

Lead isotope constraints on the mantle sources involved in the genesis of Mesozoic high-Ti tholeiite dykes (Urubici type) from the São Francisco Craton (Southern Espinhaço, Brazil)

Aplicação dos isótopos de Pb ao estudo das fontes mantélicas envolvidas na gênese dos diques toleíticos mesozoicos com alto titânio (tipo Urubici) do Cráton do São Francisco (Espinhaço Meridional, Brasil)

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ABSTRACT: The first results of Pb isotope compositions of the high-Ti Mesozoic dykes of the Southern Espinhaço are presented. The results do not show large variations and are significantly more radiogenic than the Pb isotope compositions of the high-Ti tholeiites from the Paraná Continental Flood Basalts. The data combined with published geochemical and Sr-Nd isotope results rule out crustal contamination processes in the genesis of the dykes, requiring magma generation in metasomatized subcontinental lithospheric mantle with the involvement of HIMU-type and carbonatite components. The magmas may have been also derived from a mantle source containing -4 – 5% of pyroxenite and -1% of carbonatite melts, agreeing with published Os isotope compositions of high-Ti rocks from the Paraná Continental Flood Basalts. These metasomatizing agents could be responsible for mantle source refertilization, as was also proposed in the literature to explain the characteristics of xenoliths of the Goiás Alkaline Province, which also occurs in the border of the São Francisco Craton. Additionally, to evaluate the risks of Pb contamination during sample preparation for analysis, several experimental tests were accomplished, which indicate the need of sawed surface removal and a careful washing of small-sized rock fragments before powdering, especially for rocks with [Pb] < 7 µg/g.

KEYWORDS: Mafic dyke swarms; Paraná Continental Flood Basalts; Large Igneous Provinces; Pb isotope analysis.

RESUMO: Este trabalho apresenta os primeiros resultados de composições isotópicas de Pb dos diques mesozoicos com alto titânio do Espinhaço Meridional. As composições isotópicas de Pb dos diques investigados não mostram grandes variações, sendo significativamente mais radiogênicas do que aquelas dos basaltos com alto titânio da Província Basáltica Continental do Paraná. Esses resultados foram integrados a análises geoquímicas e isotópicas de Sr-Nd realizadas nas mesmas amostras, com o objetivo de obter informações adicionais sobre a gênese desses diques. As composições isotópicas de Sr-Nd-Pb não são compatíveis com a ocorrência de processos de contaminação crustal e requerem que a geração desses magmas tenha ocorrido em manto litosférico subcontinental metassomatizado, com a participação de componentes carbonatíticos e manto do tipo HIMU. Esses magmas podem também ter sido originados em fonte mantélica contendo -4 – 5% de componentes piroxeníticos e -1% de carbonatíticos, concordando também com as composições isotópicas de Os dos basaltos com alto titânio da Província Basáltica Continental do Paraná. Esses agentes metasomatizantes foram os responsáveis pela refertilização da fonte mantélica, conforme proposto na literatura para explicar as características dos xenólitos que ocorrem na Província Alcalina de Goiás, localizada na borda do Cráton do São Francisco. Com o objetivo de avaliar os riscos de contaminação por Pb durante o processo de preparação de amostras para análise, foram também realizados vários testes experimentais que indicam a necessidade de remoção de superfícies serradas e de uma lavagem cuidadosa da rocha finamente britada antes da pulverização, especialmente para aquelas com [Pb] < 7 µg/g.

PALAVRAS-CHAVE: Enxames de Diques Máficos; Província Basáltica Continental do Paraná; Grandes Províncias Ígneas; Análise de Isótopos de Pb.

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INTRODUCTION

Large igneous provinces (LIP) have been intensively studied all around the world, occurring in both oceanic and continental environments, where vast volumes of volcanic and intrusive rocks are produced in an interval of few million years (Coffin & Eldholm 1994; Bryan & Ernst 2008; Ernst 2014). On continental areas, these provinces are mainly characterized by widespread flood basalts, often associated with sills and dyke swarms, and occasionally with acid volcanics (flows or ignimbrites).

However, the origin and evolution of such provinces remain a disputed subject, with no agreement about the role of shallow/deep mantle plumes as the triggers of the magmatic activity, as well as the participation of subcontinental lithospheric mantle (SCLM) and subduction-related materials (ancient oceanic crust and sediments) in their genesis (e.g., White & McKenzie 1989; Richards *et al.* 1989; Anderson 1994; De Min *et al.* 2003; Rocha-Júnior *et al.* 2012, 2013; Heinonen *et al.* 2014).

In this framework, the genesis of Paraná Continental Flood Basalts (PCFB), one of the largest continental igneous provinces of the world, is not an exception. According to some interpretations, PCFB tholeiites would reflect the participation of the Tristan da Cunha plume (Gibson *et al.* 1999; Milner & le Roex 1996; Ewart *et al.* 2004; Valente *et al.* 2007), which may have contributed as a source of heat and material to the magmatism. In contrast, an origin from partial melting of heterogeneous SCLM has been proposed, taking into account the elemental and Sr-Nd-Pb isotope characteristics of PCFB tholeiites (Peate 1997; Peate *et al.* 1999; Marques *et al.* 1999 and references therein).

In addition to the comparison of geochemical and isotope signatures of PCFB and Tristan da Cunha Island rocks, the role of such hypothetical plume in the magmatism was also investigated on the basis of paleomagnetic reconstructions, which indicated the plume was located about 1,000 km south of PCFB at the time of the volcanism (Ernesto *et al.* 2002). The origin of PCFB has also been explained by the breakup of the South Atlantic occurred as a result of lithospheric delamination, causing the igneous activity (Regelous *et al.* 2009).

The mantle sources of the PCFB tholeiites have been recently investigated by Rocha-Júnior *et al.* (2012, 2013) in the light of highly incompatible trace element behavior, along with radiogenic isotope (Sr, Nd, Pb, and Os) data, which indicated that the mantle sources involved in PCFB genesis require the participation of asthenospheric mantle (enriched by fluids and/or magmas related to Neoproterozoic subduction) and two enriched mantle sources (EM-I and EM-II). According to those authors, this sublithospheric metasomatized mantle source was

frozen and coupled to the base of the lithosphere above which the PCFB took place.

In order to contribute to the understanding of the mantle sources involved in PCFB, this study presents the first Pb isotope data and a review of published major, minor and incompatible trace element abundances, as well as Sr-Nd isotope data (Rosset *et al.* 2007) for tholeiitic Mesozoic dykes from the Southern Espinhaço. These rocks crop out beyond the north-northwestern limits of the Paraná Basin, located at southeastern border of São Francisco Craton (Minas Gerais State, Brazil). Previous geochemical studies about these dykes indicated geochemical characteristics similar to the high-titanium basalt flows (Urubici type) from the southern PCFB (Peate *et al.* 1999; Marques *et al.* 1999). Moreover, the Sr-Nd isotope signatures were interpreted by those authors as the result of the involvement in their genesis of a carbonatite component variably enriched in radiogenic Sr, whose isotope signatures are similar to the carbonatite complexes bordering Paraná Basin. Therefore, considering that lead isotopes have been extremely useful to characterize the sources involved in the PCFB, they were applied in this investigation in order to better constrain the genesis of the Espinhaço dykes.

In addition, taking into account the possibility of lead contamination during sample preparation, masking the true values of concentration and isotope ratios, a protocol to avoid such risks is presented. Therefore, results of experiments using different procedures of selection and washing of the small-sized rock fragments to be powdered are shown, as well as those acquired by using different grinding materials (agate vs. tungsten carbide).

THE PARANÁ CONTINENTAL FLOOD BASALT PROVINCE

The Paraná Continental Flood Basalt Province is mainly composed by flood tholeiitic basalts, with subordinate intermediate and acid volcanics, which were erupted in the Early Cretaceous. As this magmatism took place approximately 10 Ma before the South Atlantic Ocean opening, the PCFB counterpart is located in Africa, being referred to as Etendeka Province. The volume of extrusive rocks was larger than 660,000 km³, covering about 1 million km² and spreading over the sandstones of Botucatu Formation of the Paraná Basin (southern Brazil), which started to subside in the Early Paleozoic (e.g., Piccirillo & Melfi 1988). Associated with the volcanic activity, occurred subordinate intrusive magmatism represented by sills and three expressive dyke swarms (Almeida 1986; Piccirillo & Melfi 1988; Garda & Schorscher 1996; Raposo *et al.* 1998; Déckart *et al.* 1998; Ernesto *et al.* 1999; Guedes *et al.* 2005; Valente *et al.* 2007; Machado *et al.* 2007).

A considerable number of high precision $^{40}\text{Ar}/^{39}\text{Ar}$ dating, corrected for ^{40}K decay constants and age of the Fish Canyon Tuff, proposed by Renne *et al.* (2010), allowed to well constrain the age of PCFB rocks, indicating the main phase of the magmatic activity took place at 134–133 Ma (Renne *et al.* 1992, 1996; Thiede & Vasconcelos 2010). The Ponta Grossa dykes intruded mainly in a narrow interval (132–130 Ma; Renne *et al.* 1996). The Ar–Ar ages of Florianópolis dykes vary between 131 and 120 Ma (Raposo *et al.* 1998; Déckart *et al.* 1998), whereas Florisbal *et al.* (2014) reported ages of 134 Ma, determined by ID–TIMS U–Pb method in baddeleyite/zircon. Regarding the Serra do Mar swarm, the age of the main phase emplacement varies from 133 to 129 Ma (Turner *et al.* 1994; Déckart *et al.* 1998), although younger (120 Ma) and older ages (up to 193 Ma) were reported by Renne *et al.* (1993) and Guedes *et al.* (2005).

The PCFB rocks are represented by dominant tholeiitic basalts and basaltic andesites. The basic rocks are divided in two main groups: (1) Low-Ti basalts (LTiB), containing relatively low concentrations of TiO_2 (≤ 2 wt.%) and incompatible elements (e.g., P, Sr, Ba, Zr, Ta, Y and light rare earth elements), and (2) High-Ti basalts (HTiB), presenting relatively high contents of TiO_2 (> 2 wt.%) and incompatible elements. The HTiB are dominant in the northern PCFB, whereas the LTiB prevail in the southern PCFB. Minor HTiB and scarce LTiB are also found in the southern and northern PCFB, respectively.

Detailed geochemical studies revealed significant differences between LTiB from the southern (Esmeralda and Gramado types) and northern (Ribeira type) PCFB, as well as between HTiB from the northern (Pitanga and Paranapanema types) and southern (Urubici) areas of the province (Piccirillo & Melfi 1988; Marques *et al.* 1989; Peate 1997; Peate *et al.* 1999; Rocha-Júnior *et al.* 2012, 2013; Machado *et al.* 2015). The isotope studies of PCFB volcanic rocks indicated that crustal contamination significantly affected the LTiB from the southern region. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Sr_i ; back to 134 Ma) vary from 0.7046 (Esmeralda) to 0.714 (Gramado). The variation of Sr_i is also accompanied by significant differences in the Nd–Pb isotope compositions, reinforcing such petrogenetic processes (Mantovani *et al.* 1985; Piccirillo & Melfi 1988; Piccirillo *et al.* 1989; Peate 1997; Marques *et al.* 1999). Conversely, the HTiB (Pitanga and Paranapanema) and LTiB (Ribeira) from the northern PCFB have Sr–Nd–Pb isotope compositions varying in a relatively narrow range (e.g., Sr_i : 0.7054–0.7064), indicating these basalts were not significantly affected by crustal contamination (Mantovani *et al.* 1985; Petrini *et al.* 1987; Piccirillo *et al.* 1989; Marques *et al.* 1999; Rocha-Júnior *et al.* 2013).

Considering only the basalts with $\text{Sr}_i < 0.7060$, which may be considered uncontaminated by the continental crust,

their incompatible trace element distribution patterns normalized to primordial mantle have Ta–Nb negative anomalies, which are considered as a mantle source feature (Marques *et al.* 1989, 1999). This characteristic was probably caused by metasomatic processes, related to Neoproterozoic subduction, as discussed by Rocha-Júnior *et al.* (2012, 2013), taking into account Re–Os isotope data.

The tholeiites of the dyke swarms (Ponta Grossa, Serra do Mar and Florianópolis) show close geochemical and isotope characteristics of the PCFB flows, although most these intrusive rocks belong to the HTiB group (Piccirillo & Melfi 1988; Piccirillo *et al.* 1990; Peate 1997; Marques 2001; Guedes *et al.* 2005; Valente *et al.* 2007).

THE MESOZOIC SOUTHERN ESPINHAÇO DYKES

The geological context of the Espinhaço region was described in detail by Dossin *et al.* (1995) and Rosset *et al.* (2007) from which most of the following brief summary is extracted, with some additional information. The São Francisco Craton (SFC) is an extension of much larger Congo Craton of Central Africa and is the largest cratonic segment of the South American lithospheric plate (Almeida *et al.* 2000). The SFC is composed essentially by Archean and Paleoproterozoic rocks mainly covered by Mesoproterozoic and Neoproterozoic sedimentary basins, and is surrounded by Neoproterozoic mobile belts, related to the Brasiliano Orogeny (650–550 Ma), when occurred its amalgamation into West Gondwana, after the closure of the Neoproterozoic Adamastor Ocean (Almeida *et al.* 2000; Cordani *et al.* 2010).

The Espinhaço Ridge marks the limit of the SFC southeastern border, which is related to the Brasiliano Orogeny due to the collision between the São Francisco and Congo cratons, with some plates or microplates in between. According to Dossin *et al.* (1995), the Archean basement, which is composed of gneisses, migmatites and granites of the Southern Espinhaço, was intruded by Mesozoic tholeiite dykes (Fig. 1). These intrusions were interpreted to be related to the huge igneous activity of the PCFB, due to their geochemical similarities (Silva *et al.* 1995; Mazzucchelli *et al.* 2000), as well as by a K–Ar age of 120 Ma for a dyke outcropping in this area (Silva *et al.* 1995). It is important to note that the dykes are not restricted to the Southern Espinhaço, and are also found in the Southern SFC border, nearby its limit with the PCFB, as reported by Pinese *et al.* (1998), who obtained a K–Ar date of 127 ± 3 Ma for a body located nearby Lavras town.

The Mesozoic Southern Espinhaço dykes (MSED) were investigated by Rosset *et al.* (2007) for elemental and Sr–Nd isotope geochemistry, paleomagnetism, and ^{40}Ar – ^{39}Ar

geochronology. Regarding the ages, applying the ^{40}K decay constants and age of the Fish Canyon Tuff proposed by Renne *et al.* (2010), the results of the two investigated samples by those authors are slightly older (sample 9021: 132.4

± 0.6 Ma; sample 9024: 131.9 ± 0.3 Ma) than previously reported (i.e., 130.3 ± 0.6 and 129.8 ± 0.3 Ma).

The data show the dykes have high titanium contents ($\text{TiO}_2 > 3\%$), presenting major, minor and trace element

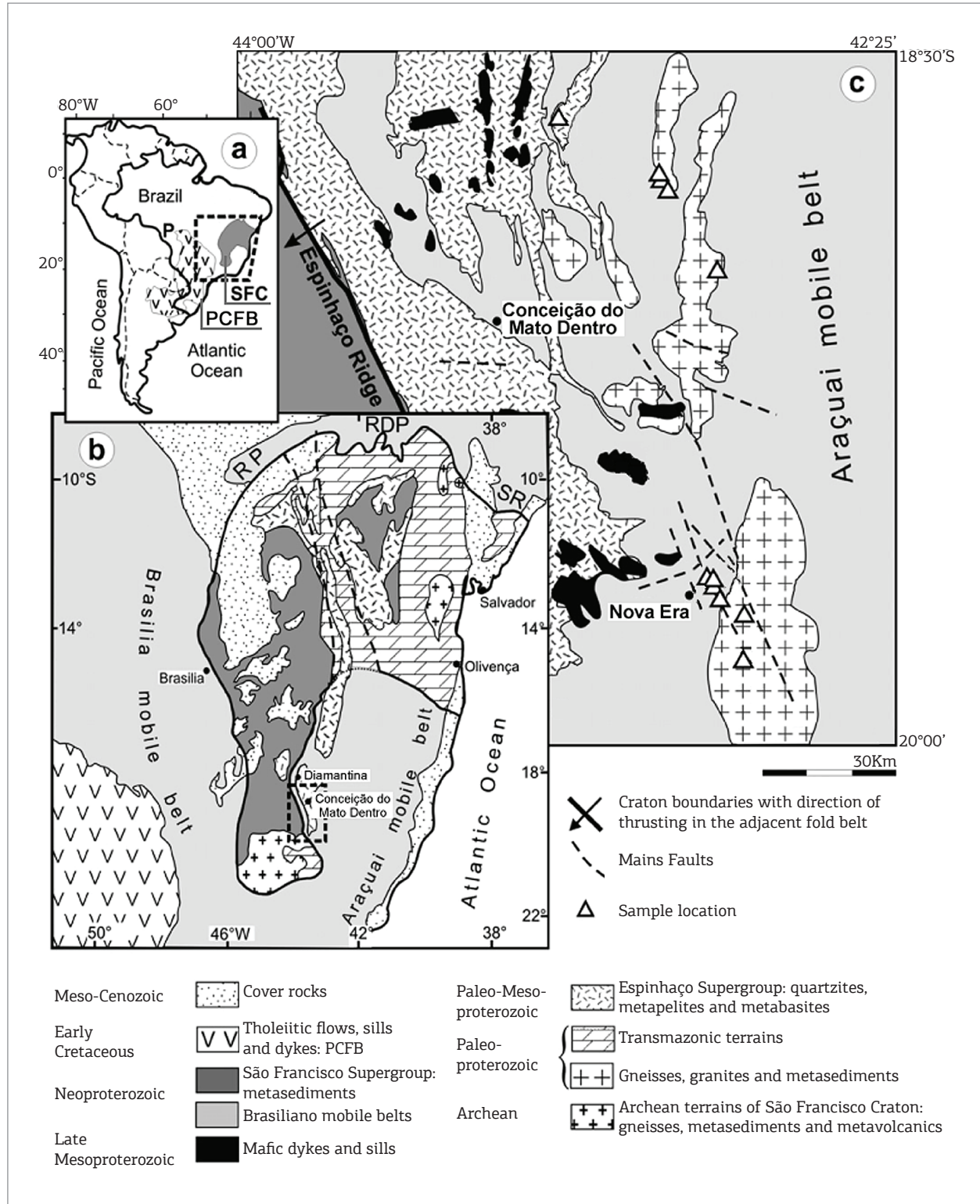


Figure 1. Geological map showing the location of the investigated dykes, extracted from Rosset *et al.* (2007).

composition close to the HTiB of Urubici type. However, the MSED have Sr_i ratios (calculated back to 132 Ma) significantly more radiogenic than Urubici basalts, for very similar initial $^{143}Nd/^{144}Nd$ ratios. These features were interpreted by Rosset *et al.* (2007) as Sr-Nd decoupling related to a chromatographic diffusion of carbonatite components, which have very high Sr concentrations and presumably different Sr isotope signature. Consequently, the diffusion process (a type of selective contamination) may have profound impact on the Sr isotope signature and very small, if any for Nd isotopes.

The role of carbonatites in the Urubici tholeiite genesis is also discussed in detail by Rosset *et al.* (2007), taking into account published Pb isotope data of HTiB from the PCFB and Etendeka, as well as of Early and Late K-alkaline rocks bordering Paraná Basin. Therefore, for the present investigation, some samples studied by Rosset *et al.* (2007) were analyzed for Pb isotope compositions, in order to better constrain the mantle sources involved in the MSED genesis.

EXPERIMENTAL PROCEDURES

Lead isotope compositions were determined in MSED selected samples at the Center of Geochronological Research (CPGeo), Universidade de São Paulo (Brazil), by thermal ionization mass spectrometry.

The analytical precision of Pb concentrations and isotope compositions has been assessed through the analysis of BRP-1 reference material (Brazilian basalt from the PCFB; Cotta & Enzweiler 2008). The results were validated by the analysis of the BCR-1 and AGV-1 USGS reference materials (Babinski *et al.* 2014). The reported means of Pb isotope ratios and their respective two standard deviation, based on 25 analyses of BRP-1, are $^{206}Pb/^{204}Pb = 17.995 \pm 0.012$, $^{207}Pb/^{204}Pb = 15.527 \pm 0.009$ and $^{208}Pb/^{204}Pb = 38.381 \pm 0.031$, with relative precision of $\pm 0.07\%$ ($^{206}Pb/^{204}Pb$), $\pm 0.06\%$ ($^{207}Pb/^{204}Pb$) and $\pm 0.08\%$ ($^{208}Pb/^{204}Pb$). The mean Pb concentration obtained by isotope dilution for BRP-1 is $5.29 \pm 0.05 \mu\text{g/g}$ (precision = $\pm 0.95\%$; accuracy = 3.8%; $n = 16$), agreeing with the certified value. The analytical blanks during the analyses were about 100 pg and replicate analyses of the SRM981 NBS standard were used to correct the lead isotope ratios for mass discrimination.

Besides the high level of accuracy and precision required for the analysis, one of the most important issues related to Pb isotope determinations is the risk of contamination during sample preparation. Recently, with the technical advances in isotope composition measurements, contamination during sample preparation proved to be a serious problem, since even some reference materials were significantly contaminated by such process (e.g., Weis *et al.* 2006). Therefore, in

order to develop a protocol to assure accurate results avoiding this kind of contamination, some PCFB literature data are critically reviewed and some experiments were carried out, as described below.

The need of sawed surface removal

There is not much detail in the literature about sample preparation of low Pb rock samples submitted to Pb isotope analysis. Marques *et al.* (1999) report the necessity of elimination of any kind of sample alteration, including the sawed sections removal, which may provoke lead contamination in high levels.

In order to assess the contamination effect of this kind of contamination in Pb concentrations and isotope compositions, the results of two samples (Urubici: GB13AF; Gramado: GB18AC) are used. Noteworthy, these samples were 1" diameter cylinders originally used for paleomagnetic studies.

These samples were firstly analyzed by Mantovani *et al.* (1985) for major, minor and trace elements, as well as for Sr isotopes, using rock powders obtained by using a tungsten carbide ball mill, without removing sawed surfaces of the cylinders. The same powdered materials were used for Pb isotope analyses, whose results were reported by Hawkesworth *et al.* (1986).

The same two samples were also analyzed for Pb isotopes by Marques *et al.* (1999), after a careful removal of all sawed surfaces of the cylinders, allowing evaluating if, in fact, there is a risk of Pb contamination by diamond saw cutting.

Sample washing and powdering process

Regarding the crushing steps, some tests were accomplished by using four samples from the PCFB, presenting very distinct Pb concentrations ($2 \mu\text{g/g}$ to about $30 \mu\text{g/g}$), in order to assess the possible effects of contamination depending on sample preparation process.

Initially, the samples were hand broken in small fragments (diameters less than 0.5 cm), using a stainless steel small hammer and tungsten carbide mortar. Then the fragments of each sample were quartered in two aliquots and were submitted to different procedures. One fragment fraction was firstly washed with deionized water, and then ultrasonically washed in double distilled water, for several times until the washing solution was clean. Finally, each sample was ultrasonically rinsed in purified 0.25N HNO_3 , for at least 3 times, and dried in class 10,000 clean room, equipped with laminar flow hoods class 100. The acid washing is necessary to eliminate some surface contamination, especially possible carbonate incrustations and sulfides present on oceanic basalts (Marques *et al.* 1999). The washing requirement was evaluated in the other fragment rock fraction, which was only rinsed with deionized water and dried in furnace at 60°C .

Each fragment rock fraction was split by quartering into three subsamples:

1. in one of them, the fragments were powdered using a tungsten carbide ring mill (CPGeo-USP), which does not introduce Pb contamination, as shown by Marques *et al.* (2003);
2. another group was crushed in a tungsten carbide ball mill (IAG-USP);
3. the last one was powdered using an agate ball mill (IAG-USP). The last two crushers are new and were used because their easiest handling.

It is important to emphasize that, in order to avoid cross contamination, before powdering each sample, the crushers were careful cleaned. The first step is the cleaning with water, neutral detergent and a sponge, followed by rinsing with alcohol and hot hair dryer or bulbs drying. Afterwards, a split of the sample to be powdered is crushed (this powder is eliminated) and, finally, the crusher is cleaned again with water and alcohol.

The Mesozoic Southern Espinhaço Dyke samples

Six samples of the MSED selected from the group previously studied by Rosset *et al.* (2007) were powdered using a tungsten carbide ring mill. The samples were hand broken in small fragments and careful washed as described above for the PCFB sample preparation.

The sample dissolution and Pb separation followed the analytical procedures described by Babinski *et al.* (1999, 2014) and Marques *et al.* (2003). The Pb isotope ratios were measured on a MAT 262 mass spectrometer. The whole procedure analytical blanks were lower than 100 pg, which are negligible in comparison to two reported lead concentrations of the MSED (Rosset *et al.* 2007), as well as to the HTiB from the PCFB. Replicate analyses of the NIST SRM981 standard was used to correct the lead isotope ratios for mass discrimination, which are about 0.095% amu⁻¹.

RESULTS AND DISCUSSION OF THE SAMPLE PREPARATION PROCEDURES

In order to establish a sample preparation protocol for Pb isotope analysis, especially in rocks with low Pb concentration, the results obtained in the different experiments are shown and discussed.

Four samples were used for the tests involving the need of washing rock fragments with double distilled water and purified diluted nitric acid. Three of them are volcanic rocks (Piccirillo & Melfi 1988; Marques *et al.* 1989) from the low-Ti association of the PCFB (B512: Esmeralda basalt; B614: Palmas rhyodacite; B716: Palmas rhyolite), whereas the other is a dyke of HTiB type (Marques 2001), belonging to the Serra do Mar Swarm (RJ7574). For the dyke, the subsamples were analyzed in duplicate in order to assess the reproducibility of the employed analytical method.

Evaluation of Pb contamination caused by diamond saw cutting

Samples GB13AF and GB18AC were used for this investigation and the results are shown in Table 1. A considerable decrease of Pb concentration is observed for GB13AF (21.2%) in the powdered aliquot without sawed surfaces. Besides that, for both samples there is a significant increase on the ²⁰⁶Pb/²⁰⁴Pb (2.8 – 3.0%), ²⁰⁷Pb/²⁰⁴Pb (0.2 – 0.4%) and ²⁰⁸Pb/²⁰⁴Pb (1.4 – 2.1%) compositions. The variations are far outside of the expected ones considering the analytical uncertainties (2σ).

It is worth mentioned that the Pb isotope compositions of some Urubici basalts reported by Hawkesworth *et al.* (1986), including the sample GB13AF, were subsequently considered doubtful by the own authors (Peate *et al.* 1999), who stated that the origin of such low ²⁰⁶Pb/²⁰⁴Pb isotope ratios was uncertain.

Therefore, external weathered portions of the samples and, especially, all sawed surfaces (including those from

Table 1. Comparison of measured Pb isotope compositions and concentrations for samples analyzed in different laboratories using different sample preparation methodologies.

Sample	GB13AF			GB18AC		
	1	2	RE (%)	1	2	RE (%)
²⁰⁶ Pb/ ²⁰⁴ Pb	17.062(19)	17.580(12)	2.9	18.068(20)	18.576(14)	2.7
²⁰⁷ Pb/ ²⁰⁴ Pb	15.447(17)	15.503(15)	0.4	15.624(17)	15.654(16)	0.2
²⁰⁸ Pb/ ²⁰⁴ Pb	37.388(41)	38.158(47)	2.0	38.323(42)	38.844(50)	1.3
Pb (µg/g)	8.232(3)	6.48(2)	27.0		5.17(2)	

The analytical uncertainties for isotope ratios (2σ) and Pb concentrations (1σ) correspond to the last figures and are denoted in parenthesis; 1: Hawkesworth *et al.* (1986); 2: Marques *et al.* (1999); RE: Relative error considering as true values the results obtained after the sawed surface removal of the cylinders, i.e. the values of Marques *et al.* (1999).

drill cores) must be eliminated prior analysis, because they can completely mask the original Pb concentrations and isotope compositions.

The use of agate versus tungsten carbide mills for sample grinding

Whichever analytical procedure is used for trace element analysis in rocks, it is traditionally recommended to use agate as the grinding material, since it does not cause any significant contamination. In contrast, tungsten carbide, although very efficient for crushing, is not adequate for some trace element analysis due to the high-level contamination of W, Os, Ta and Co, which are commonly taken into account for petrogenetic modeling.

Since rocks pulverized in agate mills are often used for the trace element analysis, it would be very suitable to use such powders for the determination of Pb concentrations and isotope compositions. For that reason, a test was carried out to verify if powdering in agate and tungsten carbide mills provide equivalent results.

For this experiment three different mills were used, two of tungsten carbide and one of agate. For easiest identification of each experimental procedure, the different subsamples were identified adding some letters after the sample numbers, as following: CW = careful washing (with double distilled water and diluted nitric acid) or SW = simple washing (only with double distilled water), C = using tungsten carbide mill or A = using agate mill, and IGC = CPGeo ring mill or IAG = IAG ball mill.

Before discussing the results obtained in the different sample preparation procedures, the data of the duplicate

subsamples are presented in order to assess the level of reproducibility of the analyses. Table 2 shows that both the Pb isotope compositions and concentrations of RJ7574-SW-C-IGC and RJ7574-SW-A-IAG subsamples, which were analyzed in duplicate, are identical considering the analytical uncertainties (for isotope ratios the uncertainties are quoted as 2σ , whereas for concentrations are 1σ). For the isotope compositions, the relative errors (RE) varied from 0.05 to 0.09%, while for Pb concentrations the RE values are 1.4 and 0.6%, reinforcing the high level of reproducibility of the employed analytical method.

For the sample preparation comparison, the following subsample pairs were considered:

1. B512-CW-C-IAG and B512-CW-A-IAG;
2. B512-SW-C-IAG and B512-SW-A-IAG;
3. RJ7574-SW-C-IGC and RJ7474-SW-A-IAG;
4. B614-CW-C-IGC and B614-CW-A-IAG.

The data for Pb isotope ratios between each pair may be considered identical, taking into account their respective (2σ) analytical uncertainties, with RE varying from 0.003 to 0.06% (Tab. 3). Using as uncertainty, the relative precision obtained by Babinski *et al.* (2014) for the analysis of the BRP-1 reference material ($^{206}\text{Pb}/^{204}\text{Pb} = 0.07\%$; $^{207}\text{Pb}/^{204}\text{Pb} = 0.06\%$; $^{208}\text{Pb}/^{204}\text{Pb} = 0.08\%$), the Pb isotope ratios of each subsample pair may be also considered as equal. Consequently, the results indicate that both agate and tungsten carbide may be used as grinder materials for the determination of Pb isotope ratios.

The Pb concentrations are equal for the pairs B512-CW-C-IAG/B512-CW-A-IAG and RJ7574-SW-C-IGC/

Table 2. Comparison of Pb isotope ratios and concentrations for duplicate analysis of samples RJ7574-SW-C-IGC and RJ-SW-A-IAG.

Sample	RJ7574-SW-C-IGC Aliquot A	RJ7574-SW-C-IGC Aliquot B	RE (%)	RJ7574-SW-A-IAG Aliquot A	RJ7574-SW-A-IAG Aliquot B	RE (%)
$^{206}\text{Pb}/^{204}\text{Pb}$	18.358(6)	18.368(7)	0.05	18.360(6)	18.369(7)	0.05
U2($^{206}\text{Pb}/^{204}\text{Pb}$)	0.012	0.012		0.012	0.012	
$^{207}\text{Pb}/^{204}\text{Pb}$	15.575(5)	15.585(6)	0.06	15.576(5)	15.588(7)	0.08
U2($^{207}\text{Pb}/^{204}\text{Pb}$)	0.009	0.009		0.009	0.009	
$^{208}\text{Pb}/^{204}\text{Pb}$	38.584(14)	38.612(15)	0.07	38.585(12)	38.618(18)	0.09
U2 ($^{208}\text{Pb}/^{204}\text{Pb}$)	0.031	0.031		0.031	0.031	
Pb ($\mu\text{g/g}$)	7.71(10)	7.60(10)	1.4	7.73(10)	7.78(10)	0.6
U1($\mu\text{g/g}$)	0.07	0.07		0.07	0.07	

The analytical uncertainties for isotope ratios (2σ) and Pb concentrations (1σ) are denoted in parenthesis; U1 and U2 are the (1σ) and (2σ) uncertainties, respectively, calculated from the relative precision of BRP-1 reference material (Babinski *et al.*, 2014); RE: Relative Error.

RJ7574-SW-A-IAG, considering the analytical uncertainties, presenting RE values of 1.1 and 0.7%, respectively (Tab. 3). Conversely, the concentrations are not statistically identical for the pairs B512-SW-C-IAG/B512SW-A-IAG (RE = 9.4%) and B614-CW-C-IGC/B614-CW-IAG (RE = 7.0%), although the RE values lower than 10.0% show that the results are quite similar. Considering the accuracy and precision of the method, as well as duplicate results, it would be expected RE less than 3.0%. These differences may be caused by sample heterogeneities, such as the presence of sporadic minerals with high Pb concentrations (e.g., sulfides) inside some rock fragments, which would increase the Pb concentrations.

Evaluation of the need of rock fragment careful washing

In order to verify the necessity of a careful washing (with double distilled water and diluted nitric acid) of the small-sized rock fragments, the following pairs of subsamples were taken into account (Tab. 4):

1. B512-CW-C-IAG and B512-SW-C-IAG;
2. B512-CW-A-IAG and B512-SW-A-IAG;

3. RJ7574-CW-C-IGC and RJ7574-SW-C-IGC;
4. B614-CW-A-IAG and B614-SW-A-IAG;
5. B716-CW-C-IGC and B716-SW-A-IAG.

Concerning the Pb isotope compositions encompassing the sample B512, which has the lowest concentration (2.40 µg/g), the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ are statistically identical, with RE ranging from 0.02 to 0.11%, whereas the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (RE = 0.2 and 0.3%) are different. Considering as uncertainty the precision of the BRP-1 reference material (Tab. 4), the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios remain distinct. For the other three subsample pairs, all isotope ratios are equal, taking into account the analytical uncertainties. It is remarkable that the statistical equality for the Pb isotope ratios tends to increase with the increasing of Pb concentrations, indicating that a careful washing is not necessary in case of relative high concentrations. This is the case of sample RJ7574, which has high enough Pb concentration (7.7 µg/g) for the elimination of the careful washing step. On the other hand, a thorough rinsing, with double distilled water and diluted purified nitric acid, is crucial for the isotope analysis of samples with low Pb concentrations.

Table 3. Comparison of Pb isotope ratios and concentrations of samples powdered in agate (A) and tungsten carbide (C) mills.

Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	U2 ($^{206}\text{Pb}/^{204}\text{Pb}$)	$^{207}\text{Pb}/^{204}\text{Pb}$	U2 ($^{207}\text{Pb}/^{204}\text{Pb}$)	$^{208}\text{Pb}/^{204}\text{Pb}$	U2 ($^{208}\text{Pb}/^{204}\text{Pb}$)	Pb (µg/g)	U1 (µg/g)
B512-CW-C-IAG	18.344(12)	0.012	15.598(12)	0.009	38.608(33)	0.031	2.41(3)	0.02
B512-CW-A-IAG	18.347(7)	0.012	15.600(7)	0.009	38.610(18)	0.031	2.39(3)	0.02
RE (%)	0.02		0.01		0.01		1.1	
Equality between results	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
B512-SW-C-IAG	18.356(8)	0.012	15.602(8)	0.009	38.5278(22)	0.031	3.09(4)	0.03
B512-SW-A-IAG	18.367(8)	0.012	15.611(8)	0.009	38.5077(21)	0.031	3.39(4)	0.03
RE (%)	0.06		0.05		0.05		9.4	
Equality between results	Yes	Yes	Yes	Yes	Yes	Yes	No	No
RJ7574-SW-C-IGC	18.358(6)	0.012	15.575(5)	0.009	38.584(14)	0.031	7.8(1)	0.07
RJ7574-SW-A-IAG	18.360(6)	0.012	15.576(5)	0.009	38.585(12)	0.031	7.7(1)	0.07
RE (%)	0.01		0.01		0.003		0.7	
Equality between results	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
B614-CW-C-IGC	18.924(6)	0.013	15.672(5)	0.009	38.891(16)	0.031	16.5(2)	0.16
B614-CW-A-IAG	18.922(9)	0.013	15.669(10)	0.009	38.878(32)	0.031	17.7(2)	0.17
RE (%)	0.01		0.02		0.03		7.0	
Equality between results	Yes	Yes	Yes	Yes	Yes	Yes	No	No

The analytical uncertainties for isotope ratios (2σ) and Pb concentrations (1σ) correspond to the last figures and are denoted in parenthesis; U1 and U2 are the (1σ) and (2σ) uncertainties, respectively, calculated from the relative precision of BRP-1 reference material (Babinski *et al.* 2014). The results obtained for the samples powdered in tungsten carbide mill were considered as true values for the relative error (RE) calculation.

Concerning the Pb concentrations, only for the sample RJ7574 the results are statistically identical (RE = 0.7%). Although the concentrations of the pairs including the samples B614 (RE = 7.6%) and B716 (RE = 3.4%) are not statistically equal, the results may be considered comparable (Tab. 4). On the contrary, there are large differences in Pb concentrations (RE = 28.1 and 41.8%) related to the two pairs encompassing the sample B512 (Esmeralda basalt; 2.40 µg/g). These variations seems too huge to be only caused by the washing step, unless there are occasional Pb-enriched sulfides on the surface some rock fragments, which were removed by HNO₃ rinsing.

It is noteworthy that a better agreement of Pb concentrations and ²⁰⁸Pb/²⁰⁶Pb ratios of the careful washed B512 subsamples in respect to other Esmeralda basalts, with similar compositions (Peate 1997; Marques *et al.* 1999). Therefore, a careful washing for Pb determination in the analysis of samples with low concentrations is recommended, irrespective of the analytical method employed.

It is also important to note that, as pointed out by Nobre Silva *et al.* (2009), several steps of sample washing with 6M HCl (leaching process) are required to eliminate sample superficial alteration due to seawater (secondary minerals) for accurate determinations of Pb isotope composition of both tholeiite and alkaline oceanic basalts. According to those authors, the leaching allows even eliminating sample contamination by drilling mud in case of rocks from boreholes.

LEAD ISOTOPE RESULTS OF THE MESOZOIC SOUTHERN ESPINHAÇO DYKES AND PETROGENETIC IMPLICATIONS

According to Rosset *et al.* (2007), the MSED tholeiites have TiO₂ ranging from 3.1 to 4.2 wt.%, present geochemical signatures similar to the HTiB of Urubici type and can

Table 4. Comparison of Pb isotope ratios and concentrations of samples submitted to different washing procedures.

Sample	²⁰⁶ Pb/ ²⁰⁴ Pb	U2 ²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	U2 ²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	U2 ²⁰⁸ Pb/ ²⁰⁴ Pb	Pb (µg/g)	U1 (µg/g)
B512-CW-C-IAG	18.344(12)	0.012	15.598(12)	0.009	38.608(33)	0.031	2.41(3)	0.02
B512-SW-C-IAG	18.356(8)	0.012	15.602(8)	0.009	38.528(22)	0.031	3.09(4)	0.03
RE (%)	0.07		0.02		0.2		28.1	
Equality between results	Yes	Yes	Yes	Yes	No	No	No	No
B512-CW-A-IAG	18.347(7)	0.012	15.600(7)	0.009	38.610(18)	0.031	2.39(3)	0.02
B512-SW-A-IAG	18.367(8)	0.012	15.611(8)	0.009	38.508(21)	0.031	3.39(4)	0.03
RE (%)	0.11		0.07		0.3		41.8	
Equality between results	Yes	Yes	Yes	Yes	No	No	No	No
RJ7574-CW-C-IGC	18.366(7)	0.012	15.585(6)	0.009	38.610(16)	0.031	7.8(1)	0.07
RJ7574-SW-C-IGC	18.358(6)	0.012	15.575(5)	0.009	38.584(14)	0.031	7.7(1)	0.07
RE (%)	0.04		0.06		0.07		0.7	
Equality between results	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
B614-CW-A-IAG	18.922(9)	0.013	15.669(10)	0.009	38.878(32)	0.031	17.7(2)	0.17
B614-SW-A-IAG	18.903(5)	0.013	15.667(5)	0.009	38.858(12)	0.031	16.3(2)	0.16
RE (%)	0.10		0.01		0.05		7.6	
Equality between results	Yes	Yes	Yes	Yes		Yes	No	No
B716-CW-C-IGC	19.052(6)	0.013	15.673(5)	0.009	38.809(13)	0.031	27.6(3)	0.26
B716-SW-A-IAG	19.047(7)	0.013	15.676(6)	0.009	38.815(16)	0.031	26.7(3)	0.25
RE (%)	0.02		0.02		0.02		3.4	
Equality between results	Yes	Yes	Yes	Yes	Yes	Yes	No	No

The analytical uncertainties for isotope ratios (2σ) and Pb concentrations (1σ) correspond to the last figures and are denoted in parenthesis; U1 and U2 are the (1σ) and (2σ) uncertainties, respectively, calculated from the relative precision of BRP-1 reference material (Babinski *et al.* 2014). The results obtained for the samples whose rock fragments were careful washed were considered as true values for the relative error (RE) calculation.

be divided in two groups based on their Sr contents. The high-Sr dykes (> 950 µg/g) are characterized by relatively low Zr/La (5.3 to 6.8) ratios and high P₂O₅ (> 0.90 wt.%) content, whereas the low-Sr rocks (< 650 µg/g) have relatively high Zr/La (7.2 to 8.2) and lower concentrations of P₂O₅ (< 0.75 wt.%).

The Pb isotope compositions of the six analyzed dykes (three of each group) do not show large variations (²⁰⁶Pb/²⁰⁴Pb: 18.202 to 18.343; ²⁰⁷Pb/²⁰⁴Pb: 15.563 to 15.593; ²⁰⁸Pb/²⁰⁴Pb: 38.499 to 38.633), although the high-Sr group has less radiogenic compositions in comparison to the low-Sr one (Tab. 5). These Pb isotope compositions are slightly higher than the most radiogenic compositions of HTiB from the PCFB, being significantly more radiogenic than those of Urubici basalts.

The petrogenetic processes that would generate such relatively high radiogenic Pb isotope signatures of the MSED are crustal contamination and/or mantle metasomatism. These two possibilities are discussed below, integrating the obtained results with published analyses of major, minor and trace elements, along with Sr-Nd isotopes (Rosset *et al.* 2007). According to those authors, the dykes have relatively high Sr_i (0.7065 – 0.7071; back to 132 Ma) and low initial Nd isotope compositions (εNd(t): -2.4 to -6.1).

Those belonging to the high-Sr group are distinct from the low-Sr one by their lower εNd(t) (-5.8 and -6.1 *versus* -2.4 and -4.3) for similar Sr_i. The data also show that the MSED have εNd(t) values very similar to those of HTiB from the PCFB. Conversely, their Sr_i are distinctly higher than those of the HTiB from the PCFB, which have in general Sr_i < 0.7060 (Piccirillo *et al.* 1989; Peate *et al.* 1999).

Crustal contamination

The role of crustal contamination processes in the genesis of the MSED tholeiites was discussed in detail by Rosset *et al.* (2007) based on major, minor and trace elements, as well as Sr-Nd isotope data. Although their conclusions preclude a significant participation of crustal interaction in the magma evolution of these dykes, this possibility is here revised in view of the significant radiogenic Pb compositions of these dykes in comparison to the HTiB from the PCFB.

Considering that the assimilation of even small amounts of felsic crustal rocks results in a sharp increase in the abundances of Ba, U, Th, and LREE, if this petrogenetic process took place in the generation of MSED, it would be expected positive correlations of these elements with the increase of

Table 5. Sr-Nd-Pb isotope compositions of Mesozoic Southern Espinhaço Dykes.

Element or Isotope Ratio	9021 (Low-Sr)	9022 (Low-Sr)	9024 (Low-Sr)	9006 (High-Sr)	9009 (High-Sr)	9020 (High-Sr)
Rb*	51	45	48	56	46	41
Sr*	630	618	641	955	968	1007
⁸⁷ Sr/ ⁸⁶ Sr*	0.70755(4)		0.70689(4)		0.70690(5)	0.70730(5)
(⁸⁷ Sr/ ⁸⁶ Sr) _i *	0.70710		0.70648		0.70664	0.70708
Sm	11.0*	9.2	9.6*	11.0	12.8*	11.9*
Nd	52.0*	46.6	46.8*	63.0	60.0*	54.6*
¹⁴³ Nd/ ¹⁴⁴ Nd*	0.51246(1)		0.51235(2)		0.51228(4)	0.51227(3)
(¹⁴³ Nd/ ¹⁴⁴ Nd) _i *	0.51234		0.51225		0.51217	0.51216
εNd(t)*	-2.4		-4.3		-5.8	-6.1
U	1.00	1.08	1.29	1.06	1.13	
Th	4.2	4.5	4.47	4.62	4.83	
Pb*	6.73		6.79			
²⁰⁶ Pb/ ²⁰⁴ Pb	18.314(10)	18.343(9)	18.341(9)	18.202(12)	18.219(11)	18.214(8)
²⁰⁷ Pb/ ²⁰⁴ Pb	15.593(11)	15.578(9)	15.577(8)	15.563(12)	15.575(11)	15.574(8)
²⁰⁸ Pb/ ²⁰⁴ Pb	38.633(10)	38.597(9)	38.604(8)	38.499(13)	38.533(11)	38.534(8)

Concentrations in µg/g; U, Th, Sm and Nd determined by INAA; analytical uncertainties for isotope ratios (2σ) correspond to the last figures and are denoted in parenthesis; initial isotope ratios corrected back to 132 Ma; *data from Rosset *et al.* (2007).

Pb isotope compositions. As it can be seen in Fig. 2, which shows the behavior of some selected major, minor and trace elements in relation to the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, the contents of SiO_2 , K_2O , Ba, Th, U and La are very similar to the Urubici flows, although the dykes have significantly higher radiogenic Pb isotope compositions. In contrast, the MSED rocks, and specially the low-Sr dykes, are more enriched in those elements and present more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than the Pitanga basalts. This suggests that MSED might reflect crustal contamination processes affecting magmatic liquids with a composition similar to that of Pitanga magmas. However, since the continental crust has Sr concentrations about $350 \mu\text{g/g}$, this process would cause a decrease of this element in comparison to the Pitanga basalts, which is not observed.

In order to evaluate the possible extent of crustal contamination on the MSED rocks, it was necessary to define the composition of the parental magma before crustal interaction, as well as that one of the crustal rocks intruded by the dykes. Considering that the northern PCFB is widely dominated by the HTiB of Pitanga type, whose geochemical characteristics also found in some dykes outcropping in the Southern SFC (Pinese *et al.* 1998), this magma-type was used as the uncontaminated end-member for the petrogenetic modeling, while Archean continental crust was considered as contaminant, as detailed below.

For modeling, the elemental and isotope composition of the uncontaminated parental magma of the MSED tholeiites was regarded as being similar to sample KS-700 ($\text{MgO} = 5\text{wt.}\%$; Rocha-Júnior *et al.* 2012, 2013), which based on its osmium isotope composition ($\gamma^{187}\text{Os}$ value = + 1.0; calculated for 134 Ma) was securely not affected by crustal contamination. Note that the osmium isotope system is a sensible tracer of crustal involvement in magma genesis, due to the extreme disparity in isotope signatures between the depleted mantle and crustal materials (e.g., Shirey & Walker 1998).

The upper crust in the adjacent area, where the MSED occur, consists of rocks with Archean ages, as previously discussed. The average Sr, Nd and Pb isotope compositions and trace element concentrations for these ancient rocks (Tab. 6) were compiled from Teixeira *et al.* (1996) and Rudnick & Fountain (1995).

The results of the mixing calculations are shown in Figures 3 and 4. Modeling calculations for the Sr-Nd isotope variations could be related to a slight Archean crustal addition (up to 4%) to the parental magma (Fig. 3) in order to explain the isotope composition of the MSED rocks. However, the radiogenic Pb compositions of the MSED tholeiites are not reached through such process (Fig. 4), requiring the involvement of another component in their genesis.

Carbonatites in the mantle source(s)

Using geochemical and Sr-Nd isotope data, Rosset *et al.* (2007) proposed the involvement of carbonatite components to explain the genesis of both the Urubici basalts and the MSED, which may be represented by the SE Brazilian carbonatites (Ponta Grossa region) and by the Asunción Sapucaí Graben (ASU) analogues, located at Eastern Paraguay (Comin-Chiaramonti & Gomes 2005; Antonini *et al.* 2005). Also according to Rosset *et al.* (2007), the Pb isotope compositions of the HTiB from PCFB suggested that the potassic magmatism of the ASU (K-ASU) may also reflect a SCLM component for Urubici basalts.

The Sr-Nd mixing modeling between the Pitanga flows (represented by KS-700) from the PCFB and the K-ASU carbonatites indicated that the last one component contributed with about ~10% for the generation of the MSED tholeiites (Fig. 3), in accordance with the proposition of Rosset *et al.* (2007). However, this is not verified when the Pb isotopes are taken into account, because the HTiB (sample KS-700 included) from the PCFB have more radiogenic compositions than K-ASU rocks (Fig. 3 and 4). This requires the participation of a HIMU-type mantle component, which is characterized by its very radiogenic Pb isotope composition. According to Nd-Pb binary mixing between HIMU and K-ASU components, the participation of latter is about ~4 – 5%. The participation of a HIMU component was also proposed by Antonini *et al.* (2005) to explain the isotope characteristics of the PCFB extension into eastern Paraguay. Comin-Chiaramonti *et al.* (2007) emphasized that the HIMU signature is not restricted to the oceanic basalts, but may be present in the heterogeneous SCLM, as proposed for the Eastern Paraguay rocks (belonging to the PCFB and K-alkaline carbonatites).

Pyroxenite metasomatism in the SCLM-type source

Melting of heterogeneous SCLM-type and/or mantle wedge above ancient subduction zones (frozen and coupled to the base of the lithospheric mantle), which may have been enriched by fluids and/or magmas, are good candidates to generate the geochemical and isotope characteristics of the MSED.

In this respect, Rocha-Júnior *et al.* (2013) proposed a new hypothesis about the genesis of the HTi basalts and associated intrusives from the northern PCFB. According to their proposition, the geochemical and isotope characteristics of tholeiites from the PCFB may be explained by fluids and/or small-volume melts related to metasomatic processes, probably caused by Neoproterozoic subduction, which gave rise to Gondwanaland, as also suggested by Comin-Chiaramonti *et al.* (1997, 2014). In this

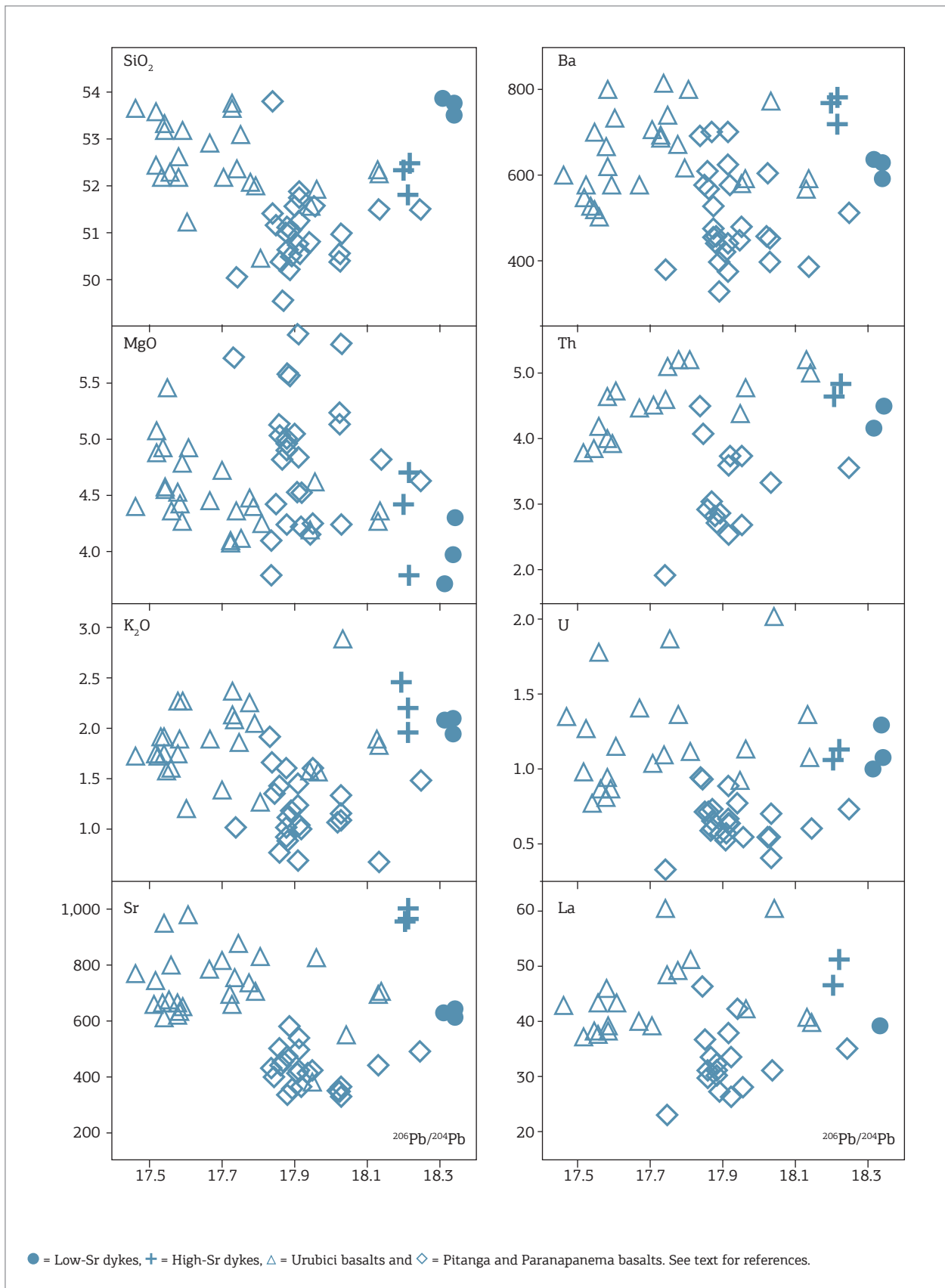


Figure 2. Diagrams for selected major and minor (wt.%), as well as trace elements ($\mu\text{g/g}$) versus measured $^{206}\text{Pb}/^{204}\text{Pb}$.

context, the source of these magmas is not related with a mantle plume and was a mixture of sublithospheric peridotite veined and/or interlayered with mafic components (e.g., pyroxenites or eclogites). This sublithospheric mantle region may have been frozen and coupled to the lithosphere of the investigated area and surrounding region (Goiás Alkaline Province (GAP) and northern PCFB). Note that the sources of the HTiB from the PCFB, as well as the alkaline rocks that surround the Paraná Basin and the oceanic basalts with DUPAL signatures have isotope characteristics of the EM-I component, which is associated with processes derived from mixtures of eclogites or pyroxenites with peridotites (e.g., Bizzi *et al.* 1995; Carlson *et al.* 2007).

The basis of the proposed model is the initial γ_{Os} values for the HTiB from the northern PCFB (γ_{Os} calculated back to 134 Ma range from +0.1 to +1.4; Rocha-Júnior *et al.* 2012), which overlap the compositions of fertile SCLM xenoliths from the spatially associated GAP (γ_{Os} calculated for 85 Ma range from -5.1 to +2.2; Carlson *et al.* 2007). These isotope similarities are indicative that their source(s) might be physically continuous. The GAP is located in a circum-cratonic area, whose underlying mantle experienced several subduction events during the Neoproterozoic related to the events of the Brasiliano/Pan-African orogenic cycle.

The model proposed by Rocha-Júnior *et al.* (2013) to explain the petrogenesis of the HTiB from the northern PCFB is broadly compatible with origin of the MSED rocks. For both, the main source involved in their genesis would include depleted mantle (DMM component) enriched by fluids and/or magmas (pyroxenite), related to the Neoproterozoic subduction processes, which may have been frozen and coupled to the base of the SCLM. However, distinctly of HTiB from the northern PCFB, the

Sr-Nd-Pb isotope diagrams show that three end-members are required to explain the origin of the MSED tholeiites, which are a DMM component (representing the asthenospheric composition) and two metasomatizing agents, carbonatite (represented by K-ASU carbonatite component) and pyroxenite melts. The pyroxenite component is assumed as the same hypothetical “mafic vein” material (pyroxenite EN89-2; Carlson and Irving 1994) used by Rocha-Júnior *et al.* (2013) to explain the genesis of the HTiB from the northern PCFB. The model suggests a partial melting of a metasomatized peridotite mantle source (originally of DMM-type), containing ~4 – 5% of pyroxenite and ~1% of carbonatite melts (Figs. 3 and 4). Although it was not considered in the petrogenetic modeling, a possible participation of a HIMU-type source cannot be ruled out.

In this respect, the experimental petrology has been used to argue that pyroxenites or eclogites are important constituents in the source regions of some OIBs and flood basalt provinces. Besides that, pyroxenites and eclogites might be generated by hybridizing mantle peridotite with recycled components (Sobolev *et al.* 2005, 2007), or via high-temperature intramantle metasomatism. According to Yaxley (2000), a series of progressive mixing and reaction processes might re-homogenize eclogite components back into the peridotite mantle, producing hybrid, re-fertilized peridotites. Because mafic components in the mantle (e.g., pyroxenites or eclogites) have lower solidus temperatures than those of peridotites, low-degree partial melts will preferentially sample such components (Yaxley & Green 1998).

It is noteworthy that this model is corroborated by electromagnetic surveys (Bologna *et al.* 2005; Pinto *et al.* 2010), whose results revealed highly conductive intrusions in the circum-cratonic area of SFC. According to Pinto *et al.* (2010), carbonatite melts may have metasomatized the resistive cratonic lithosphere, becoming it rejuvenated

Table 6. Parameters of the different components used for the petrogenetic modeling of the Mesozoic Southern Espinhaço Dykes.

Element or Isotope Ratio	KS700 ¹	Archean Continental Crust ²	K-ASU ³	DMM ⁴	Pyroxenite EN89-2 ⁵	HIMU ⁶
Sr (µg/g)	474	347	12,000	7.66	30	623
⁸⁷ Sr/ ⁸⁶ Sr	0.70538	0.7573	0.7072	0.7019	0.70915	0.7028
Nd (µg/g)	38	26	100	0.581	9.7	46.3
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512247	0.51087	0.5118	0.5135	0.51087	0.5129
Pb (µg/g)	3.84	6	500	0.018	10	3.1
²⁰⁶ Pb/ ²⁰⁴ Pb	17.658	18.38	17.29	15.80	19.44	21.20

¹Rocha-Júnior *et al.* (2012); ²Teixeira *et al.* (1996), Rudnick & Fountain (1995); ³Antonini *et al.* (2005), Comin-Chiaramonti & Gomes (2005); ⁴Workman & Hart (2005), Handler *et al.* (2005), GERM data base (<http://earthref.org/GERM/>); ⁵Carlson & Irving (1994), Rehfeldt *et al.* (2008); ⁶Hofmann (2003), Jackson & Dasgupta (2008), GEOROC data base (<http://georoc.mpch-mainz.gwdg.de/georoc/>).

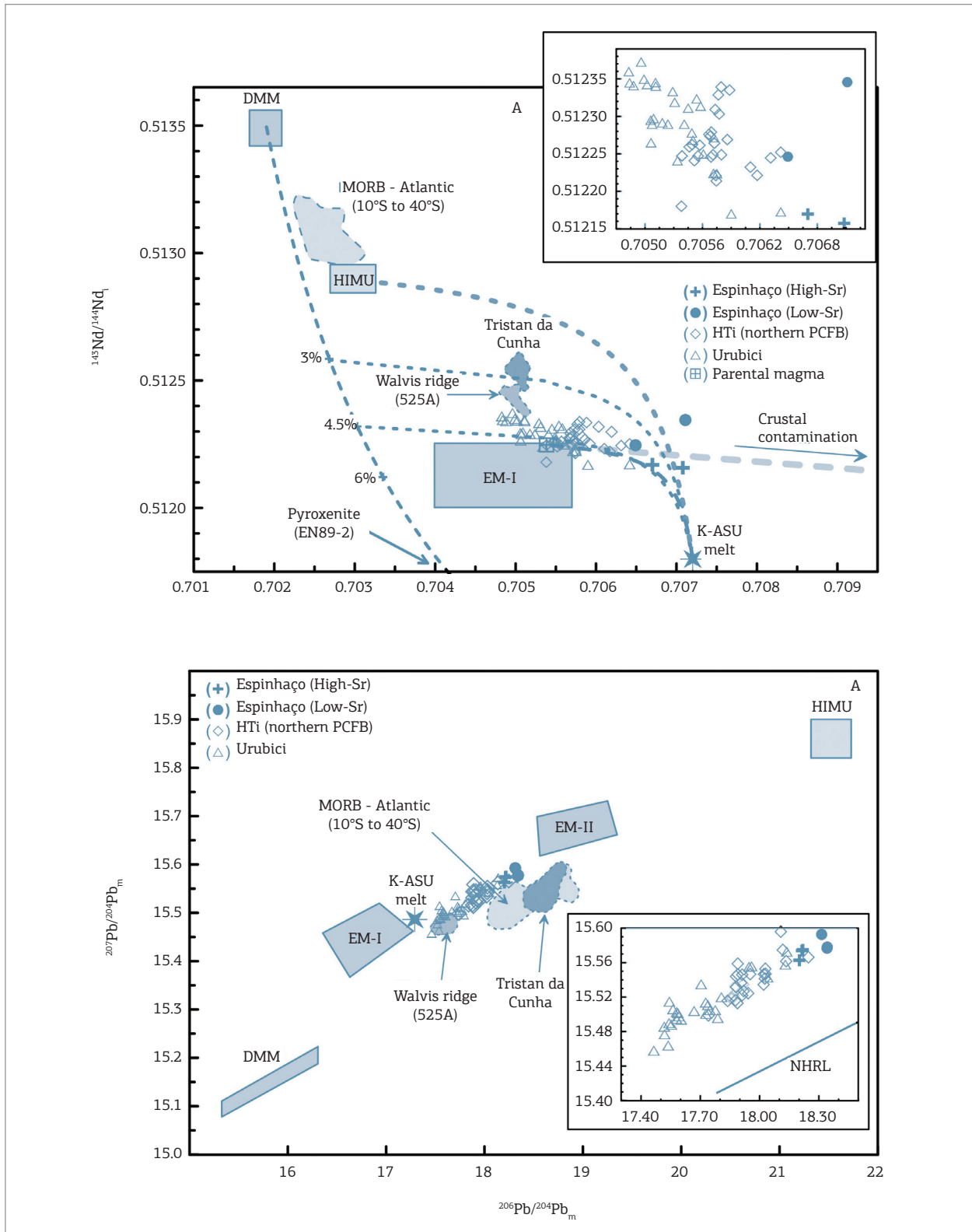


Figure 3. (A) Initial $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against initial $^{143}\text{Nd}/^{144}\text{Nd}$. (B) Measured $^{206}\text{Pb}/^{204}\text{Pb}$ plotted against measured $^{207}\text{Pb}/^{204}\text{Pb}$. Northern Hemisphere Reference Line (NHRL; Hart 1984). Atlantic (10° – 40°S) MORB (PET-DB database (<http://www.petdb.org>)). The mixing lines between the components KS700 (representing the isotope signature of the mantle source of the Pitanga basalts), Archean Continental Crust, K-ASU, DMM, HIMU and EN89-2 pyroxenite are shown (used modeling parameters are in Tab. 6). The EM-I and EM-II mantle components are from Zindler & Hart (1986). Tristan da Cunha is based on data from the GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>).

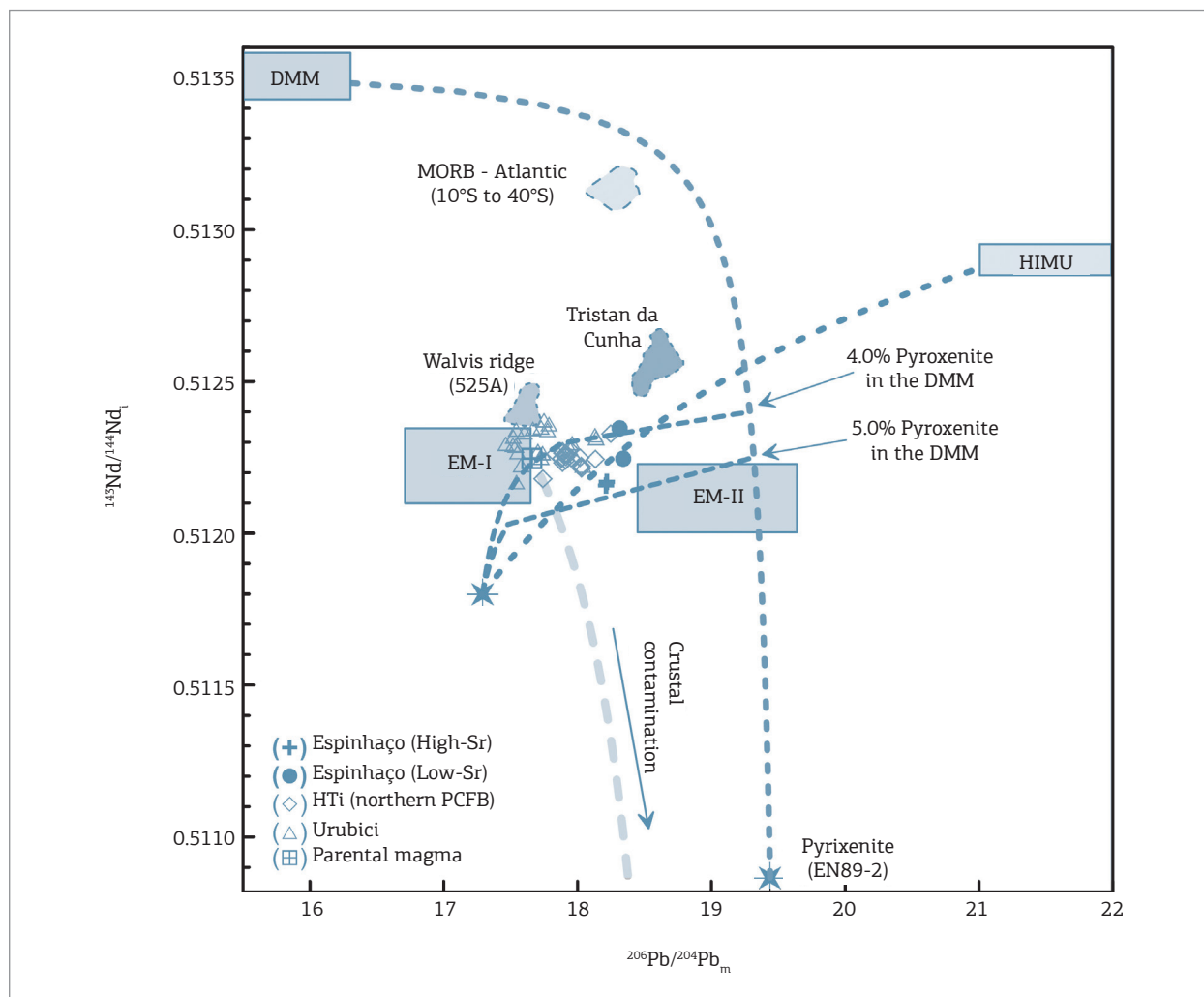


Figure 4. Plot of initial $^{143}\text{Nd}/^{144}\text{Nd}$ versus measured $^{206}\text{Pb}/^{204}\text{Pb}_m$. The components used in the mixture modeling are the same of Fig. 3 (used parameters are in Tab. 6). The EM-I and EM-II mantle components are from Zindler & Hart (1986). Tristan da Cunha is based on data from the GEOROC database (<http://georoc.mpch-mainz.gwdg.de/georoc/>).

and re-oxidized. Additionally, the SCLM refertilization process is supported by GAP xenoliths, which have major and trace element compositions similar to modern fertile mantle (Carlson *et al.* 2007). Most GAP peridotites have fertile $^{187}\text{Os}/^{188}\text{Os}$ (0.1261-0.1292), which are similar to the HTi basalts from the northern PCFB ($^{187}\text{Os}/^{188}\text{Os}$ = 0.12623-0.12793; Rocha-Júnior *et al.* 2012), used as the parental magma of the MSED.

CONCLUDING REMARKS

The main results of the present study are summarized below:

1. The first Pb isotope compositions for the Mesozoic Southern Espinhaço Dykes are presented. Although the dykes have significant radiogenic Pb compositions in

comparison to the high-Ti basalts (Pitanga and Urubici types) from the Paraná Continental Flood Basalts, the Sr-Nd-Pb isotope compositions rule out crustal contamination processes in their genesis.

2. Differently of the most common high-Ti basalts of Pitanga type, which dominate the northern PCFB, the Sr-Nd-Pb isotope compositions of the investigated dykes reinforce that their genesis require metasomatized subcontinental lithospheric mantle source, with the involvement of HIMU and carbonatite mantle components. Agreeing with the Os isotope data of the HTiB from the PCFB (Rocha-Júnior *et al.* 2012, 2013), the magmas might be derived from a metasomatized-SCLM source containing ~4 – 5% of pyroxenite and ~1% of carbonatite melts, although a possible participation of HIMU-type component cannot be ruled out. These metasomatizing agents

were responsible for the refertilization process, as evidenced in the xenoliths from the GAP that surround the investigated region, whose major and trace element compositions are similar to the modern fertile mantle (Carlson *et al.* 2007), also explaining the high electrical conductive character of the lithosphere in this region (Bologna *et al.*, 2005).

3. The investigation about the risks of Pb contamination during sample preparation showed that it is essential to remove sawed surfaces before powdering the rocks. Another crucial procedure for obtaining reliable results of Pb concentrations and isotope compositions is the washing of small-sized rock fragments to be powdered with double distilled water and diluted purified nitric acid, particularly for samples presenting [Pb] < 7 µg/g. In addition, the results of Pb concentrations and isotope compositions of

samples powdered in agate and tungsten carbide mills are identical, considering the analytical uncertainties, indicating that both materials can be used as grinding material for this analysis.

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