical and preferentially NE-SW trending, with thicknesses ranging from centimeters to tens of meters. Most of the SMS intrusive rocks have relatively high concentrations of $TiO_2$ (>3wt%), except for occurrences in the Região dos Lagos (Costa Azul Suite), as well as around Nova Friburgo Town (Serrana Suite), where they are characterized by basic rocks with low $TiO_2$ (<2wt%) contents, whose genesis are still not completely understood. Therefore, a detailed study is being carried out in rocks of the Suite Serrana, with the determination of the concentrations of the rare earth (REE: La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) and other trace (Ta, Th, U, Hf, Cs, Sc, and Co) elements by instrumental neutron (thermal and epithermal) activation analysis, which has accuracy and precision required for petrogenetic studies. The data obtained so far show a substantial enrichment of highly incompatible trace elements (light REE, Th and U) and a remarkable geochemical similarity with the low-TiO2 basaltic flows of Gramado type found in southern PMP, suggesting important processes of crustal contamination during the genesis of the investigated dykes.

## 1. INTRODUCTION

During the Mesozoic, one of the most significant intracontinental volcanic events preceded the rifting process and the opening of the South Atlantic Ocean, located mainly in Southern Brazil,

spreading over Uruguay, Northern Argentina, and Eastern Paraguay, with a volume larger than 660,000 km³. Such volcanism, of tholeiitic nature and associated with significant intrusive magmatism (sills and dyke swarms) is referred as the Paraná Magmatism Province (PMP; [1], [2],[3],[4]). Even though many studies have been carried out on these rocks, there is no consensus about mantle source features, as well as the sequence of tectonic processes involved in their generation and the relationship with the South American and African continental breakup.

The PMP volcanic rocks are mostly composed by tholeiitic basalts and basaltic andesites (>90% of volume). These rocks are chemically divided according to their $TiO_2$ contents ([5],[6],[7],[8],[3]). The high-$TiO_2$ (HTi) group is dominant in the northern PMP and subdivided into three basalt magma types: Pitanga (northern PMP; $TiO_2$ > 2.9wt%; Sr > 350 mg/kg; Ti/Y > 350; Zr/Y > 5.5), Paranapanema (northern PMP; 1.7 < $TiO_2$ < 3.2wt%; 200 < Sr < 450 mg/kg; Ti/Y > 330; 4 < Zr/Y < 7) and Urubici (southern PMP; $TiO_2$ > 3.3wt%; Sr > 550 mg/kg; Ti/Y > 500; Zr/Y > 6.5),). In contrast, the low-$TiO_2$ (LTi) group, dominant in the southern PMP, it is subdivided into three basalt magma types: Gramado (southern PMP; 0.75 < $TiO_2$ < 1.9wt%; 140 < Sr < 400 mg/kg; Ti/Y < 300; 3.5 < Zr/Y < 6.5), Esmeralda (southern PMP; 1.1 < $TiO_2$ < 2.3wt%; 120 < Sr < 250 mg/kg; Ti/Y < 330; 2 < Zr/Y < 5) and Ribeira (northern PMP; 1.5 < $TiO_2$ < 2.3wt%; 200 < Sr < 375 mg/kg; Ti/Y > 300; 3.5 < Zr/Y < 7).

Intrusive magmatic bodies occur as sills and in three expressive dyke swarms, namely Serra do Mar, Ponta Grossa and Florianópolis ([1],[2],[9],[10],[3]), which are interpreted by some authors as arms of triple junctions ([11], [4]). These intrusive rocks have close elemental and isotope characteristics to the PMP flows, although the vast majority of the dykes belong to the HTi group.

The Serra do Mar Dyke Swarm (SMDS) occurs along coast of the São Paulo and Rio de Janeiro states (southeastern Brazil), entering to the continent up to Paraíba River valley ([12], [13], [14], [10], [15]). These intrusive rocks are vertical to subvertical, with most of them trending ENE, and their thicknesses vary from a few centimeters to hundreds of meters. The dykes are relatively evolved (most with MgO contents varying from 8 to 4wt%), encompass basic and intermediate lithotypes, and the majority have relatively high concentrations of $TiO_2$ (>3wt%). Subordinately, the occurrence of low-$TiO_2$ (<2wt%) dykes have been found in Rio de Janeiro State, particularly in the Região dos Lagos (Costa Azul Suite) and Região Serrana (Serrana Suite), whose genesis are still not completely understood.

Previous studies on the LTi tholeiitic dykes of the Serrana Suite indicate that these rocks are similar to Gramado-type basalts, commonly encountered in southern PMP, regarding major, minor and trace elements, as well as Sr initial (back to 130 Ma) isotope compositions ($^{87}Sr/^{86}Sr_i$ ≥ 0.7060), indicating significant crustal contamination processes in their genesis ([3], [10]). These geochemical characteristics are opposite to those observed for the low-$TiO_2$ Costa Azul Suite tholeiitic dykes, which are depleted in incompatible elements and in radiogenic Sr ($^{87}Sr/^{86}Sr_i$ < 0.7060), resembling the Esmeralda-type basalt features and/or even to E-MORB types ([16], [10],[17]).

The low-$TiO_2$ dykes that outcrop around the Bom Jardim, Macuco and Nova Friburgo (Lumiar District) towns (Figure 1), located in the Serrana Region, are mainly focused in this study, since they are poorly investigated (e.g. [12], [18]), requiring additional geochemical data to understand the role of the low-$TiO_2$ magmatism in the SMDS genesis. Therefore, a detailed

investigation is being carried out in such rocks, with the determination of the concentrations of the rare earth (REE: La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) and other trace (Ta, Th, U, Hf, Cs, Sc, and Co) elements by instrumental neutron (thermal and epithermal) activation analysis, which has accuracy and precision required for petrogenetic studies. Considering that the HTi dykes also occur in the same region, they have also been analyzed for comparison.
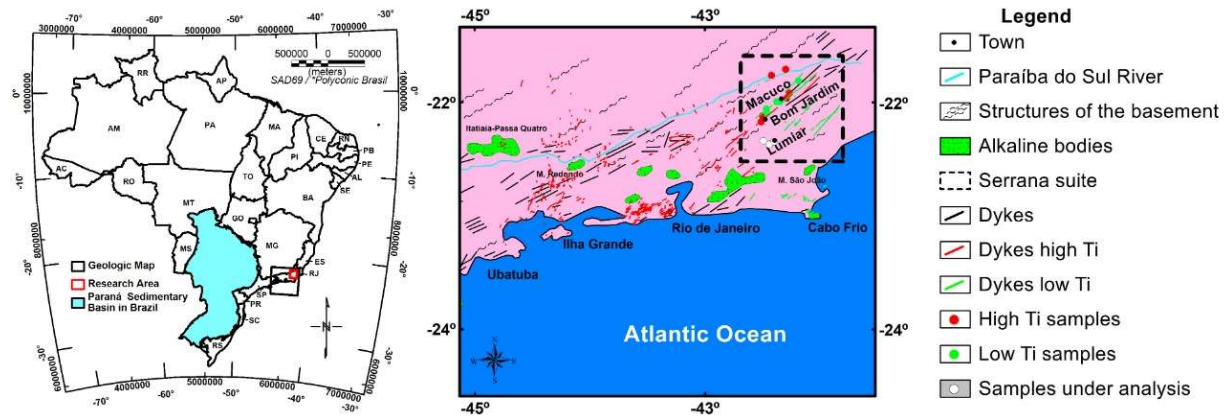


**Figure 1: Sketch map of part the Serra do Mar Swarm, with the location of the investigated samples. Dykes high Ti (red lines) and low Ti (green lines) are based on [10]. The dyke samples of low-TiO₂ group are represented by green circles, and the high-TiO₂ group in orange circles. Modified from [12].**

## 2. METODOLOGY

The analytical method used to determine the trace element concentrations in the dykes is the Instrumental Neutron Activation Analysis (INAA), since it is non-destructive (without chemical separation) and allows highly precise simultaneous determination of several chemical elements ([19], [20]). The method is accurate and has high sensitivity concerning the determination of trace elements, particularly those, which are crucial fingerprints of the petrogenetic processes of igneous rocks.

### 2.1. Principles of INAA

For INAA, samples are irradiated by neutron beams. In this process, stable isotopes present in the rock capture neutrons, become radioactive and decay according to their half-life characteristics, emitting particles and γ-rays with specific energies. The radioactive nuclides are then measured using high precision γ-ray spectrometry and based on their characteristic peaks in the γ-ray spectrum, the respective activities are calculated [19].

In this study, the following chemical elements were determined: La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Ta, Th, U, Hf, Cs, Sc, and Co. Different reactions may occur depending on the neutron energies and those which induce γ-ray emission involve the incidence of thermal (0 – 0.026 eV) and epithermal (0.027-1000 eV) neutrons. For the present study, the samples were irradiated by both thermal and epithermal neutrons. The first one provided more accurate results on determinations of Nd, Eu, Lu, and Yb (e.g. [19], [21]). In order to irradiate the

samples with epithermal neutrons, the samples are packed with a Cd foil 1mm thick, which significantly reduces the thermal neutron flux.

1. **Table 1: Main characteristics of radioisotopes determined in the study and irradiation condition (adapted from [22]).**

| Elements | Measured radioisotope | Half-life | Energy (keV) | Irradiation Conditions |
|---|---|---|---|---|
| La | $^{140}$La | 47.27 h | 328.6 1595.4 | Epithermal |
| Ce | $^{141}$Ce | 32.5 d | 145.4 | Epithermal |
| Nd | $^{147}$Nd | 11.1 d | 91.4 531 | Thermal |
| Sm | $^{153}$Sm | 47.1 h | 103.2 | Epithermal |
| Eu | $^{152}$Eu | 12.2 y | 1407.5 | Thermal |
| Tb | $^{160}$Tb | 73 d | 879.4 | Epithermal |
| Yb | $^{175}$Yb | 101 h | 396.1 | Thermal |
| | $^{169}$Yb | 30.6 d | 197.8 | |
| Lu | $^{177}$Lu | 6.75 d | 208.4 | Thermal |
| Ta | $^{182}$Ta | 115.1 d | 1188.8 1221.6 | Epithermal |
| Th | $^{233}$Pa | 27 d | 311.8 | Epithermal |
| U | $^{239}$Np | 2.35 d | 277.5 | Epithermal |
| Hf | $^{181}$Hf | 44.6 d | 482.2 | Epithermal |
| Cs | $^{134}$Cs | 2.7 y | 795.8 | Epithermal |
| Sc | $^{46}$Sc | 83.9 d | 889.4 | Epithermal |
| Co | $^{60}$Co | 5.24 y | 1332.2 | Epithermal |

## 2.2. Reference geological materials

As mentioned before, one of the advantages to using INAA is the fact that the samples do not need any chemical treatment, neither before nor after the activation, reducing the risk of contamination due to limited sample handling operations [20]. Since the comparative method has been used in this study, the investigated rocks were irradiated along with three international geological reference materials with well-known (recommended) concentration values of the analyzed trace elements.

The used reference geological materials are the basalt BE-N (International Working Group – Groupe International de Travail), the granite GS-N (Association Nationale de la Recherche Technique) and basalt BCR-1 (United States Geological Survey), which recommended values are reported by [23]. These standards are silicate rocks with distinct compositions, encompassing the concentrations of trace elements present in the investigated rocks.

The trace element concentrations in the samples were obtained by the Equation 1, where $C_a^I$ is the $I$ element concentration in the sample, $A_a^I$ is radioisotope activity considered in the sample at time $t$, $M_s$ and $M_{st}$ are the sample and standard mass, respectively, $C_{st}^I$ is the $I$ element concentration in the reference material, $t$ is the elapsed time between counting the sample and the standard, and $\lambda$ is the decay constant of $I$ element.

$$C_s^I = \frac{A_s^I . M_{st} . C_{st}^I . e^{\lambda t}}{A_p^I M_s} \qquad (1)$$

## 2.3. Sample comminution

Comminution consists of a process in which the rock is reduced to grains of suitable sizes required for geochemical analyses, without changing its chemical property. For INAA the samples must be pulverized to less than 100 mesh (0,149 mm of diameter). The sample preparation followed the steps:

1. Fresh rock selection, with the elimination of possible weathering or sawn surfaces;
2. Sample crushing to small chips with diameters of about 0.5cm;
3. Manual splitting to obtain a representative fraction (~50 g) of the sample;
4. Fragment washing with deionized water using an ultrasonic bath;
5. Drying the fragments in an oven at 60°C;
6. Pulverization in an agate mechanical ring mill;
7. Sample homogenization.

## 2.4. Irradiation and counting

After the pulverizing procedure, each aliquot was precisely weighted (~100 mg), packed in two polyethylene bags and enclosed in a commercial aluminum foil. The samples along with the reference materials were irradiated for 16 hours (thermal irradiation) and 24 hours (epithermal irradiation) in a neutron flux of about $5 \times 10^{12}$ neutrons cm$^{-2}$s$^{-1}$ at the IEA-R1 research reactor,

with a maximum power of 5MW. All these processes have been made at the Centro de Reator de Pesquisa (CRPq) of Instituto de Pesquisas Energéticas e Nucleares (IPEN)

The γ-ray emission measurements were carried out using a high-resolution hyperpure Ge detector with resolution (FWHM) of 1.90 keV for the 1332 keV γ-ray of [60]Co. The gamma-ray spectra were processed using the VISPECT software, which discriminates the peak locations, determines the respective energies of the gamma-rays, and calculates their net activities.

Two series of measurements were done after the epithermal irradiations. The first one was carried out around 5-7 days after the end of irradiation, and time counting was at least 50 minutes. The second one was performed about 15-20 days after the irradiation, with a counting time of at least 100 minutes. For the samples activated with thermal neutrons, only one counting of at least 100 minutes was conducted around 10-15 after the end of the irradiation.

## 3. RESULTS AND DISCUSSION

Eleven dykes that outcrop around the Macuco and Bom Jardim towns were analyzed for major and minor element oxides, as well as for some trace elements (Cr, Ni, Ba, Rb, Sr, La, Ce, Nd, Y, Nb, and Zr) by X-ray fluorescence at the University of Trieste, following the analytical procedures reported by [24]. The precision and accuracy are better than 3% and 10%, respectively.

All the samples were also analyzed by INAA, allowing determining fifteen trace elements, including REE (La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu) and Ta, Th, U, Hf, Cs, Sc, and Co. In general, accuracy and precision are better than 5% and 10%, respectively [12].

Up to now, for the Lumiar region only 2 samples were analyzed for major and minor elements at the Instituto de Geociências e Ciências Exatas (UNESP-RC). The results concerning the dykes collected around Macuco and Bom Jardim include those already presented by [12] in the study of SMDS.

### 3.1. Chemical nomenclature and classification

As also observed for the PMP volcanism, the dykes have sub-alkaline nature [25] and may be separated in low-$TiO_2$ (LTi) rocks, containing 7 samples, and high-$TiO_2$ (HTi) rocks, encompassing 6 samples. The LTi group (MgO: 3.22 - 5,58%wt) is characterized by basic and intermediate rocks and according to TAS nomenclature [26] is chemically represented by 1 basalt and 6 basaltic andesites, while the HTi one (MgO: 2.68 – 5.13%wt) is also composed of basic and intermediate rocks and represented by 3 basalts and 5 basaltic andesites (Figure 2).
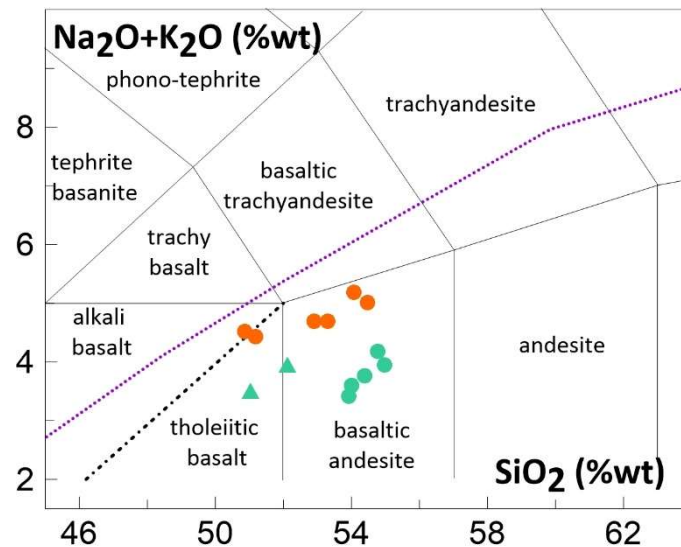
**Figure 2: Classification and nomenclature of the Bom Jardim, Macuco and Lumiar dykes. Low TiO₂ group = green circles (Macuco and Bom Jardim) and green triangles (Lumiar), high TiO₂ group = orange circles. The purple dotted line divides the rocks between alkalic and sub-alkalic magma series [25]. The black dotted line divides alkali basalts and tholeiitic basalts from [27].**

### 3.1.1. Major, Minor and Trace Element Geochemistry

For similar MgO contents, the HTi dykes are enriched in $TiO_2$, $Fe_2O_3t$, $Na_2O$, $K_2O$, and $P_2O_5$ and depleted in $SiO_2$ and CaO in comparison to the LTi rocks (Figure 3). The two groups of rocks are also distinct concerning the behaviour of highly incompatible trace elements, such as the light rare earth elements, U, Th, Ta, and Hf, as evidenced in the variation diagrams using Zr as an index of differentiation presented in Figure 4. The HTi group (orange circles) is clearly distinguished from the LTi one (green circles), which are significantly depleted in La, Sm, Hf, Ta and Zr.
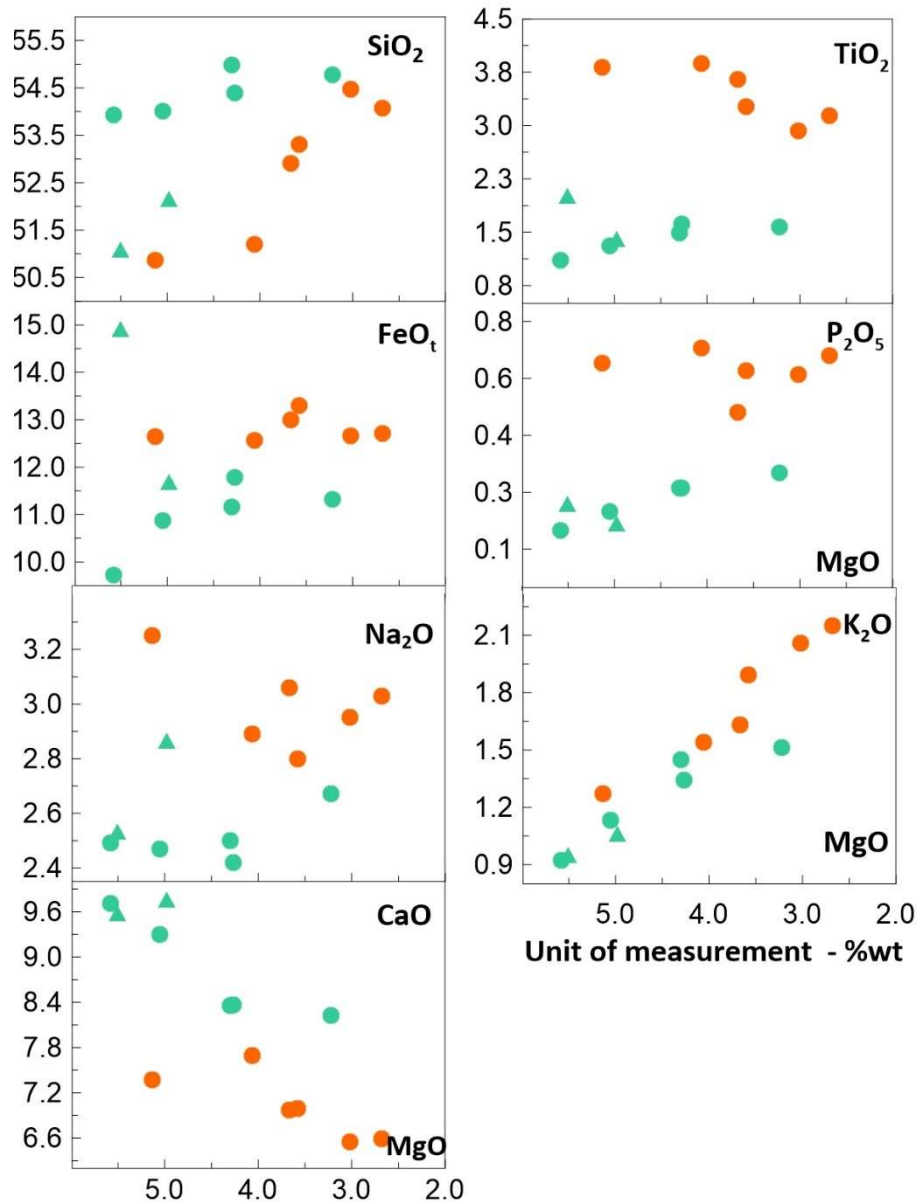
**Figure 3:** Variation diagrams, with MgO contents as abscissa, for the Bom Jardim, Macuco and Lumiar dykes. Low TiO₂ group = green circles and green triangles (Lumiar region), high TiO₂ group = orange circles.

Considering the ensemble of the LTi and HTi rocks, it is observed that the trends of highly incompatible elements (Figure 4) do not fit straight lines passing through the origin, as expected for the evolution by fractional crystallization process operating on a unique parental magma. Therefore, corroborating the major and minor element behaviour, the analysed incompatible trace elements indicate the involvement of different mantle sources in the genesis of LTi and HTi dykes.

The LTi and HTi groups also present considerable differences on the abundance patterns of rare earth elements (REE), normalized to CI chondrite [28], as seen in Figures 5 and 6, respectively. It is important to note that the data agree with those published data [14]. Although fractionation

of the light REE (more incompatible) in relation to the intermediate and heavy REE exists on both rock groups, they are more significant in the HTi dykes (< $(La/Lu)_N$: 8.9-10.1; $(La/Sm)_N$: 2.3-3.1; $(Sm/Lu)_N$: 3.0-3.8) than in the LTi rocks ($(La/Lu)_N$: 4.8-5.7; $(La/Sm)_N$: 2.6-2.9; $(Sm/Lu)_N$: 1.6-2.1). Slight Eu negative anomalies are observed in the LTi group ($0.88 \leq Eu/Eu^*$ $\leq 0.93$), whereas, except for two samples with $Eu/Eu^*$=0.92/0.93, slight Eu positive anomalies are present in HTi group ($1.02 \leq Eu/Eu^* \leq 1.14$; average: $1.04 \pm 0.05$).
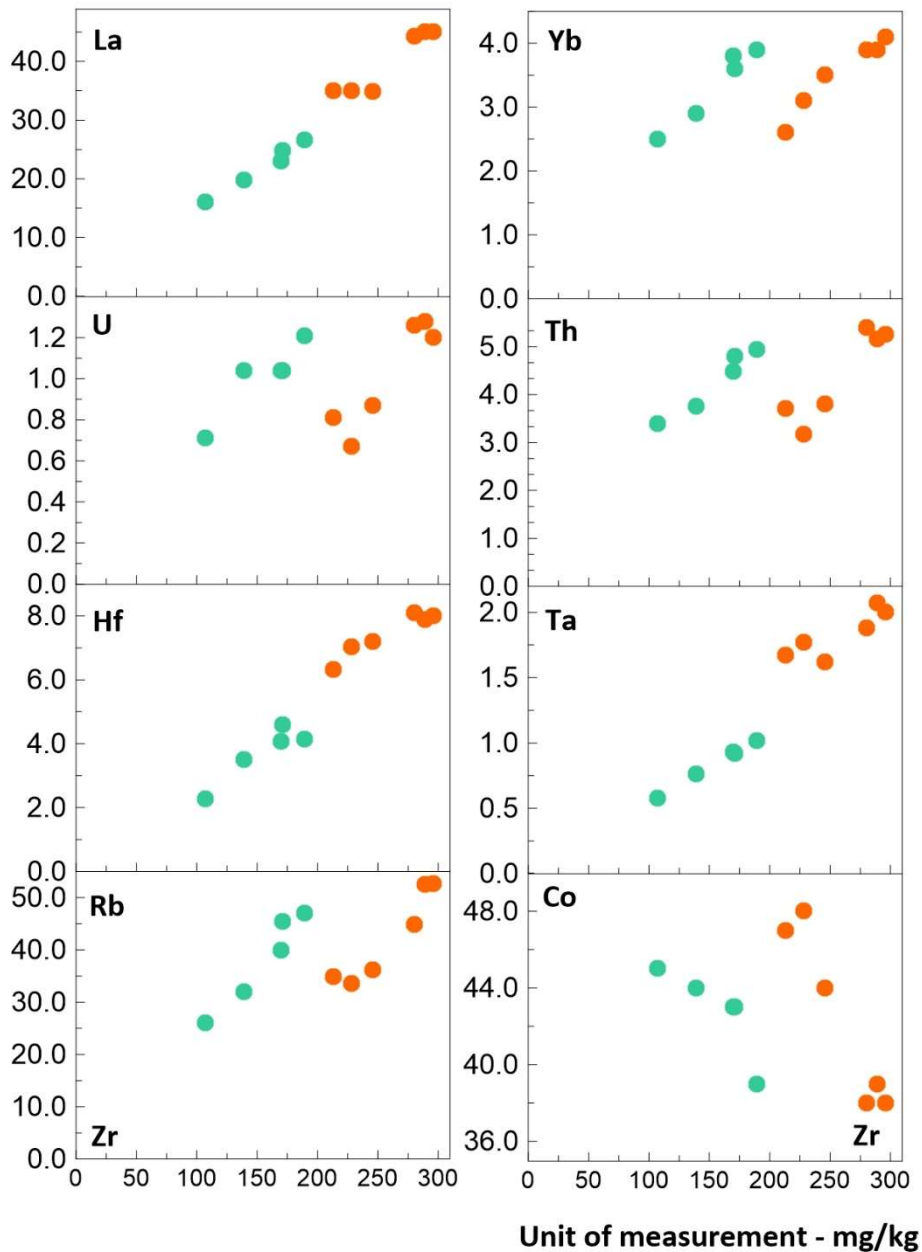


**Figure 4: Variation diagrams of trace elements (mg/kg), against Zr, considered as an index of magmatic evolution, for the Bom Jardim and Macuco dykes. Low TiO₂ group = green circles, and high TiO₂ group = orange circles.**

Although the major, minor and trace elements of the LTi and HTi dykes indicate that they originated in a heterogeneous mantle source, considering each group separately, the data are broadly compatible with evolution by fractional crystallization. Such process involved mainly Ca-clinopyroxene and plagioclase, and subordinate titanomagnetite, as evidenced by the decrease of $TiO_2$, $Fe_2O_3$, CaO and $Al_2O_3$ with the magmatic differentiation (Figure 3), that is, with the increase of $SiO_2$ and decrease of MgO.
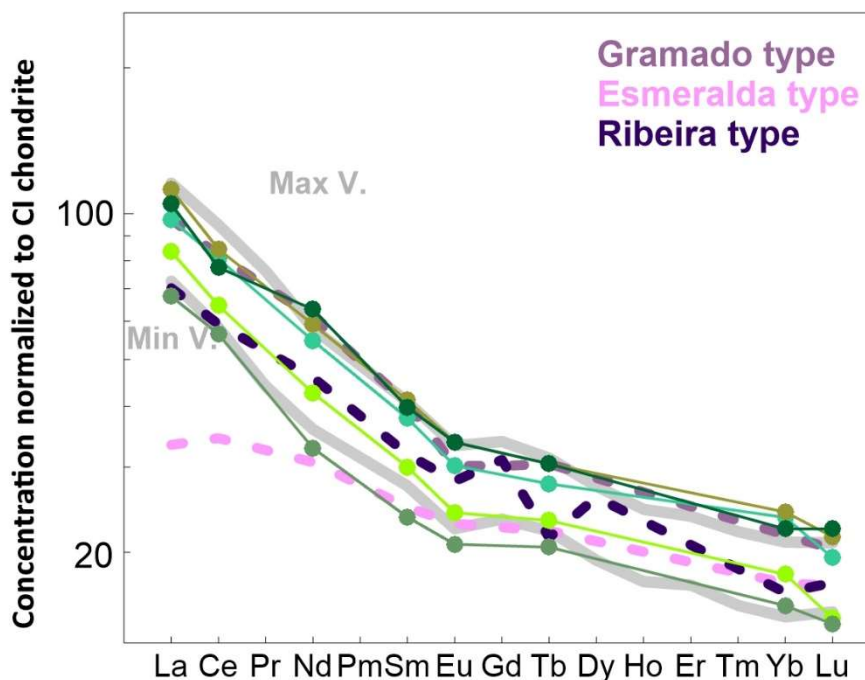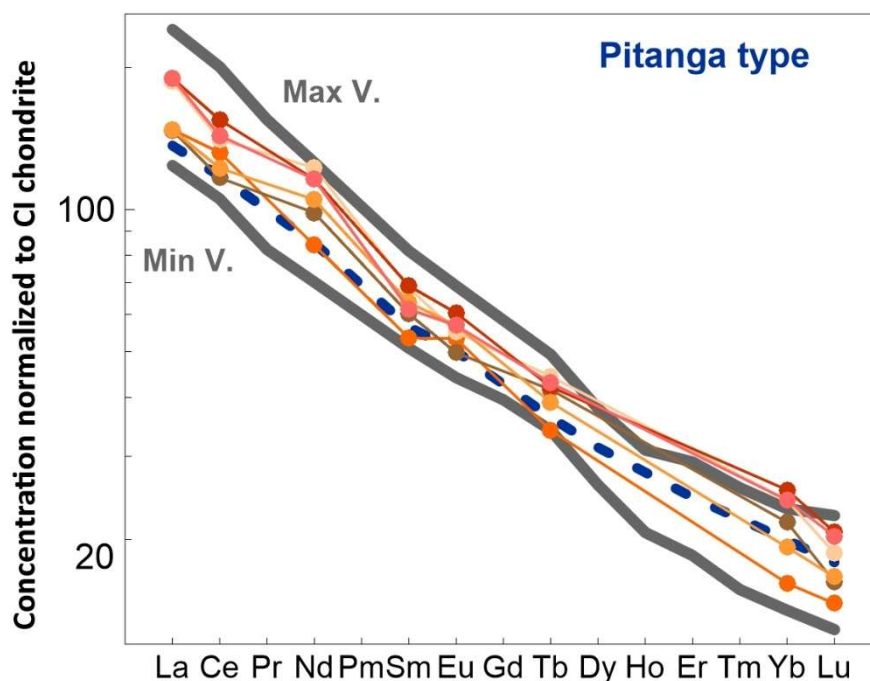


**Figure 5:** **Rare earth element distribution patterns normalized to CI chondrite [28] of the low-TiO2 dykes from Macuco and Bom Jardim. Min.V = minimum values of [14], Max.V = maximum values of [14].**

According to the classification proposed by [7], it is not possible to identify if the LTi dykes belong to Esmeralda or Gramado basalts. However, the U and Th concentrations of such intrusive have an unusual geochemical behavior since they are considerably enriched in comparison with other highly incompatible trace elements, such as La, Ta, and Zr (Figures 4 and 5). This is an indication that the magmas that originated these dykes were contaminated by the continental crust. Therefore, the fractional crystallization process probably did not take place in a closed system. Crustal contamination is also reinforced by the relatively high Rb/Ba ratios (1.0 < (Rb/Ba)Primitive Mantle < 1.2), normalized to the primitive mantle [28]. It is important to note that the LTi dykes have REE distribution patterns (Figure 5), that resemble those of the LTi basalts of Gramado type from southern PMP, which were expressively affected by crustal contamination in their genesis ([2], [8],[29]).

In relation to the magma-types encountered in the PMP [7], the HTi dykes have Sr concentrations (< 526 mg/kg) that match those of Pitanga basalts from northern PMP. The REE patterns of such dykes and flows are similar (Figure 6). However, in contrast to the Pitanga flows, some HTi dykes have relatively high Rb/Ba ratios (0.6 < (Rb/Ba)Primitive Mantle < 0.9),

which are accompanied by U and Th enrichments (Figure 4), suggesting that assimilation fractional crystallization (AFC) process cannot be ruled out in their evolution.



**Figure 6:** **Rare earth element distribution patterns normalized to CI chondrite [28] of high-TiO2 dykes from the Macuco and Bom Jardim. Min.V = minimum values of [14], Max.V = maximum values of [14].**

## 4. CONCLUSIONS

Thermal and epithermal INAA allowed determining REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu), as well as Ta, Th, U, Hf, Cs, Sc and Co on 11 samples of the SMDS, which outcrop in the neighborhood of Bom Jardim and Macuco towns (RJ), with precision (better than 10%) and accuracy (better than 5%), as required for petrogenetic studies.

Two magmatic groups, easily distinguished by their $TiO_2$ contents, were identified in the investigated area. The LTi and HTi dykes are also distinguishable in terms of other major and minor element oxides, as well as by their trace element contents. The trends of the incompatible trace element observed in the variation diagrams point to the involvement of different mantle sources in the magmatism and, consequently, that these two groups are not cogenetic.

Concerning the LTi group, data show a substantial enrichment of Th and U highly incompatible and a remarkable geochemical similarity with the LTi basaltic flows of Gramado type found in southern PMP, suggesting significant processes of crustal contamination during the genesis of the investigated dykes.

The HTi dykes have geochemical characteristics comparable to the HTi flows of Pitanga-type from northern PMP, indicative of mantle source melting with similar characteristics.

At present, the dykes located at Nova Friburgo town (Lumiar district) are being analyzed by INAA, in order to investigate in more detail, the extent of the LTi magmatism and better understand the SMDS genesis.

## ACKNOWLEDGMENTS

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