Lu-Hf ANALYSIS BY LA-MC-ICP-MS: METHODS AND APPLICATION IN CAPIVARITA ANORTHOSITE ZIRCONS

Anelise Losangela BERTOTTI[1]
Farid CHEMALE JÚNIOR[2]

[1] Geóloga, Dra. Geociências. Professora Visitante do Departamento de Geologia, Universidade Federal de Sergipe – UFS. aneber79@gmail.com
[2] Geólogo, Dr. Geociências. Professor Titular do Instituto de Geociências da Universidade de Brasília - UNB. faridchemale@gmail.com

ABSTRACT. This paper presents a comparative study of Lu-Hf analytic technique performed by methods developed in two laboratories, applied to magmatic and metamorphic zircons from Capivarita Anorthosite, located in southern Brazil. The analyzes were carried out first in the Laboratório de Geologia Isotópica at Universidade Federal do Rio Grande do Sul, Brazil, and after in the Microanalysis Facilities Inco Innovation Centre at Memorial University of Newfoundland, Canada. Both laboratories used the same model of MC-ICP-MS, Thermo Finnigan Neptune, but different lasers and different methodologies. The main differences besides the use of different lasers, lies in its being used during analysis in the LGI a larger spot size for laser and nitrogen. Results from both laboratories show good reproducibility in Hf analyses. T_{DM} ages and $\varepsilon_{Hf}(t)$ values obtained are in agreement within experimental errors.

Key words: Capivarita Anorthosite, Lu-Hf Methodology, LA- MC-ICP-MS, Zircon.

***RESUMO*. Análise de Lu-Hf por MC-ICP-MS: métodos e aplicação em zicões do Anortosito de Capivarita.** *O presente artigo apresenta um estudo comparativo da técnica analítica Lu-Hf realizada por métodos desenvolvidos em dois laboratórios, aplicado a zircões magmáticos e metamórficos do Anortosito de Capivarita, localizado no sul do Brasil. As análises foram realizadas primeiramente no Laboratório de Geologia Isotópica da Universidade Federal do Rio Grande do Sul, Brasil, e depois no* Microanalysis Facilities Inco Innovation Centre *da* Memorial University of Newfoundland, *Canada. Ambos os laboratórios utilizaram o mesmo modelo de MC-ICP-MS, o Neptune da Thermo Finnigan, mas diferentes lasers assim como diferentes metodologias de trabalho. As principais diferenças além de diferentes lasers residem no fato de ter sido utilizado durante as análises no LGI um diâmetro maior para o furo do laser e nitrogênio. Os resultados dos dois laboratórios mostram boa reprodutibilidade nas análises de Hf. As idades TDM e os valores de epsilon Hf obtidos são concordantes dentro dos erros experimentais.*

Palavras-chave: *Anortosito de Capivarita, Metodologia de Lu-Hf, LA-MC-ICP-MS, Zircão.*

INTRODUCTION

The isotopic system of Lutetium-Hafnium (Lu-Hf) has been widely used in geochronology as a tracer to understand the crustal evolution and differentiation of the Earth's mantle (PATCHETT; TATSUMOTO, 1980; THIRWALL; WALDER, 1995; BLICHERT-TOFT; ALBAREDE, 1997; VERVOORT; BLICHERT-TOFT, 1999; GOODGE; VERVOORT, 2006). Numerous studies in the past three decades have shown that the combined use of different isotope systems can be effective in obtaining information on the crustal evolution, metamorphism and sediment provenance (GRIFFIN et al., 2000; GERDES; ZEH, 2006; 2009; NEBEL et al., 2007).

Zircon is a mineral with a geochemistry capability unmatched, easily datable by several radiometric methods (WOODHEAD et al., 2004; WU et al., 2006). This mineral is important in Hf methodology due the fact the initial Hf isotope ratios are preserved in it, a characteristic that can be used in provenance studies and as petrogenetic indicator. Among the several issues to be addressed by the Hf in zircon, like your high concentration, one stands out its applicability in the use combined with the age of zircon crystallization provided by the Uranium-Lead (U-Pb) method.

Furthermore, the high ionization efficiency in inductively coupled plasma instruments made the MC-ICP-MS the method for Hf analysis in zircon (LONGERICH et al., 2008). Although, analysis by laser ablation presents low accuracy comparative with TIMS and in solution analysis by ICP-MS, this disadvantage can be overcome by speed and convenience of combining U-Pb and Hf in-situ isotopic measurements in a single zircon grain, providing information in high resolution.

In this paper, are presented the Lu-Hf methodology and also its applications in zircons from Capivarita Anorthosite. Analysis were performed in two distinct labs, at LGI (Laboratório de Geologia Isotópica, Federal University of Rio Grande do Sul (UFRGS), Brazil), data already published in Chemale Jr. et al. (2011), and MAF-IIC (Microanalysis Facilities Inco Innovation Centre, Memorial University of Newfoundland (MUN), Canada), this paper, in order to test the reproducibility of the Hf method developed at LGI.

Lu-Hf GEOCHEMISTRY

The Lu-Hf isotopic system proves to be very effective in complementing the other isotopic systems (Faure 1986). But the most important factor on this method is that the study of these radiogenic elements provides evidence regarding as the differentiation of the mantle and the growth of continental crust (PATCHETT et al., 1981).

Lu is a heavy rare earth elements (HREE), trivalent, part of the lanthanides group and the element that has the smallest atomic radius in this group (0.93 Å). Lu is present in all types of rocks (FAURE, 1986), but in low concentrations and always with the ytterbium (Yb). The mineral that has the highest concentration of Lu is monazite, approximately 0.003%. Lu is also found in other minerals such as zircon, garnet and xenotime (KINNY; MAAS, 2003; FAURE, 2005).

The Hf element belongs to the IVB group (+4), has ionic radius of 0.81 Å and chemical properties similar to zirconium (Zr +4, 0.80 Å). This makes the zircon one of the minerals with the highest concentrations of Hf by the fact that it easily replaces Zr in its structure. Most zircons have concentrations of Hf around 0.5-2% (HOSKIN; SCHALTEGGER, 2003), its distribution is uneven in other accessory minerals, causing heterogeneity in the rock (FAURE, 1986).

In addition to zircon, Hf can also be found in high concentration in baddeleyite, around 13,340 ppm (FAURE, 2005). Because Hf is an HFSE, High Field Strength Element, it differs chemically from the REE, including Lu, Sm and Nd. The HFSE's are less soluble in aqueous fluids than LILE’s, Large Ion Lithophile Elements, and REE's. Thus, the Lu-Hf pair is different from Sm-Nd isotopic systems in tectonic environments, being less mobile in convergent plates comparing to Sm-Nd during the dehydration in subducting oceanic crust (FAURE, 1986).

Sm and Nd are geochemically very similar elements; same radius, charge and electronegativity. Lu and Hf are different in charge and radius. Despite these differences, the geochemical properties of Lu-Hf are similar to the Sm-Nd pair when it takes into account to their behavior in the partial melting of the mantle, as Nd to Sm, Hf relative to Lu is more concentrated in the liquid silicate. Thus, mantle-derived basaltic magmas has low Lu/Hf ratio than the source rock, and the solid residue is depleted in Hf and higher Lu/Hf ratio than the rock before differentiation.

Dating Lu-Hf

Hafnium has six naturally occurring isotopes, ^{174}Hf (0.16%), ^{176}Hf (5.2%), ^{177}Hf (18.6%), ^{178}Hf (27.1%), ^{179}Hf (13.63%) and ^{180}Hf (35.1%). Lutetium has only two isotopes, ^{175}Lu (97.4%) and ^{176}Lu (2.59%) (FAURE, 2005). Since the isotope ^{176}Hf increases with time in rocks and minerals due to the beta decay of ^{176}Lu. Because of this decay, the Lu-Hf age of rocks and minerals can be given by Equation 1:

$$\frac{^{176}Hf}{^{177}Hf} = \left(\frac{^{176}Hf}{^{177}Hf}\right)_I + \frac{^{176}Lu}{^{177}Hf}\left(e^{\lambda t} - 1\right) \qquad \text{(Eq. 1)}$$

where t is the time elapsed since the formation of rock or mineral and λ is the decay constant of ^{176}Lu. Different values for λ have been proposed in the past by several authors. Patchett and Tatsumoto (1980) proposed the value 1.94×10^{-11} y^{-1}, calculated from the slope of a Lu-Hf isochron for eucrite meteorites of known age. The decay constant assumed in this work is the value of $1.867 \times 10^{-11} y^{-1}$ proposed recently by Söderlund et al. (2004).

The Isotopic Evolution of Hf

Hf isotopic evolution in the BSE (Bulk Silicate Earth) reservoir is assumed to be equal to the chondritic meteorites (CHUR), according to Faure (2005). The initial ratio for ^{176}Hf/^{177}Hf was determined by Patchett and Tatsumoto (1980) in an isochron of 13 chondrites with a value of 0.27978 ± 0.00009 and 0.334 for Lu/Hf ratio. If the age of the chondrite patterns reservoir is 4.55×10^9 years, then the present value for ^{176}Hf/^{177}Hf is 0.28286. In Figure 1, is illustrated the Earth isotopic evolution from a primordial solar nebula in 4.55 Ga, with initial ratio of 0.279718 to the presumed current ratio 0.282772 (FAURE, 1986), such as in chondrites.

The most significant modification of the Lu/Hf ratio occurs in the mantle-crust differentiation event. The magma from the mantle arises in the crust and the Lu/Hf ratio is modified by radioactive decay or by events that crustal material undergoes during its geological history. This crust-mantle differentiation can occur through partial melting processes, fractional crystallization, or both (DICKIN, 2005).

The Lu/Hf methodology enables, beyond the age determination, to establish a petrogenetic parameter, the Epsilon Hf (ε_{Hf}), which support the identification of sources of magmas and processes of rock formation and mineralization. The parameter ε_{Hf} basically consists in comparing the ratio ^{176}Hf/^{177}Hf of the sample at the time of its formation or its current value, with a standard uniform chondrite patterns reservoir (CHUR), which would be representative of the Bulk Earth and is expressed as Equation 2.

$$\varepsilon^{t}(Hf) = \left[\frac{\left({}^{176}Hf/{}^{177}Hf\right)_{sm}^{i}}{\left({}^{176}Hf/{}^{177}Hf\right)_{ch}^{t}} - 1 \right] \times 10^{4} \qquad \text{(Eq. 2)}$$

Where the chondritic values used to calculate the (^{176}Hf/^{177}Hf)$_{ch(t)}$) ratio were 0.0336 to ^{176}Lu/^{177}Hf and 0.282785 to ^{176}Hf/^{177}Hf for present day (BOUVIER et al., 2008). If at the time of the rock crystallization the parent magma has a ^{176}Hf/^{177}Hf higher than the CHUR, the ε_{Hf} is positive, meaning that the source of this magma had Lu/Hf ratio higher than the chondrite, ie the source is the upper mantle (Faure 2005). Moreover, when the formation of the rock, its parent magma has ^{176}Hf/^{177}Hf ratio lower than CHUR, the ε_{Hf} value is negative and therefore the source of these rocks have a Lu/Hf lower than the chondrite, this is the case of magmas of crustal origin. Therefore, when the ε_{Hf} is positive the source is the mantle and when the ε_{Hf} is negative value, the source is a crustal magma.

Depleted Mantle Model Age

The Hf depleted mantle model age is the generation of continental crust from a mantle reservoir causing the depletion in the lighter elements (LILE - Large Ion Lithophile Elements) and also the light rare earth elements (LREE) in this reservoir, resulting what is called as "depleted mantle" (DM) (NEBEL et al., 2007). Therefore, this model assumes the mantle had suffered episodes of fractionation involving the extraction of basaltic magmas, remaining then a residual mantle enriched in the ratio Lu/Hf and geochemically depleted in LILE's. The Hf model age adopted to this work can be calculated by Equation 3, which is the possible evolution curve of Hf for the depleted mantle.

$$T_{DM} = \frac{t_{(U/Pb)}}{1000} + \frac{1}{0.01867} \times \ln\left(1 + \frac{\left({}^{176}Hf/{}^{177}Hf\right)_{sm}^{t} - \left({}^{176}Hf/{}^{177}Hf\right)_{DM}^{t}}{\left({}^{176}Lu/{}^{177}Hf\right)_{sm}^{t} - \left({}^{176}Lu/{}^{177}Hf\right)_{DM}^{0}} \right)$$

(Eq. 3)

Where t is the U/Pb age. The depleted mantle values in present day are 0.28325 for ^{176}Hf/^{177}Hf ratio and 0.0388 for ^{176}Lu/^{177}Hf ratio (GRIFFIN et al., 2000; updated by ANDERSEN et al., 2009); and 0.015 to (^{176}Lu/^{177}Hf)$_{sm(t)}$ an assumed value for Bulk Silicate Earth (GOODGE; VERVOORT, 2006).

INSTRUMENTATION AND ANALYTICAL PROCEDURES

The MC-ICP-MS is a high-resolution mass spectrometer for isotopic ratio measurements with a special configuration for a wide range of nuclides simultaneously detecting. The sample in the ICP-MS can be analyzed by solution or laser ablation. In both forms, the sample is transported by Argon to the ICP sector. The effects of fractionation in the processes of ablation and aspiration are monitored daily by internal and external standards, which in this study are GJ-1, Plešovice and 91500 zircon standards.

In situ analysis of Hf in zircon from LGI and MAF-IIC were made using the ThermoFinnigan Neptune MC-ICP-MS, but different laser microprobe. A laser ablation system from New Wave Research UP213 (Nd:YAg) and GeoLas (ArF Excimer) were used, respectively. The zircons were firstly analyzed at LGI by U-Pb and Lu-Hf methods then after at MAF-IIC for Lu-Hf analysis. Details of the instrumental operating conditions from both labs were as given in Table 1 and the methodologies from each lab are described separately below. In both labs, to minimize aerosol deposition around the ablation pit and improve transport efficiency, the helium gas was flushed into the ablation cell (EGGINS et al., 1998).

LGI Methodology

The isotopic data of Lu-Hf are acquired by the static mode with spot size of 55 µm, a repetition rate of 10 Hz and a density of energy of ~5-6 J/cm^2. The laser ablation system used was a New Wave Research UP213 (Nd:YAg), which provides flats craters and high absorption or the analysis of opaque and transparent materials alike.

To obtain further improvements in precision of the Hf isotopic data from zircon material, a N_2 mixing technique was applied (IIZUKA; HIRATA, 2005; GERDES; ZEH, 2006), with the purpose to reduce the oxide signals by an addition of small amounts of N_2 (~ 4 mL/min) into the carrier gas and an increase of 30% on Hf signals could be seen (BERTOTTI et al., 2013). The N_2 was addicted directly in the Argon line.

Before proceeding with the Hf isotopic calculations, all raw signals are blank corrected using the mean of 50 points recorded as the gas blank baseline before ablation of the grains and standards. The analyses sequence was made by one standard, five unknown and one standard again. A user-selected interval of ~45 data points (~45 seconds of data since the integration time is ~1 data point per second) covering the sample transient peak (~50 seconds of ablation) is used for calculation of the Hf ratio.

In order to calibrate the MC-ICP-MS, we analyzed the reference material JMC-475 in solution (Tune solution 200 ppb) and obtained a value of 0.282156 ± 0.000015 (2SD), which reproduced the isotopic values of Hf reported in the literature (WU et al., 2006; CHU et al., 2002). The standard used during Hf *in situ* analysis was the GJ-1, its reference value for ^{176}Hf/^{177}Hf is 0.282000

± 0.000005 (2MSWD) (MOREL et al., 2008). The obtained value for GJ-1 was 0.282017 ± 0.000009 (n=5, 2SD) with an intensity of 2.03 ± 0.08 V in ^{178}Hf. The sample cell was not opened between the analyses.

Table 1 - Operating conditions used for LA-MC-ICPMS at LGI and MAF-IIC

	LGI	**MAF-IIC**
MC-ICP-MS	Finnigan Neptune	Finnigan Neptune
Ion Source		
Power	1200W	1200W
Extraction	-2000 V	-2000 V
Ion Detection	Faraday	Faraday
Analysis Mode	Static	Static
Gas flow rate		
Cool (l/min)	15.0	16.0
Auxiliar (l/min)	0.73	0.75
Carrier Ar (l/min)	0.74	0.75
Carrier N_2 (ml/min)	4.0-5.0	-
Data acquisition		
Integration Time (s)	1,049	1,049
Integrations	1	1
Laser Ablation		
Instrument	UP-213 New Wave, Nd: YAG, 213 nm	GeoLas, Lambda Physik Compex Pro 110 ArF Excimer,193nm
Spot Size (µm)	55	49
Energy Density (J/cm^2)	5-6	5
Repetition rate (Hz)	10	10
Total ablation time (s)	50	60
He gas flow rate (l/min)	0.7	1.3

MAF-IIC Methodology

A GeoLas (ArF excimer laser) operating at a wavelength of 193nm and a pulse width of 20 ns laser ablation system linked to the MC-ICP-MS was used for the in situ analyses at MAF-IIC. The wavelength from the laser of 193 nm produces a fine distribution of particles, which increases the efficiency in transporting the material resulting in better sensitivity and minimal deposition in the plasma, but also has a fractionation that must be corrected by standards.

A laser fluence of approximately 5 J/cm^2, repetition rate of 10 Hz and spot size of 49 µm were used for all analyses. Here all raw signals are also blank corrected using the mean of ~20-25 points recorded as the gas blank baseline before each ablation. A user-selected interval of ~50 data points from the ~60 seconds of ablation is used for calculation of the Hf ratio in the Excel sheet.

The Plešovice (PL) and 91500 zircons were analyzed as quality control standards. The sequence of the analyses were one PL, one 91500, seven unknowns, one PL and one 91500 again. The reported value for Plešovice for ^{176}Hf/^{177}Hf ratio is 0.282482 ± 0.000013 (2SD) (SLAMA et al., 2008) and the obtained value during our analysis was 0.282480 ± 0.000049 (2SD). The reference value for 91500 can be found in Blichert-Toft (2008) with ^{176}Hf/^{177}Hf = 0.282308 ± 0.000006 (2SD) and the obtained value was 0.282312 ± 0.000061 (2SD).

Isobaric Interference Corrections

Lu, Yb and Hf isotopes are measured simultaneously during the analysis *in situ* in MC-ICP-MS. The configuration used at LGI and MAF-IIC for Lu-Hf analysis is the same and is described in Table 2. The isotopic ratios measured during the analyses of Lu-Hf were: ^{173}Yb/^{171}Yb, ^{179}Hf/^{177}Hf, ^{178}Hf/^{177}Hf, ^{176}Lu/^{177}Hf, ^{176}Yb/^{177}Hf and ^{176}Hf/^{177}Hf. Data were corrected and normalized following the procedure of the laser ablation analyses in the Excel sheet, both labs use the same equations and values to correct the isobaric interference as follow bellow.

Table 2 - Cup configuration used during Lu-Hf measurements in both labs

	L4	**L3**	**L2**	**L1**	**C**	**H1**	**H2**	**H3**
Isotopes	^{171}Yb	^{173}Yb	^{174}Hf	^{175}Lu	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf
Interferences			^{174}Yb		^{176}(Yb+Lu)			

During the *in situ* analysis of Hf in zircon, the isotope ^{176}Lu and ^{176}Yb were analyzed together with the ^{176}Hf. The isotopes ^{175}Lu, ^{171}Yb and ^{173}Yb were monitored during analysis and their relative abundances were used to calculate ^{176}Lu and ^{176}Yb interferences, which were subtracted from ^{176}Hf. Due this reason the ratio ^{176}Hf/^{177}Hf was carefully corrected using a exponential law (WASSERBURG et al., 1981). A mass bias factor β is calculated for Hf and Yb for unit of atomic mass, they are defined as:

$$\beta_{Hf} = \frac{\ln\left[\dfrac{\left(\dfrac{^{179}Hf}{^{177}Hf}\right)_m}{\left(\dfrac{^{179}Hf}{^{177}Hf}\right)_N}\right]}{\ln\left[\dfrac{M_{179(Hf)}}{M_{177(Hf)}}\right]} \qquad \beta_{Yb} = \frac{\ln\left[\dfrac{\left(\dfrac{^{173}Yb}{^{171}Yb}\right)_m}{\left(\dfrac{^{173}Yb}{^{171}Yb}\right)_N}\right]}{\ln\left[\dfrac{M_{171(Yb)}}{M_{173(Yb)}}\right]} \qquad \text{(Eq. 4 and 5)}$$

The measured (m) signals are the blank corrected signals from the instrument, while the corrected values (corr) are the expected natural values for these isotopic ratios. Where the corrected value for ^{179}Hf/^{177}Hf is 0.7325 (PATCHETT; TATSUMOTO, 1980), and the corrected values for ^{173}Yb/^{171}Yb and ^{176}Yb/^{173}Yb are 1.1301 and 0.7938 (SEGAL et al., 2003), respectively.

The signal measured for the 176 mass is a combination of ^{176}Hf, ^{176}Yb and ^{176}Lu. In order to determine ^{176}Hf, the interferences from Yb and Lu must be subtracted. The intensity of ^{176}Hf can be calculated using Equation 6 (IIZUKA; HIRATA, 2005):

$$^{176}Hf = {}^{176}(Hf + Lu + Yb)_m - \left[\begin{array}{l} ^{175}Lu_m \times \left(\dfrac{^{176}Lu}{^{175}Lu}\right)_N \times \left(\dfrac{M_{176(Lu)}}{M_{175}}\right)^{\beta(Lu)} \\ + ^{173}Yb_m \times \left(\dfrac{^{176}Yb}{^{173}Yb}\right)_N \times \left(\dfrac{M_{176(Yb)}}{M_{173}}\right)^{\beta(Yb)} \end{array}\right] \qquad \text{(Eq. 6)}$$

Where the corrected value assumed for ^{176}Lu/^{175}Lu is 0.2656 (CHU et al*.*, 2002) and M is the mass of the isotope.

For ^{176}Yb/^{177}Hf and ^{176}Lu/^{177}Hf, the mass bias correction is approximated using the mass bias factor for Hf, β(Hf):

$$\left(\frac{^{176}Yb}{^{177}Hf}\right)_{corr} = \left(\frac{^{176}Yb}{^{177}Hf}\right)_m \times \left(\frac{M_{176(Yb)}}{M_{177(Hf)}}\right)^{\beta(Hf)}$$

(Eq. 7)

$$\left(\frac{^{176}Lu}{^{177}Hf}\right)_{corr} = \left(\frac{^{176}Lu}{^{177}Hf}\right)_m \times \left(\frac{M_{176(Lu)}}{M_{177(Hf)}}\right)^{\beta(Hf)}$$

(Eq. 8)

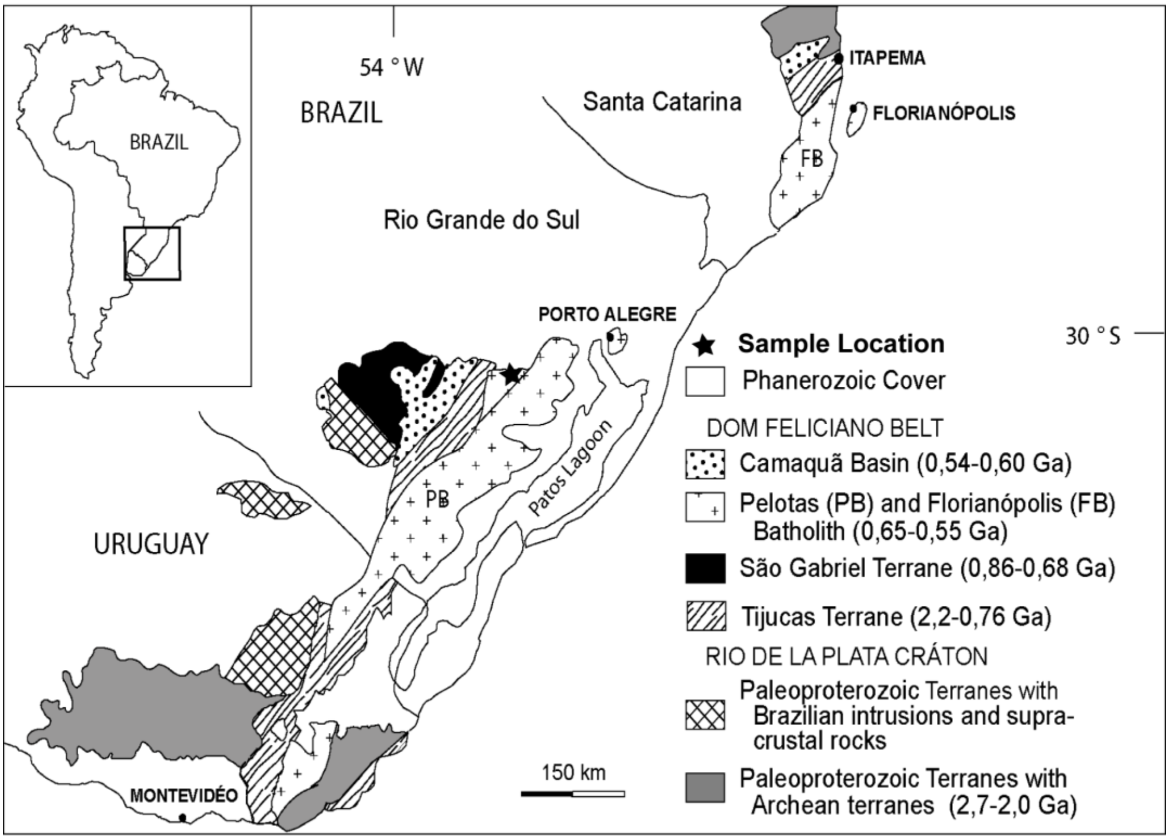
RESULTS FROM CAPIVARITA ANORTHOSITE ZIRCONS

The Capivarita Anorthosite is situated in the Pantano Grande locality in the NE portion of the Sul-Rio-Grandense Shield, Rio Grande do Sul State, Brazil (Figure 1). This anorthosite is part of the Dom Feliciano Belt (DFB), an orogenic belt formed during the Neoproterozoic (860-550 Ma). Many studies (RIBEIRO et al., 1966; TESSARI; PICADA, 1966; FORMOSO; CARRARO, 1968; FORMOSO, 1973; FERNANDES et al., 1992; BABINSKI et al., 1997; PHILIPP; MACHADO, 2005; CHEMALE JR., 2000; CHEMALE JR. et al., 2011) were made on this anorthosite to define better the nature of this massif-type anorthosite.

Anorthosites are unique rocks, both in terms of occurrence, composition (> 90% of plagioclase) and genesis. The anorthosites are mainly found in Archean and Proterozoic terrranes in all continents with significant occurrences in North America, Africa, Europe and Antarctica (PHILIPP; MACHADO, 2005). Furthermore, they are also important in the reconstruction and evolution of ancient continents such as the Columbia and Rodinia, occurring in the final stages of continental consolidation or later, in the early stages of continental fragmentation.

In the Capivarita Anorthosite the major components are the anorthosite rocks with associated mafic rocks, metagabros and amphibolites tabular bodies, cogenetic related. The composition of plagioclase is homogeneous (An$_{50}$-An$_{64}$), one special occurrence displays An$_{94}$ (PHILIPP; MACHADO, 2005). Large crystals (7 to 20 centimeters) and a protoclastic texture are typical. The obtained ages for inherited zircons is 2028 ± 17 Ma and for igneous zircons is 1573 ± 21 Ma (CHEMALE JR. et al., 2011). These ages agree with those of Proterozoic massif-type anorthosites.

Figure 1 - Location of the Capivarita Anorthosite in the NE portion of the Sul-Rio-Grandense Shield, Rio Grande do Sul State, Brazil (modified from Philipp et al. (2010)



Previous Lu-Hf Data

A detailed description of sample preparation for Capivarita Anorthosite's sample is in Chemale Jr. et al. (2011). In this previous work, magmatic and metamorphic minerals were dated using the LA-MC-ICP-MS *in situ* method. The magmatic and metamorphic zircons, totalizing of 15 zircons, were first analyzed by U-Pb method which yielded an age of 1573 ± 21 Ma and of 606 ± 6 Ma, respectively. Some titanites were also analyzed, igneous titanites yielded an age of 1530 ± 33 Ma and for metamorphic titanites yielded ages of 651 ± 9 Ma and 601 ± 5 Ma.

To obtain information about the provenance of the zircon, the authors carried out Lu-Hf in situ LA-ICP-MS analyses in the zircons that were chosen for U-Pb dating (see Table 3). The Lu-Hf model ages showed two clusters from 1.81 to 2.03 Ga with ε_{Hf}(t) values from +2.21 to +6.42 and 2.55 to 2.62 Ga with ε_{Hf}(t) values from -4.59 to -5.64. All dated metamorphic zircons have T_{DM} and ε_{Hf}(t) similar to those of the crustal zircons with Hf model ages ranging from 2.47 to 2.54 and ε_{Hf}(t) values from -15.34 to -16.58 for time of metamorphic recrystallization of 0.6 Ga. The baddeleyite grain (Zr-170-A-I-02) displays similar values as those of the metamorphic zircons, with Hf model age of 2.45 Ga and ε_{Hf}(t) value of -15.4.

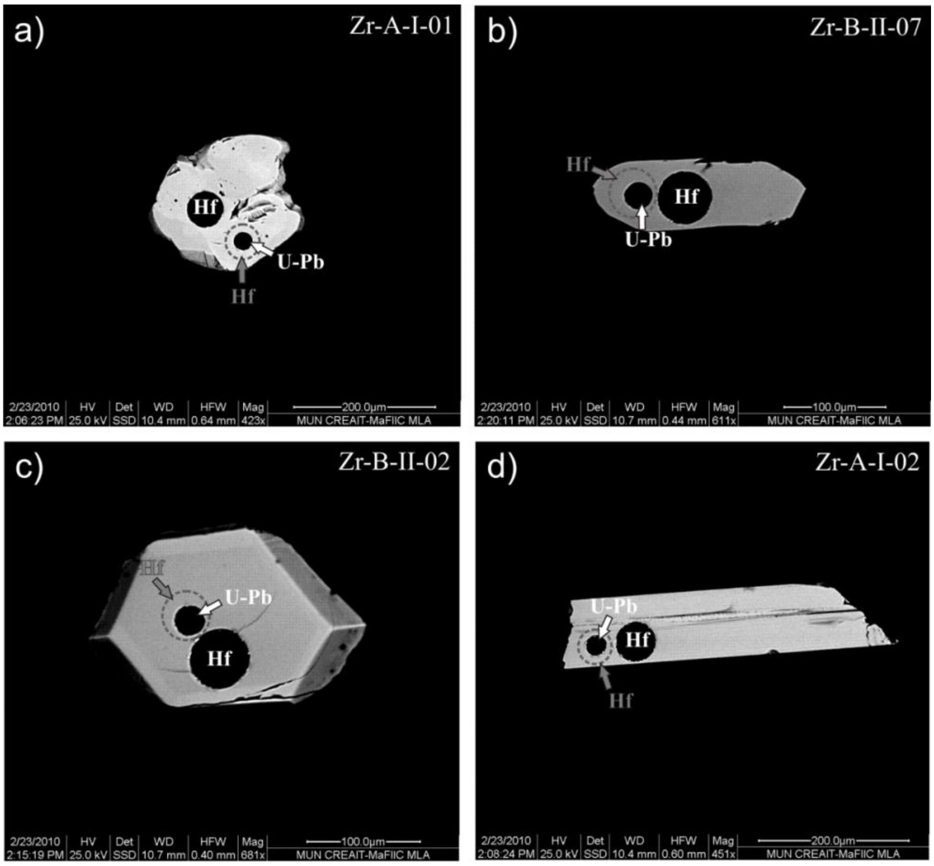
New Lu-Hf Data

The Hf analyses in the Capivarita Anorthosite at MAF-IIC were made in twelve zircons, seven magmatic and five metamorphic and one baddeleyite in the same sample as used in previous study described in Chemale Jr. et al. (2011). Hf analyses were not performed in all dated zircons in LGI. Three igneous zircons (Zr-170-C-III- 05, 10 e 16) have not been analyzed at MAF-IIC because they were too small to permit a new laser spot for Hf isotopes analyses. The hole of the laser was made on the top of the U-Pb analysis or close as possible to the U-Pb spot (see Figure 2).

Table 3 - Results of Lu-Hf analyses from Capivarita Anorthosite zircons at LGI

Sample	U/Pb Age	±2s	^{178}Hf (V)	^{176}Hf/^{177}Hf	±2SE	^{176}Lu/^{177}Hf	±2SE	^{176}Hf/^{177}Hf (t)	ε_{Hf} (t)	T_{DM} Age (Ga)
Igneous Zircons										
Zr-170-A-I-01	1573	21	2.61	0.281636	0.000029	0.000359	0.000006	0.281625	-5.64	2.62
Zr-170-B-II-11	1573	21	3.52	0.281643	0.000019	0.000298	0.000004	0.281635	-5.29	2.60
Zr-170-C-III-08	1573	21	1.69	0.281665	0.000039	0.000372	0.000004	0.281654	-4.59	2.55
Zr-170-B-II-06	1573	21	2.81	0.281899	0.000023	0.000028	0.000001	0.281898	4.05	2.01
Zr-170-B-II-07	1573	21	2.56	0.281885	0.000026	0.000060	0.000009	0.281884	3.55	2.04
Zr-170-C-III-02	1573	21	1.77	0.281894	0.000039	0.000773	0.000061	0.281871	3.10	2.07
Zr-170-C-III-05	1573	21	1.42	0.281849	0.000035	0.000093	0.000005	0.281846	2.21	2.13
Zr-170-C-III-10	1573	21	1.63	0.282003	0.000067	0.001288	0.000018	0.281965	6.42	1.86
Zr-170-C-III-16	1573	21	1.48	0.281903	0.000044	0.000083	0.000006	0.281901	4.15	2.01
Metamorphic Zircons										
Zr-170-B-II-01	611	4.8	2.41	0.281951	0.000022	0.000842	0.000012	0.281942	-16.21	2.52
Zr-170-B-II-02	611	4.8	2.59	0.281970	0.000027	0.000431	0.000004	0.281965	-15.39	2.47
Zr-170-B-II-03	611	4.8	2.81	0.281934	0.000027	0.000206	0.000003	0.281931	-16.58	2.54
Zr-170-B-II-04	611	4.8	2.38	0.281969	0.000022	0.000253	0.000002	0.281966	-15.34	2.47
Zr-170-B-II-08	611	4.8	3.16	0.281960	0.000026	0.000875	0.000032	0.281950	-15.90	2.50
Baddeleyite										
Zr-170-A-I-02	608	14	3.01	0.281978	0.000029	0.000315	0.000005	0.281975	-15.12	2.45

Figure 2 - Zircon backscattering images showing the spots from Hf (big hole) and U-Pb (small hole) analyses at LGI. Dotted circles are the Hf analyses at MAF-IIC. Mineral images: a) and b) are igneous zircons, c) is a metamorphic zircon and d) is a baddeleyite



In the magmatic zircons were founded two groups of zircons (see Figure 3 and Table 4). The first one yielded negative ε_{Hf}(t) values of -5.9 to -4.4 and T_{DM} model ages between 2.54 to 2.63 Ga. The second group is reworked zircons from a Paleoproterozoic source with positive ε_{Hf}(t) values of +2 to +3.5 and with younger T_{DM} model ages between 2.05 to 2.14 Ga. For metamorphic zircons the ε_{Hf}(t) values were very negative of -15.8 to -17.2 with T_{DM} model ages between 2.49 to 2.58 Ga. And the only one baddeleyite (Zr-170-A-I-02) yielded ε_{Hf}(t) value of -15.4 and T_{DM} model age of 2.47 Ga.

Figure 3 – ε_{Hf}(t) values (a) and Hf isotope (b) are evolution diagrams from Capivarita Anorthosite zircons. Shadowed areas indicate the evolution trend for this massif

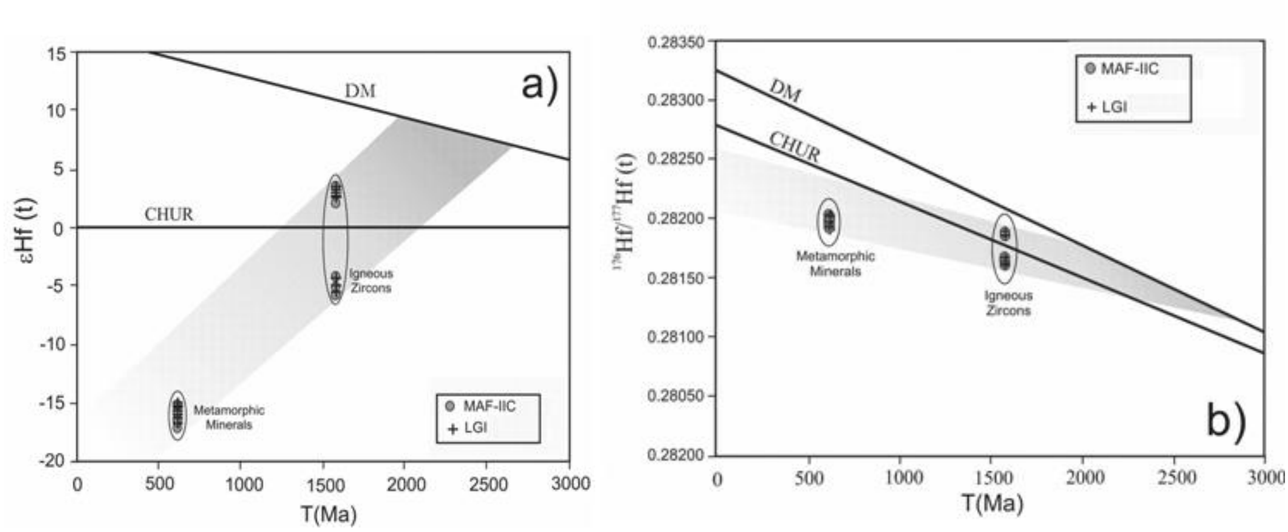
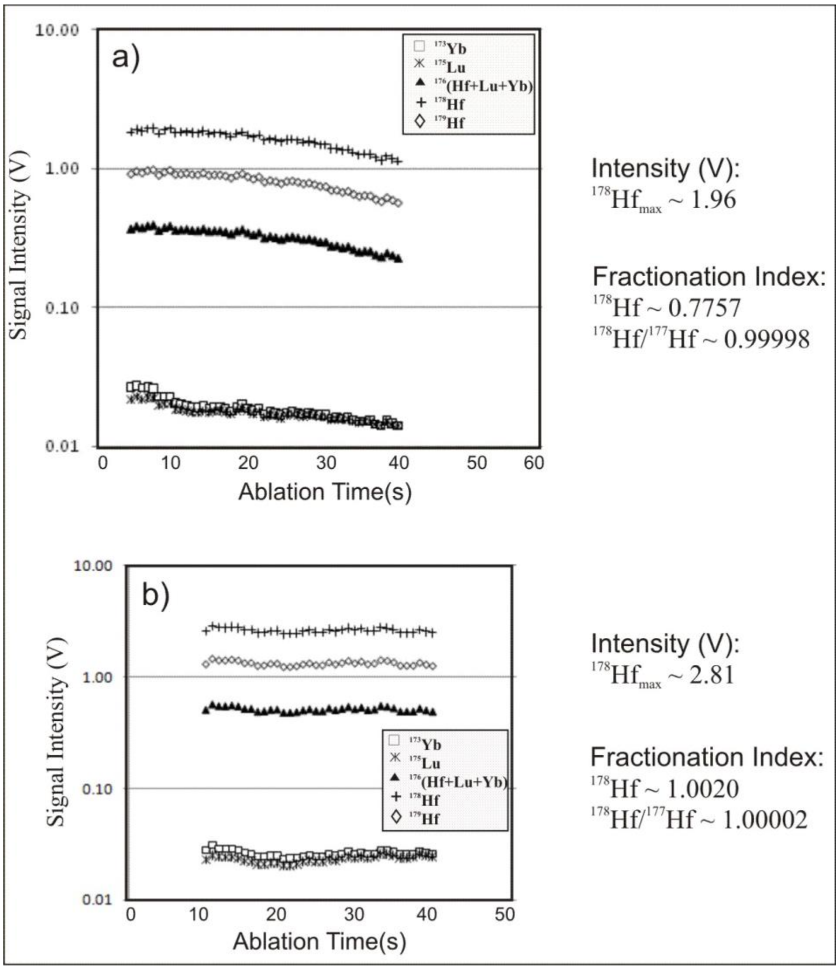


Table 4 - Results of Lu-Hf analyses from Capivarita Anorthosite zircons at MAF-IIC

Sample	U/Pb Age(Ma)	±2s	^{178}Hf (V)	^{176}Hf/^{177}Hf	±2SE	^{176}Lu/^{177}Hf	±2SE	^{176}Hf/^{177}Hf (t)	ε_{Hf}(t)	T_{DM} Age (Ga)
Igneous Zircons										
Zr-170-A-I-01	1573	21	1.60	0.281630	0.000049	0.000435	0.000010	0.281617	-5.9	2.63
Zr-170-B-II-11	1573	21	1.78	0.281643	0.000064	0.000265	0.000006	0.281635	-5.3	2.60
Zr-170-C-III-08	1573	21	1.99	0.281671	0.000033	0.000340	0.000004	0.281661	-4.4	2.54
Zr-170-B-II-06	1573	21	1.92	0.281841	0.000035	0.000033	0.000001	0.281840	2.0	2.14
Zr-170-B-II-07	1573	21	1.67	0.281883	0.000043	0.000036	0.000001	0.281882	3.5	2.05
Zr-170-C-III-02	1573	21	2.01	0.281901	0.000034	0.000614	0.000013	0.281883	3.5	2.05
Metamorphic Zircons										
Zr-170-B-II-01	611	4.8	1.29	0.281952	0.000053	0.000823	0.000004	0.281943	-16.2	2.52
Zr-170-B-II-02	611	4.8	1.59	0.281918	0.000042	0.000440	0.000003	0.281913	-17.2	2.58
Zr-170-B-II-03	611	4.8	1.71	0.281940	0.000040	0.000216	0.000003	0.281937	-16.4	2.53
Zr-170-B-II-04	611	4.8	1.52	0.281941	0.000047	0.000175	0.000004	0.281939	-16.3	2.53
Zr-170-B-II-08	611	4.8	1.64	0.281966	0.000056	0.001117	0.000059	0.281953	-15.8	2.49
Baddeleyite										
Zr-170-A-I-02	608	14	1.81	0.281971	0.000047	0.000319	0.000003	0.281967	-15.4	2.47

Figure 4 – Example of time-resolved Hf isotope spectra, intensity and fractionation index for Zr-A-I-01 grain in (a) from MAF-IIC and in (b) from LGI. The fractionation index (f) is a measure of changes in analyte signals during laser ablation (see text for explanation)



DISCUSSION OF RESULTS

In order to discuss details in Hf analyses, it is presented in Figure 4 an example of time-resolved Hf isotope spectra, intensity and fractionation index for Zr-A-I-01 grain from MAF-IIC and LGI, respectively. The fractionation index (f) is a measure of changes in analyte signals during laser ablation. It is calculated by the intensity of a measured isotope in the second half of the ablation interval divided by the intensity of the same measured isotope for the first half of the ablation interval (SOUDERS; SYLVESTER, 2010). The obtained fractionation index is close to 1 for all Hf isotope ratios, which indicates that there is no fractionation during the ablation in both lasers (Figure 4).

The Lu-Hf isotope results from both labs are presented in the Tables 3 and 4. The obtained intensity in Capivarita Anorthosite zircons at the LGI ranges from 1.7 to 3.5 V for ^{178}Hf in igneous zircons and 2.38 to 3.16 V in metamorphic zircons, whereas in the MAF-IIC ranges from 1.6 to 2.0 V and 1.29 to 1.81 V, respectively. In general the intensities are approximately 30-50% higher at the LGI. The main reason is related to the larger spot size used at LGI (55 µm) against the smaller spot size at MAF-IIC (49 µm). Other reason for this is because the spot was performed on the top of U/Pb analysis in the MAF-IIC and part of the material was already removed as well the use of nitrogen during the analyses which increases de signal at the LGI.

On other side, the measured ^{176}Hf/^{177}Hf isotope ratios in both labs are almost the same (Table 4), usually differing in the in sixth position after point, whereas ^{176}Lu/^{177}Hf values are somewhat different due to very low content of ^{176}Lu compared to ^{177}Hf. The errors (in 2SE) are in the expected values for this method, with better precision for those values obtained at the LGI (due to higher intensity and consequently stability of the signal). ε_{Hf}(t) values and T$_{DM}$ ages are very consistent and similar for analytical results of both labs, even for igneous and metamorphic zircons as well for inherited zircons, with of Zr-170-B-II-06 zircon that presents substantial differences in the Model ages and ε_{Hf}(t) values. The results obtained in this study supported the conclusion from previous study (CHEMALE JR. et al., 2011) in the Capivarita zircons, that Lu–Hf zircon data suggests a juvenile source for the melt with some degree of Paleoprotrozoic crustal contamination.

CONCLUSIONS

The Lu-Hf methodology in zircon presented in this work was very important, because it provided additional information for studies of provenance and crustal growth in the Capivarita Anorthosite. Furthermore, the high stability of Hf in zircon, really makes Hf as a good geochemistry tracer, this feature allowed the isotopes of Hf to contribute in understanding the discrepancy in age from U-Pb zircon and assist in the interpretation of zircon ages of high-grade metamorphic rocks as the case of Capivarita Anorthosite.

We had in our study not just different lasers (213 and 193 nm) but many other differences as: different standards, different region for spots in the zircon, and just one Hf analysis in each lab (the grains were very tiny) and differences during the analysis. Although it is necessary to determine more than 15 parameters interact mutually and the experiment needs to perform under identical laser ablation conditions, the obtained results and therefore interpretation are quite similar in both labs. Despite the differences between methods used in each lab we could see good reproducibility of the Hf analysis from LGI and MAF-IIC. All obtained Hf isotope ratios, T_{DM} model ages and epsilon Hf values were in agreement within experimental errors.

ACKNOWLEDGMENTS

We thank the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for the PhD scholarship (140922/2008-3). We also thank the technicians from LGI/UFRGS and MAF-IIC/MUN for helping in the sample preparation and during the Hf analysis in the LA-MC-ICP-MS. We are very grateful to E. Koester and K. Kawashita for critical reading of the manuscript and helpful suggestions.

REFERENCES

ANDERSEN, T., ANDERSSON, U. B., GRAHAM, S., ÅBERG, G., SIMONSEN, S. L. Granitic magmatism by melting of juvenile continental crust: new constraints on the source of Palaeoproterozoic granitoids in Fennoscandia from Hf isotopes in zircon. **J. Geol. Soc**., v. 166, p 233-247, 2009.

ASHWAL, L. D. Anorthosites. In: **Minerals and rocks.** Berlin: Springer-Verlag, xix, 1993, 422 p.

BABINSKI, M., CHEMALE JR., F., VAN SCHMUS, W. R., HARTMANN, L. A., SILVA, L. C. U-Pb and Sm-Nd Geochronology of the Neoproterozoic Granitic Gneissic Dom Feliciano Belt, Southern of Brazil. **J. South Amer.Earth Sci**., v. 10, p. 263-274, 1997.

BERTOTTI, A. L., CHEMALE JR., F., KAWASHITA, K. Lu-Hf em Zircão por LA-ICP-MS: Aplicação em Gabro do Ofiolito de Aburrá, Colômbia. **Pesquisas em Geociências (Online)**, v. 40, n. 2, p. 117-127, 2013.

BLICHERT-TOFT, J., ALBARÈDE, F. The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle crust system. **Earth Planet. Sci. Lett.,** v. 148, p. 243-258, 1997.

BLICHERT-TOFT, J. The Hf isotopic composition of zircon reference material 91500. **Chem. Geol**., v. 253, n. 3-4, p. 252-257, 2008.

BOUVIER, A., VERVOORT, J. D., PATCHETT, P. J. The Lu–Hf and Sm– Nd isotopic composition of CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. **Earth Planet. Sci. Lett.**, v. 273, p. 48–57, 2008.

CHEMALE JR., F. Evolução Geológica do Escudo Sul-rio-grandense. In: HOLZ M AND DE ROS LF (Eds.). **Geologia do Rio Grande do Sul**. Porto Alegre: CIGO, p. 13-52. 2000.

CHEMALLE JR., F., PHILLIP, R. P., DUSSIN, I. A., FORMOSO, M. L. L., KAWASHITA, K., BERTOTTI, A. L. Lu-Hf and U-Pb age determination of Capivarita Anorthosite in the Dom Feliciano Belt, Brazil. **Prec. Res**., v. 186, p. 117-126, 2011.

CHU, N.C., TAYLOR, R.N., CHAVAGNAC, V., NESBITT, R.W., BOELLA, M., MILTON, J. A. Hf isotope ratio analysis using multi-collector inductively coupled plasma mass spectrometry: an evaluation of isobaric interference corrections. **J. Anal. At. Spectrom.**, v. 17, p. 1567–1574, 2002.

DICKIN, A. P. **Radiogenic Isotope Geology**. 2nd ed. Cambridge University Press, 2005, 492 p.

EGGINS, S. M., KINSLEY, L. P. J., SHELLEY, J. M. G. Deposition and element fractionation processes occurring during atmospheric pressure laser sampling for analysis by ICPMS. **Appl. Surf. Sci.,** v. 127–129, p. 278–286, 1998.

FAURE, G. **Principles of Isotope Geology**. 2nd ed. New York: John Wiley and Sons, 1986, 589 p.

FAURE, G. **Isotopes: Principles and Applications**. 3rd ed., New York: John Wiley & Sons, 2005. 897 p.

FERNANDES, L. A. D, TOMMASI, A. D., PORCHER, C. C. Deformation patterns in the southern Brazilian branch of the Dom Feliciano Belt: A reappraisal. **J. Sou. Am. Ear. Sci.**, v. 5, p. 77-96, 1992.

FORMOSO, M. L. L., CARRARO, C. C. Anorthosito de Capivarita, Rio Pardo, RS. **An. Acad. Bras. Ciênc.,** v. 40, p. 361-372, 1968.

FORMOSO, M. L. L. **Geologia da folha Capivarita – RS, Anortosito de Capivarita.** 1973. 215f. Tese (Doutorado) - Instituto de Geociências, Universidade de São Paulo, São Paulo. 1973.

GERDES, A., ZEH, A. Combined U-Pb and Hf isotope LA-(MC)-ICP-MS analyses of detrital zircons: Comparison with SHRIMP and new constraints for the provenance and age of Amorican metasediment in central Germany. **Earth Planet. Sci. Lett.,** v. 249, p. 47-61, 2006.

GERDES, A., ZEH, A. Zircon formation versus zircon alteration – New Insights from combined U-Pb and Lu-Hf in-situ LA-ICP-MS analyses, and consequences for the interpretation of archean zircon from the Central Zone of the Limpopo Belt. **Chem. Geol.,** v. 261, p. 230-243, 2009.

GOODGE, J. W., VERVOORT, J. D. Origin of Mesoproterozoic A-type granites in Laurentia: Hf isotope evidence. **Earth Planet. Sci. Lett.**, v. 243, p. 711-731, 2006.

GRIFFIN, W. L., PEARSON N. J., BELOUSOVA, E., JACKSON, S. E., VAN ACHTERBERGH, E., O'REILLY, S. Y., SHEE, S. R. The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in Kimberlites. **Geochim. Cosmochim. Acta**, v. 64, p. 133-147, 2000.

HOSKIN, P., SCHALTEGGER, U. The Composition of Zircon and Igneous and Metamorphic Petrogenesis. In: **Reviews in Mineralogy and Geochemistry,** v. 53, p 27-62, 2003.

IIZUKA, T., HIRATA, T. Improvements of precision and accuracy in situ Hf isotope microanalysis of zircon using the laser ablation-MC-ICPMS technique. **Chem. Geol.**, v. 220, p. 131-137, 2005.

KINNY, P., MAAS, R. Lu-Hf and Sm-Nd Isotope systems in zircon. In: **Rev. Min. Geoc., v.** 53, p 327-341, 2003.

LONGERICH, H. Laser Ablation – Inductively Coupled Plasma – Mass Spestometry (LA-ICP-MS): an introduction. In: S?YLVESTER, P. (Ed.). **Laser Ablation ICP-MS in the Earth Sciences:** current practices and Outstanding Issues.. Vancouver, BC, v. 40, 2008. (Short Course Series).

MOREL, M. L. A., NEBEL, O., NEBEL-JACOBSEN, Y. J., MILLER, J. S., VROON, P. Z. Hafnium isotope characterization of the GJ-1 zircon reference material by solution and laser-ablation MC-ICPMS. **Chem. Geol.**, v. 255, p. 231–235, 2008.

NEBEL, O., NEBEL-JACOBSEN, Y., MEZGER, K., BERNDT, J. Initial Hf isotope compositions in magmatic zircon from early Proterozoic rocks from the Gawler Craton, Australia: A test for zircon model ages. **Chem. Geol.,** v. 241, p. 23-37, 2007.

PACHETT, P. J., TATSUMOTO, M. Lu-Hf total rock isochron for the eucrite meteorites. **Nature**, v. 288, p. 571-574, 1980.

PATCHETT, P. J., KOUVO, O., HEDGE, C. E., TATSUMOTO, M. Evolution of continental crust and mantle heterogeneity: evidence from Hf isotopes. **Contrib. Mineral. Petrol**., v. 78, p 279-297, 1981.

PHILIPP, R. P., MACHADO, R. The Late Neoproterozoic 541 granitoid magmatism of the Pelotas Batholith, Southern Brazil. **J. Sou. Am. Ear. Sci.**, v. 19, p 461-478, 2005.

PHILIPP, R. P., FORMOSO, M. L., DUSSIN, I., CHEMALE Jr., F., CAMPOS, R. S. Estruturas primárias e tectônicas do Anortosito Capivarita, Pântano Grande, RS: significado e implicações para o entendimento da evolução petrológica. **Rev. Bras. Geoc.**, v. 40, p. 99-110, 2010.

RIBEIRO, M., BOCCHI, P. R., FIGUEIREDO, F., TESSARI, R. I. **Geologia da Quadrícula de Caçapava do Sul, RGS**. DNPM/DFPM, Rio de Janeiro, Boletim 127, 232 p, 1966.

SEGAL, I., HALICZ, L., PLATZNER, I. T. Accurate isotope ratio measurements of ytterbium by multiple collection inductively coupled plasma mass spectrometry applying erbium and hafnium in an improved double external normalization procedure. **J. Anal. At. Spectrom.**, v. 18, p. 1217–1223, 2003.

SLAMA, J. ET AL. Plešovice zircon — A new natural reference material for U–Pb and Hf isotopic microanalysis. **Chem. Geol.,** v. 249, p. 1-35, 2008.

SÖDERLUND, U., PATCHETT, J. P., VERVOORT, J. D., ISACHSEN, C. E. The ^{176}Lu decay constant determined by Lu–Hf and U–Pb isotope systematics of Precambrian mafic intrusions. **Earth Planet. Sci. Lett.**, v. 219, p. 311–324, 2004.

SOUDERS, A. K., SYLVESTER, P. J. Accuracy and precision of non-matrix-matched calibration for lead isotope ratio measurements of lead-poor minerals by LA-MC-ICPMS. **Journal of Analytical Atomic Spectrometry, v.** 25, p. 975-988, 2010.

TESSARI, R. I., PICADA, R. S. **Geologia da quadrícula de Encruzilhada do Sul, RS, Brasil**. DNPM/DFPM, Rio de Janeiro, Boletim 124, p 1-147, 1966.

THIRWALL, M. F., WALDER, A. J. In situ hafnium isotope ratio analyses of zircon by inductively coupled plasma mass spectrometry. **Chem. Geol.,** v. 122, p. 241-247, 1995.

VERVOORT, J., BLICHERT-TOFT, J. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. **Geochim. Cosmochim. Acta**, v. 63, p. 533-557, 1999.

WASSERBURG, G. J., JACOBSEN, S. B., DEPAULO, D. J., MCCULLOCH, M. T., WEN, T. Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standards solutions. **Geochim. Cosmochim. Acta,** v. 45, p. 2311-2323, 1981.

WOODHEAD, J., HERGT, J., SHELLEY, M., EGGINS, S., KEMP, R. Zircon Hf-isotope analysis with an excimer laser, depth profiling, ablation of complex geometries and concomitant age estimation. **Chem. Geol.,** v. 209, p. 121-135, 2004.

WU, F-Y., YANG, Y-H., XIE, L-W., YANG, J-H., XU, P. Hf isotopic compositions of the standard zircons and baddeleyites usedin U-Pb geochronology. **Chem. Geol.**, v. 234, p. 105-126, 2006.