Sr ISOTOPES BY LA-MC-ICP-MS PROCEDURES COUPLED WITH THE MACS3 REFERENCE MATERIAL IN A CORAL SAMPLE: A RECORD OF ENVIRONMENTAL CHANGES

ISÓTOPOS DE Sr POR LA-MC-ICP-MS ANALISADOS COMO MATERIAL DE REFERÊNCIA MACS3 EM UMA AMOSTRA DE CORAL: UM REGISTRO DE MUDANÇAS AMBIENTAIS

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RESUMO - O objetivo principal deste trabalho é demonstrar que a espectrometria de massa com plasma indutivamente acoplado e ablação a laser (LA-MC-ICP-MS) é uma ferramenta poderosa para a análise de isótopos de Sr em corais. Este trabalho discute estratégias de certificação para determinação de isótopos de Sr, usando análises de material de referência e o detalhamento do tratamento dos resultados adquiridos em materiais biológicos (coral). Para obter resultados confiáveis, é essencial ajustar adequadamente o espectrômetro de massas e o sistema de ablação a laser de forma a obter a intensidade máxima e em seguida promover as correções para obter as razões ^{87}Sr / ^{86}Sr corretas. Nestes termos, a otimização do espectrômetro de massa foi realizada usando o material de referência NIST SRM-987 (em solução) que em sequência foi migrado para a ablação a laser com ajuste da razão isotópica Sr correta para o material de referência (NIST-612, vidro), antes de cada sessão analítica. O protocolo incluiu a utilização material de referência sólido USGS MACS3 com razão isotópica ^{87}Sr / ^{86}Sr de 0,72000. Os valores obtidos para esta RM variaram entre 0,7012 e 0,7014, com fator de correção calculado entre 0,990 e 0,988. A fim de contabilizar possíveis desvios no espectrômetro de massa durante uma sessão analítica, sugere-se a aplicação de correção de *bracketing* e o uso do material de referência com a mesma matriz. Os resultados das técnicas de ablação são reproduzíveis dentro do erro analítico, o que indica que esta técnica produz resultados robustos quando aplicada a carbonatos de coral. Além disso, várias medições comparativas de diferentes materiais de referência (por exemplo, USGS MACS3 e NIST 612) e a comparação das suas respectivas razões ^{87}Sr / ^{86}Sr destacam a robustez do método. Os resultados ao longo dos eixos de crescimento do coral mostraram uma diminuição na razão ^{87}Sr / ^{86}Sr da camada interna para a externa do coral (de 0,70920 para 0,70627). Estes resultados sugerem variações na disponibilidade de material particulado durante o crescimento do coral, provavelmente relacionado a mudanças ambientais marinhas locais.

Palavras-chave: Carbonato biológico. Isótopos de Sr. LA-MC-ICP-MS. Materiais de referência. Metodologia. Ambiente marinho.

ABSTRACT - The main aim of this work is to demonstrate that the Laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) is a powerful tool for the analysis of strontium (Sr) isotopes in corals. This work discusses certification strategies for Sr isotopes determination, using reference material (RM) analyses and the results treatment based on detailed data acquired in biological materials, a coral sample. To obtain reliable results, it is essential to properly adjust the mass spectrometer and laser ablation system. Adjusting the equipment to its maximum intensity does not always result in correct ^{87}Sr/^{86}Sr ratios. Therefore, the optimization of the mass

spectrometer was performed using the reference material NIST SRM-987 (solution) and adjusting the correct Sr isotope ratio to the reference material (USGS MACS3 and NIST-612, solids) before each analytical session. The protocol applied the solid reference material USGS MACS3 with an isotopic ratio $^{87}Sr/^{86}Sr$ of 0.72000. The values obtained for this RM varied between 0.7012 and 0.7014, with a correction factor calculated between 0.990 and 0.988. In order to account for potential drifts in the mass spectrometer during an analytical session, the application of bracketing correction and the use of the most convenient reference material are suggested. The analytical uncertainty of Sr data obtained by LA-MC-ICP-MS is comparable to studies carried out on other carbonate materials. The results of ablation techniques were reproducible within the analytical error, which indicates that this technique produces robust results when applied to coral carbonates. In addition, several comparative measurements of different reference materials (e.g., USGS MACS3 and NIST 612) and the comparison of the $^{87}Sr/^{86}Sr$ ratios highlight the robustness of the method. The results along the coral growth axes showed a decrease in the $^{87}Sr/^{86}Sr$ ratio from the inner to the outer layer of the coral (from 0.70920 to 0.70627). These results indicate variations in the availability of particulate matter during the coral growth, probably related to local marine environmental changes.

Keywords: Biological carbonate. Sr isotopes. LA-MC-ICP-MS. Reference materials. Methodology. Coastal environment.

INTRODUCTION

The Laser Ablation Multi-Collector Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICP-MS) is a very efficient equipment for analyzing the composition of samples with very low levels of chemical elements and to perform isotopic precision analysis (Perkins et al., 1991; Vander Putten et al., 1999). The versatility of its results in multiple applications is based on the machine architecture composed of a plasma ionization along with a magnetic separator, in addition to multi-collectors combined with laser ablation, which allows to perform microanalysis and material studies in a non-destructive way. Due to these characteristics the LA-MC-ICP-MS has wide and varied applicability (Pickhardt et al., 2005; Jochum et al., 2012) and thus, laboratories, in different countries, have developed new ways of applying this equipment in remarkably diverse scientific contexts.

The development of the laser ablation technique has made it possible: to cheapen the dates based on the U-Pb method of geological samples; to reduce the procedure time of this analysis compared to conventional methods and; to carry out innovative plasma analysis for the Lu-Hf method and stable isotope analysis (such as for S, Ca and B, among others). Nowadays, techniques involving radiogenic isotopes (such as Sr, Nd and Pb) are routine in several laboratories (Bizzarro et al., 2003). These techniques were initially developed for the analysis of geological samples, and metallic alloys, but currently they are producing results in several areas of knowledge, such as medicine, biology, oceanography, food engineering, environmental pollution, archeology and forensic sciences (Richardson et al., 2001; Meija et al., 2012). In fact, the LA-ICP-MS techniques have been applied in varied applications and multiple areas (Lutze et al., 1985; Lutze & Ewing, 1988; Grambow, 2006). The expansion of themes of study depends on the researcher's creativity, a potential that can be multiplied when different disciplines interact to solve scientific problems.

Mass spectrometers can be applied to track and monitor the negative influence of the use of nuclear energy on the environment. Therefore, they are currently being applied in the characterization of radioactive elements, such as U, for civil use, in thermonuclear plants and in nuclear reactors and to identify nuclides formed during nuclear experiments, whose emissions remain for several decades with high risk for the natural ecosystems (Price & Pearce, 1997; Weiner & Dove, 2003).

The use of the laser ablation has been reported in pollution studies in order to identify degrees of hazard and forms of storage (Zhou et al., 2008). Work on the impact of pollution on living organisms or their remains preserved in the sedimentary record has increased significantly. Some studies focus on the contamination of gastropods and bivalves, fish, and seawater in coastal environments (Hodell et al., 1989; Bordalo et al., 2007). Studies on birds to characterize migration trajectories and investigations of contamination by metals on trees, turtles, crocodiles and plants, are some examples that can be mentioned (Price & Pearce, 1997; Weiner & Dove, 2003).

Recently analyses with ICP-MS have been increased in archeology research. These studies have reported dating human teeth, bones and hair of mummies to identify contamination by metals in ancient civilizations (Lutze et al., 1985; Lutze & Ewing, 1988; Grambow, 2006; Price, 2008). Important applications of this technique are made in famous paints to characterize chemical signatures and to combat document forgery. Another application in art valuable was made in Chinese ceramics from different periods of the oriental culture, through chemical characterization (concentrations of trace and rare earth elements and isotopic analyses) (Carriquiry et al., 1994). Studies on ceramics, soils, coins, adornment materials and metallurgical materials have been

carried out to identify commercial exchanges of materials between ancient cultures (Cruz Jr et al., 2005; Bentley, 2006; Campos, 2014).

Temperature change and coral growth

Sclerochronology characterizes growth patterns that reflect annual, monthly, fortnightly increases associated with tides, solar intensity, and salinity delimited by a set of environmental and astronomical markers aiming to understand the organism life history and to reconstruct records of environmental variations and climatic changes in spatial and in temporal dimension (Hudson et al., 1976; Jones, 1983; Grocke & Gillikin, 2008; Schwarcz et al., 2010). It also includes Sr isotopes (Quitmyer & Jones, 1997; Oppitz et al., 2015). Corals are sensitive to physicochemical and ecological changes and their skeletal growth rate depends on the sea-water temperature and alkalinity and photosynthetic activity, which allows their application as a proxy for environmental conditions (Weber & Woodhead, 1970; Carriquiry et al., 1994). Temperature is the main factor influencing the formation of coral-growth bands. It is known that the high-density of coral-growth bands coincides with periods of warmer water (Barnes & Lough, 1993; Allemand et al., 2004; Corrège, 2006; Carré et al., 2013).

Elements such as O, C, Ca and Sr are incorporated throughout the skeletal calcification of corals during which density bands with annual periodicity are formed. The elemental assimilation is controlled by oceanographic parameters of seawater that form density bands with annual periodicity (Gattuso et al., 1999; Merks et al., 2004; McFarlane & McCulloch, 2008).

The use of the Sr/Ca ratio, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ isotopes in corals has been used to reconstruct the recent ocean temperature curve, although several other element ratios have been proposed, namely Mg/Ca (Mitsuguchi et al., 1996) and U/Ca (Dunbar et al., 1994; Quitmye & Jones, 1997; Gagan et al., 2000).

Thus, the values of $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ ratio, in addition to Sr/Ca ratio in coral skeleton, allow the quantification of the influence of climatic parameters on the incorporation of these isotopes and elements as a proxy to indicate sea surface temperature (Edwards et al., 1987; Dunbar et al., 1994; Gagan et al., 1998; Felis & Pätzold, 2004). The environmental parameters in corals are defined based on current conditions and historical series of temperature and salinity. Instrumental temperature records can be corre-lated with geochemical and isotopic indicators (Oomori et al., 1982; Mitsuguchi et al., 1996). Thus, corals that calcify their skeletons at rates ranging from approximately 3 to 15 mm per year, can be used to establish a very precise chronology based on their geochemical and isotopic signature (Quinn et al., 1993).

A recent study analyzed metal concentrations in *Porites* corals aiming to identify the impact of the anthropogenic input of river runoff into a coral reef from an urbanized area, Okinawa (Japan) (Ramos et al., 2004a). Inspired by this line of research, this work aims to develop a methodology aiming to obtain high quality Sr isotope data through LA-MC-ICP-MS in a coral sample from Espírito Santo state (SE Brazil; Figure 1). Several reference materials (USGS MACS3 and NIST 612, solids; and NIST SRM-987, solution) were used in the analysis.

The coral used in this investigation is *Mussismilia braziliensis* (Verrill, 1868). This species has a colonial habit and is quite common in coral reefs as observed in Brazilian coast, where it has been observed from very shallow waters (0.5 - 0.1 m) up to 3.9 m depth, but mainly between 2.5-2.9 m depth. This coral develops massive colonies, commonly globular, with hemispherical shapes, and are strongly attached to the substrate. A colony can reach up to more than 1 m diameter and has polygonal goblets; the columella is reduced and has delicate septa (Nogueira, 2003). In large colonies there is a tendency to form elongated goblets, with more than three centers. The living colonies have gray and yellow-white colors.

LA-ICP-MS for Sr isotope analysis

In situ analysis of Sr isotopes has experienced a systematic improvement over the past two decades, mainly due to the availability of reference materials (Pearce et al., 1997). The identification, quantification and correction of factors influencing the results quality made possible the acquisition of accurate data with spatially high-resolution. Therefore, this technique has become routine in many isotope geochemistry laboratories worldwide. The versatility of the LA-MC-ICP-MS analyses has made it feasible for use in the numerous applications, on a wide variety of materials, including magmatic minerals (Schmidberger et al., 2003; Ramos et al., 2004b; Guo et al., 2014), biogenic carbonate (Adams et al., 2005; McCulloch et al., 2005; Carré et al., 2006, 2013) and human tooth enamel

(Simonetti et al., 2008). In addition, the results of Sr isotope data acquired by LA-MC-ICP-MS are comparable to those obtained by thermal ionization mass spectrometry (TIMS) (Coelho et al., 2017), but allows for faster data acquisition, which is very advantageous.
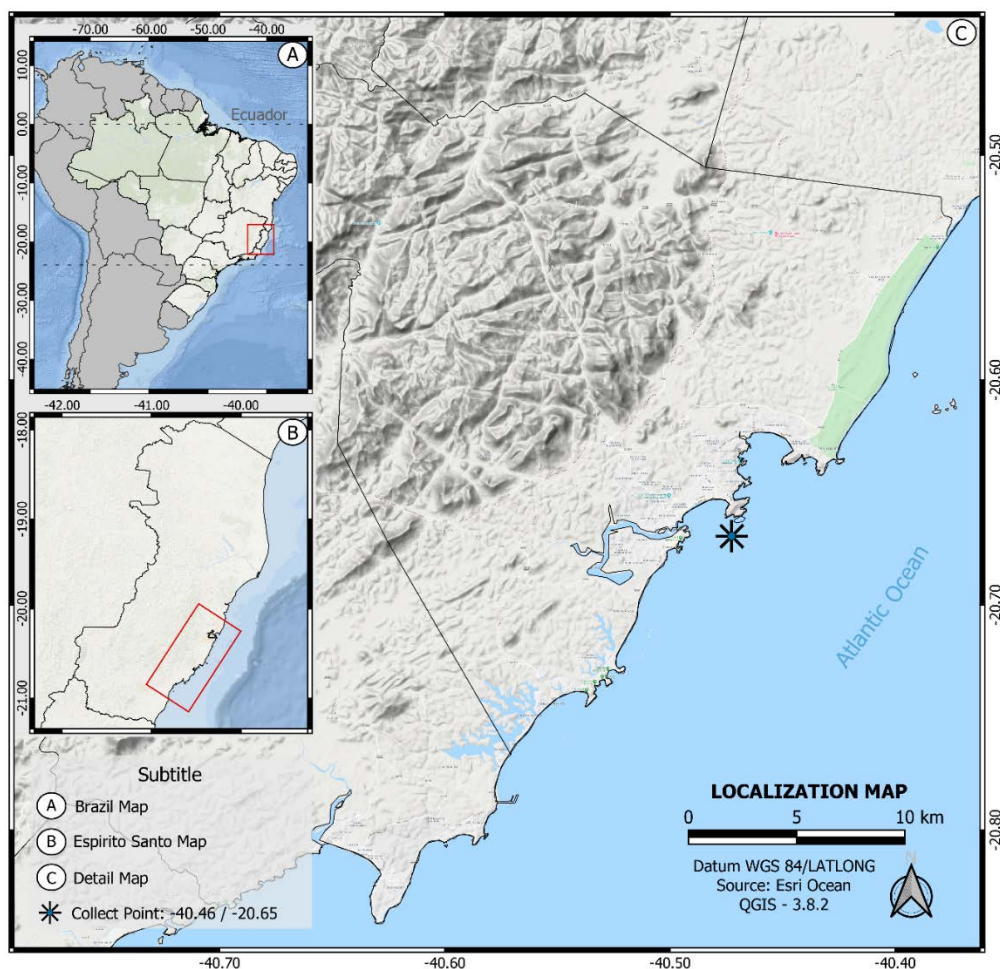

Figure 1 - Map indicating the site where the analysed material was collected.

The growth of the coral colony involves an increase in its tissue and skeleton. Tissue growth involves the increasing of number of polyps that make up the colony (Pitombo et al., 1988; Quinn & Sampson, 2002). The division of polyps occurs when they reach their maximum diameter, which is characteristic of each species of coral. The polyps build an external aragonite skeleton, forming carbonate sheets under its base. Since the skeleton is deposited by the polyp tissue, the growth of the coral tissue and skeleton is closely linked (Cohen & McConnaughey, 2003; Merks et al., 2004), although they are not necessarily controlled or limited by the same environmental factors (Barnes & Lough, 1993; Allemand et al., 2004; Corrège, 2006). Coral growth occurs continuously through the formation of the skeleton characterized by patterns of density bands with annual cyclicity. Changes in the density of these bands are influenced by the variations of environmental and climatic conditions. These regions are visible in imaging (optical microscopy, X-ray and electron microscopy, cathodoluminescence, among others) so that a set of bands of high and low density (and compositional variations), represent a year of growth (Knutson et al., 1972; Pingitore et al., 2002).

The recovery of biogeological data is important for assessing climate models and understanding the causes of climate fluctuations (Wei et al., 2000; Watanabe et al., 2001). These "proxies" are also important paleoclimatic indicators in the assessment of the disturbances of natural climatic variability caused by anthropogenic action. Thus, a better understanding of the climate favors the study of major events in the global climate system, with socio-economic implications due to their large-scale effects (Swart & Leder, 1996).

Procedures on mass spectrometry

The advent of multi-collector mass spectrometers in the early 1980s was a promise of substantially improved accuracy in isotope ratio measurements, as well as of reduced measurement

time. Many laboratories with multicollector equipments divulge internal precision similar to the values obtained in single collector machines (Thirlwall, 1991). In addition, the laboratories are capitalizing on the time-saving using multi-collectors and increasing the volume of data.

Recent applications that report Sr isotope ratios in biological carbonates have been evaluated as a powerful tool for environmental studies (Guo et al., 2014; Coelho et al., 2017). Nowadays, both thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry with multicollectors (MC-ICP-MS) can be considered reference methods for Sr isotope ratios measurements in human and other organism hard tissues and can provide insight into present and past ecological/environmental issues. Therefore, has become an indispensable method in different research disciplines in environmental geochemistry.

The analysis of $^{87}Sr/^{86}Sr$ isotopes in archaeological remains, such as human teeth and bones, has more often been carried out with portions mechanically removed from the original peace, followed by acid digestion, separation of Sr by chromatography and, finally, solution-based analysis by MC-ICP-MS. This analytical approach allows to obtain Sr isotope ratios comparable to TIMS data. However, although plasma mass spectrometry inductively coupled to multicollectors and laser ablation (LA-MC-ICP-MS) offer great advantages over other well-established methodologies, the results may have lesser measurement accuracy. This technique is particularly useful for its attributes: it is semi-invasive; provides quick and direct analysis of Sr isotopic ratios; requires minimal sample preparation; allows the analysis of solid samples in high spatial resolution. This last aspect became a key issue considering the growing diversity of the investigated samples, such as human teeth or hard parts of fish (Walther & Thorrold, 2009). These matrices based on Sr isotopes, continuously increase their resolution, recording chemical information from the environment where the organism lived, in small spatial (for example, 100 μm) and temporal scales. For this reason, this methodology can allow obtaining useful data in paleoceanographic and paleoclimate research (Klein et al., 1996).

The problems to be solved: interferents and fractionations

The continuous use of the LA-MC-ICP-MS has allowed the identification of physical factors that control the quality of data (Jochum et al., 2007). Among these, there are factors such as: (a) isobaric and molecular interferences (Table 1; Waight et al., 2002); (b) mass fractionation of the instrument; (c) background levels and; (d) counting statistics. These are the main concerns associated with the acquisition of accurate Sr isotope data (Vroon et al., 2008). In general, data reduction involves the quantification of mass bias and isobaric interference corrections, and the background level effects on Sr isotopes and, therefore, most data reduction procedures involve the correction of these interferences.

Table 1 - The isobaric interference of the ^{87}Rb mass on the ^{87}Sr can be seen in the specific masse of each atomic particle of interest for the Rb-Sr method. The equation $^{87}Sr* = (^{87}Sr+^{87}Rb) = {}^{85}Sr*^{87}Rb$ can be used to correct this interference [83].

Isotope	Mass	Abundance (%)
^{84}Sr	83.9134	0.56
^{85}Rb	84.9118	72.17
^{86}Sr	85.9093	9.86
^{87}Sr	86.9089	7
^{87}Rb	86.9092	27.83
^{88}Sr	87.9056	82.58

Several quantification procedures are used for the analysis of LA-ICP-MS, namely a standardization procedure, which compensates the variations in the ICP-MS signals caused by laser ablation processes, the efficiency of the transport of volatilized material by laser and plasma ionization processes (Czas et al., 2012; Diwakar et al., 2014). The most widely used method is the external calibration, allowing the analysis of trace elements by LA-ICP-MS with spatial resolution of dozens of μm units in diameter, which makes this method a powerful tool for chemical elemental mapping. This resource is widely explored in the study of the elemental distribution in biological tissues (Bonta et al., 2017).

Fractionation corrections

The fractionation of stable Sr isotopes during mass spectrometer analysis occurs as an instrumental effect and is mass dependent, requiring the parallel use of different reference values, such as that of the $^{85}Sr / {}^{88}Sr$ ratio. This ratio can be used for simultaneous corrections to the analytical procedure and is considered when Sr radiogenic isotope ratios (consequently time-dependent) are evaluated. This is important, since conventional Sr isotope ratio measurements apply instrumental isotopic fractionation corrections following an internal correction approach to

correct the $^{88}Sr/^{85}Sr$ isotope ratio, using also the $^{88}Sr/^{85}Sr$ ratio of the same sample.

In this approach, the $^{88}Sr/^{86}Sr$ ratio is considered invariant in nature. However, this strategy should be reconsidered, since the values of $^{88}Sr/^{86}Sr$ isotope ratio vary significantly in natural samples. The reported variation of δ ($^{88}Sr/^{86}Sr$) ranges from -1.06 ± 0.02‰ to +1.373 ± 0.007‰, although most of the published values vary between 0.1 and 0.5 ‰ (Jochum et al., 2012).

Interference corrections

The interferences in Sr isotopes analyzed by the LA-MC-ICP-MS have been the subject of countless debates and discussions during the last years, since several sources of interference have been detected and corrections have been approached differently. Correction of Ca-Ar interference in the ^{87}Sr /^{86}Sr ratios obtained from carbonate matrices has been considered necessary, since it can result in abnormally higher values for TIMS measurements compared to LA-MC-ICP-MS (Yang et al., 2011). However, reports have shown that these corrections are now necessary in laser analysis with long periods (over several minutes) and unnecessary for measurements on the second scale. Jochum et al. (2009) and Yang et al. (2011) presented a correction strategy for the interference caused by rare earth element (REE) ions doubly charged in geological samples as accessory minerals, namely in the case of apatite, monazite, and zircon, among others.

^{87}Rb interference

Potential interference resulting from isotopic analysis of Sr by LA-ICP-MS is admitted without prior separation of Rb/Sr; however, Ca-based interference is negligible (Berglund & Wieser, 2011). The remarkable number of publications clearly shows that the analysis of the Sr isotope ratios by LA-MC-ICP-MS remains a challenging task, since the presence and level of interferences are understood in different ways. Therefore, this topic requires further investigation to allow reliable treatment of data before it can be making solid interpretations of results in any field of research.

In this sense, it is important to perform the final step in the $^{87}Sr/^{86}Sr$ ratio correction procedure, for ^{87}Rb interference. Due to the previous corrections, the mass 85 consists only of ^{85}Rb, which can be used to calculate the fraction of ^{87}Rb with the constant ratio of $^{87}Rb/^{85}Rb=0.3857$ (Irrgeher et al., 2015). This Rb correction is only considered necessary for samples with a Rb/Sr ratio <0.02 (Müller & Anczkiewiczb, 2016). For samples with higher Rb content, an alternative Rb correction is required (Ingle et al., 2003).

Mass bias

The trend of mass bias needs to be corrected before adjusting instrumental deviations, from the $^{86}Sr/^{88}Sr$ ratio. Based on the corrected signals, the values obtained for $^{86}Sr/^{88}Sr$, $^{84}Sr/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios are calculated. Then, a mass fractionation factor α is calculated to correct the instrumental mass fractionation based on the $^{86}Sr/^{88}Sr$ ratio and the exponential law described in Ehrlich et al. (2001). The mass fractionation factor α is calculated as described in Steiger & Jager (1977) where the $^{86}Sr/^{88}Sr$ ratio of 0.1194 is an accepted value (Figg & Kahr, 1997; Kimura et al., 2013).

MATERIALS AND METHODS

This study is based on the analysis of Sr isotopes through the ablation technique along a coral growth axes of the species *Mussismilia braziliensis*, from Espírito Santo state (SE Brazil; Figure 1) by LA-MC-ICP-MS. The LA-MC-ICP-MS measurements for Sr isotopes were performed perpendicularly to the growth axis of the coral in samples (with 100 μm of diameter) using material from 40 craters obtained by laser ablation (Figure 2). The mixture of material from different growth layers was avoid. The applied 100 μm crater sampling methods have the advantage of obtaining and maintaining a high signal strength over a relatively long measurement interval (about seconds), enough to obtain a statistically robust count. The craters were spaced by a distance of ~1000 μm from each other. This sampling pattern corresponds to different growth layers and allow to verify the isotopic evolution along different phases of the animal life.

This sampling approach allows us to identify changes in the $^{87}Sr/^{86}Sr$ ratio at extremely high spatial resolution. The first 5 seconds of analysis (or the first 5 results) can have abnormal values and can be discarded due to the high intensities when the laser is started. This effect is typical of the laser ablation analysis. Four analysis batteries were performed with 100 measurements. Different reference materials (i.e., USGS MACS3 and NIST 612, solids; and NIS SRM-987, solution) were applied in this study according to the methodology presented and discussed in the following items.
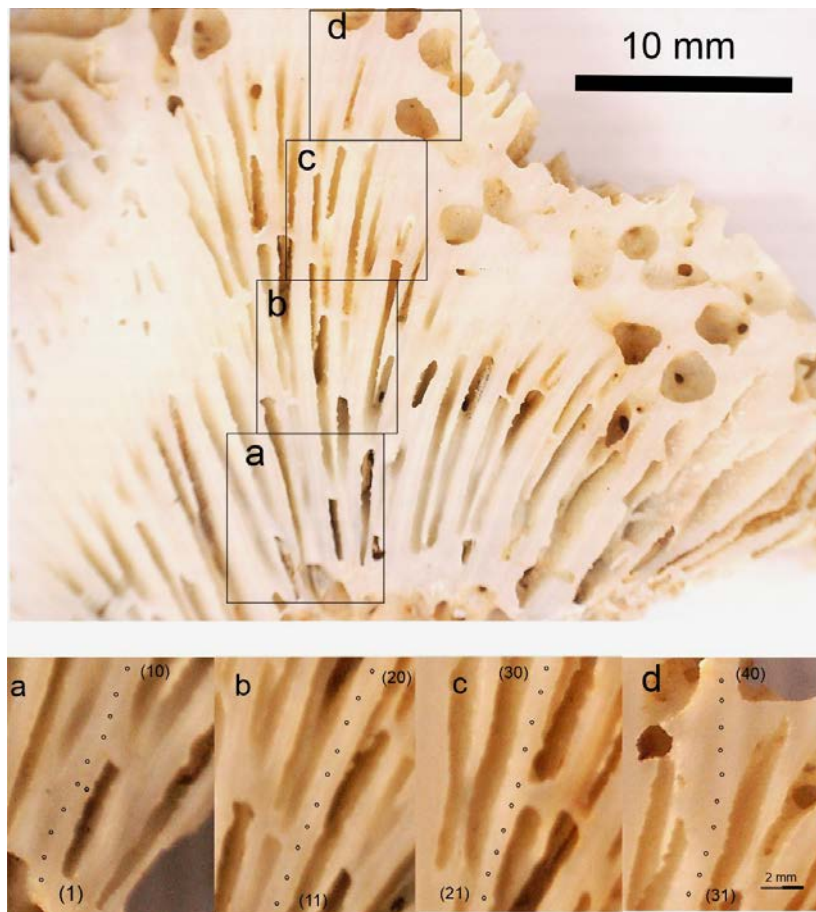
Figure 2 - Photos of the coral cut showing the craters. Profile (a) craters 1 to 10; Profile (b) craters 11 to 20; Profile (c) craters 21 to 30; and Profile (d) craters 31 to 40.

A series of three NIST reference materials (NIST SRM 610, 612, 614) and a series of three USGS reference materials (BCR-2G, BHVO-2G, BIR-1G) were produced with different matrices for laser ablation research (Thirlwall, 1991; Ciucci et al., 1999; Eggins & Shelley, 2002; Elburg et al., 2005). NIST SRM 610, 612 and 614 synthetic glass reference materials have similar and sufficient trace elements (e.g., Ca 50 μg g^{-1} for NIST SRM 612 or NIST-612) for accurate primary calibration. However, the composition in its main chemical element is quite different from any geological matrix, which can lead to significant analytical bias due to the matrix effects. The value used for the $^{87}Sr/^{86}Sr$ ratio of the NIST SRM-987 reference material obtained in the literature (Ciucci et al., 1999) was 0.71034 ± 0.00026 and the value obtained in this investigation is 0.71042 (Figure 3).
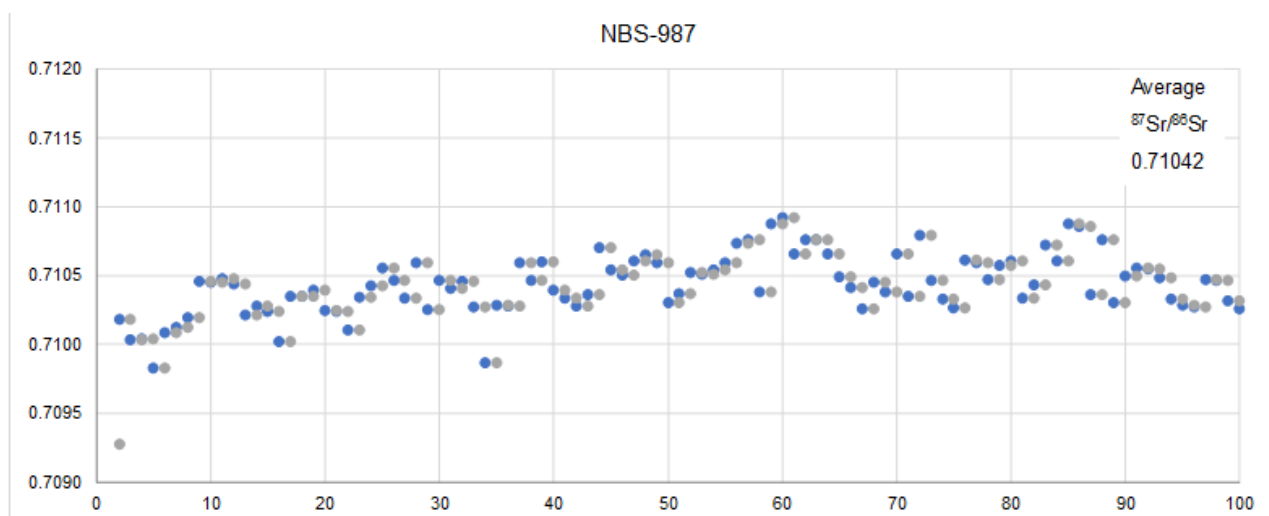

Figure 3 - $^{87}Sr/^{86}Sr$ ratio of the *NBS-987*, isotopic standard, during the calibration of the Neptune mass spectrometer used in this investigation. In this diagram the results of three runs with 100 analyzes in each run (totalizing 300 measurements) are plotted. The average value of $^{87}Sr/^{86}Sr$ = 0.71042.

Criteria for choosing the reference material (RM)

It is essential to use an appropriate reference material (RM) with similar Sr concentration and a matrix similar to the unknown sample (Albarède & Beard, 2004; Weber et al., 2017). In the case of different matrices and/or large differences in Sr concentration, the $^{87}Sr/^{86}Sr$ ratio resulting from the unknown sample needs to be treated with care. Since different RMs and samples have variable Sr content, the laser energy and crater size may have to be adjusted to avoid signal intensities higher than ~ 10 V in faraday cups (^{88}Sr signal). It is important to use similar measurement parameters for RMs and unknown samples when the bracketing technique with RM correction factor calculation is applied. Therefore, comparative measurements of different reference materials (e.g., USGS MACS3 and NIST-612, solids; and NIST SRM-987 solution) were realized.

Sr isotope results from reference material NIST SRM-987

Using the procedures proposed by Jochum et al. (2005) and Lugli et al. (2020), the NIST SRM-987 reference solution was used to optimize the peak shape and the best position of the collectors that measure the abundance of Sr isotopes (^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr). It was also used to test the influence of different adjustment parameters, such as gas flows, the position of the torch, the adjustment of the high voltage lenses and variations in the intensities of the radio frequency (RF) generators, which have a significant effect on $^{87}Sr/^{86}Sr$ ratios (Appendix 1).

Calculation Procedures

As reported by McFarlane & McCulloch (2008) and Weber et al. (2017), the main advantage of the analysis of Sr isotopes with LA-MC-ICP-MS is that Sr isotopes are measured *in situ*, without the need for chemical separation. Therefore, previous studies based on the analysis of Sr isotopes by LA-MC-ICP-MS required the application of a sequence of corrections for interference and mass polarization fractionations (Jochum et al., 2011). Therefore, our raw data and background signals were reduced in an offline Excel spreadsheet and the correction sequence followed the order: subtracting the laboratory blank contributions; subtraction of ^{87}Rb interference; correction of Sr mass bias through bracketing. The results are calibrated using the $^{87}Sr/^{86}Sr$ ratios of the reference material USGS MACS3, recommended as a calibration strategy for Sr isotope analysis. Normally, the final $^{87}Sr/^{86}Sr$ ratios obtained for RMs differ slightly from the reference values, requiring an additional correction step. Each sample is, therefore, delimited by a set of ten individual measurements alternating with the selected RM. For unknown samples the correction value used is the certified value of $^{87}Sr/^{86}Sr$. Thus, the correction factor of the two sets of RMs (measured before and after the sample) were used and applied to the $^{87}Sr/^{86}Sr$ ratio of the unknown sample.

Multicollector Mass Spectrometer and Laser Ablation procedures

Neptune MC-ICP-MS (Finnigan) was used for isotopic analysis. The instrumental parameters for the routine analysis of digested samples of carbonate, as well as for measurements involving reference materials, are summarized in table 2. Operating parameters of the Laser Ablation instrumentation and sample introduction systems are presented in table 3.

Table 2 - Operating parameters of the MC-ICP-MS instrumentation and sample introduction systems.

MC-ICP-MS Operating Parameters	
Masses monitored	82, 83, 84, 85, 86, 87, 88
Mass resolution (M/ΔM)	~300
Cones	Ni
Detectors	Faraday cups
Data acquisition mode for laser ablation time-resolved analysis (LA-TRA)	Time resolved analysis
Dwell time/s	2
Radio-frequency (RF) power/ Watts (W)	1300
Plasma gas flow/L min	15
Auxiliary gas flow/L min (Ar)	0.8

Table 3 - Operating parameters of the Laser Ablation (LA) instrumentation and sample introduction systems.

LA parameters (Photon Machine)	
Ablation mode	Static point ablation
Laser wave length/nm	193
Ablation gas	He
LA-gas flow/L/ min	0.7
Repetition rate/Hz	10
Ablation duration/s	30s
Spot size/μm	100

RESULTS

In addition to Sr, the isotopic analysis of reference materials for Rb and Zr and mixtures of them were carried out to investigate the instrumental isotopic fractionation.

Daily, the instrument was adjusted for maximum sensitivity and stability. The gas and laser configurations have been optimized for the expected peak and alignment for different sets of axial masses. The blank correction of the solution-based MC-ICP-MS analysis was performed using the measurement before and after each group of 10 unknown samples.

Sr isotope results from reference material NIST-612

The analytical results of Sr isotopes in NIST-612 reference material are shown in Appendix 2 and plotted in figure 4, with an average for the ratio $^{87}Sr/^{86}Sr = 0.710446$.
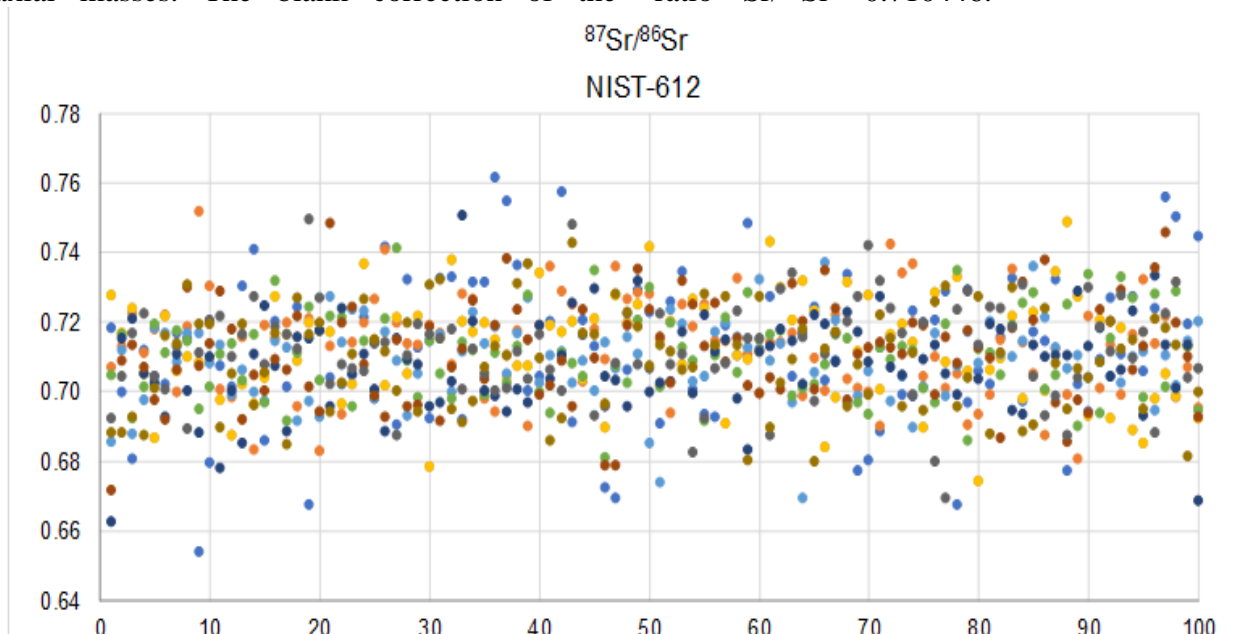

Figure 4 - Analytical results (run data) of Sr isotopes of NIST-612 standard. The mean value for the ratio $^{87}Sr/^{86}Sr$ is 0.710446. The reference value in the literature for $^{87}Sr/^{86}Sr$ is 0.709063±0.000020 (Woodhead & Hergt, 2001).

The composition certificate stated by National Institute of Standards and Technology U.S. (NIST) gives the value of 0.709063±0.000020 for the ratio $^{87}Sr/^{86}Sr$, according to Jochum et al. (2011, 2019), Weber et al. (2018) and Willmes et al. (2018). The obtained Sr isotope ratio for NIST 612 should be corrected since the high concentration of Rb and REEs in comparison to Sr causes interferences (Christensen et al., 1995; Horsky et al., 2015).

Sr isotopes results from reference material MACS03

The pressed powder of synthetic carbonate ($^{87}Sr / ^{86}Sr = 0.7075532 \pm 0.0000037$; 93) was analyzed in this investigation and used as reference material to correct fractionation of unknown samples. In addition, this reference material is also certified for the ratio $^{84}Sr/^{86}Sr = 0.05603$, but this ratio was not used in the correction calculations. The reference material USGS MACS03 has Sr concentration of 6760 μg/g (4) and is suitable for laser analysis. Therefore, this RM was used to calculate the concentration of unknown coral samples.

Four batteries of analyses were performed with 100 measurements and the results are shown

in Appendix 3 and plotted in the diagrams of figure 5. Each battery was analyzed at the beginning of the unknown analyses (group of 10 analyses) and was used, respectively, for calculating corrections using the bracketing technique. The average value of the ratio $^{87}Sr/^{86}Sr$ values for: battery A is 0.71926 and the estimated correction factor (CF) was 0.988 (Figure 5A); for battery B is 0.71925 and the CF=0.988 (Figure 5B); for battery C is 0.71926 and the CF=0.978 (Figure 5C); and for battery D is 0.71813 and the CF=0.962 (Figure 5D). In this sense, the repeatability in this investigation of the certified values varied between 96% and 98%.
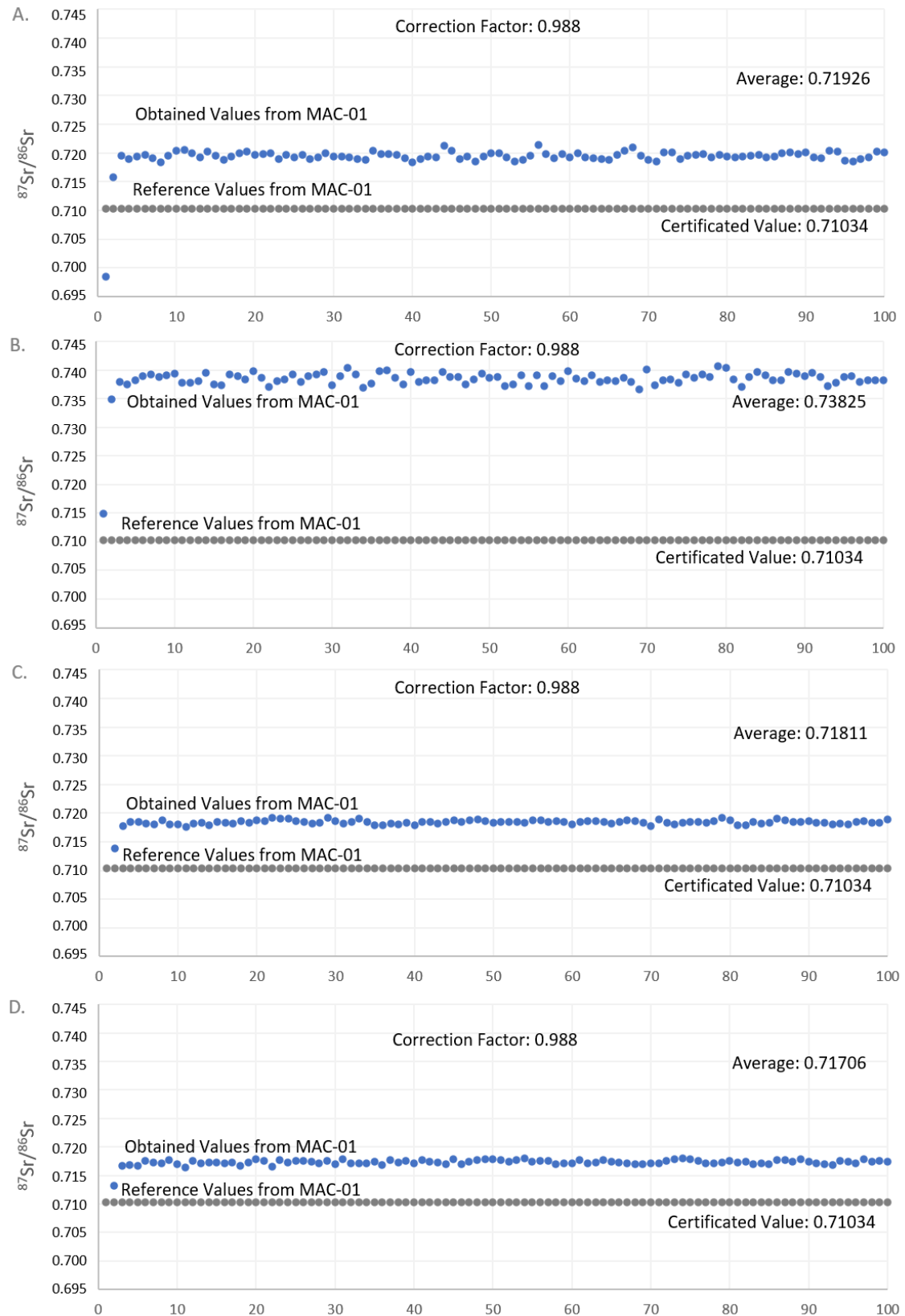

Figure 5 - The values obtained from the $^{87}Sr/^{86}Sr$ ratio plotted with the reference value of battery A, B, C and D.

Rb and Sr isotopes in corals

The results obtained in the coral (carbonate material), from the total number of 40 different layers, where Sr isotope values were measured are presented in the Appendix 4.

The $^{87}Sr/^{86}Sr$ ratio values were plotted in figure 6. It is important to emphasize that between 1 to 40 spot layers, the distance from the beginning of the coral growth to the end is about 18 mm.

The $^{87}Sr/^{86}Sr$ ratios decrease from the inner to the outer layer of the coral, from 0.70920 to 0.70627. The average $^{87}Sr/^{86}Sr$ ratio for all the points is 0.70892 ± 0.00006 (n = 40).

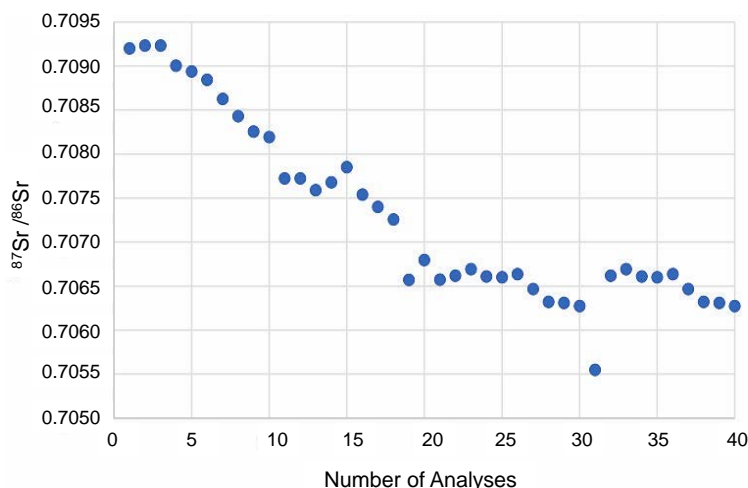**Figure 6** - Results of the $^{87}Sr/^{86}Sr$ ratio for the profile of 40 craters obtained in the coral growth axis. The results are corrected for fractionation and for ^{87}Rb isobaric interferences.

The values of $^{84}Sr/^{86}Sr$ ratio (from the inner to the outer layer of the coral) remained quite similar (average 0.0565). This indicates that there was no fractionation between the analyzed isotopes (Figure 7A), which was also confirmed by the almost invariable $^{85}Sr/^{88}Rb$ values around the average 0.119 (Figure 7B).

To quantify the interference of the ^{87}Rb in the H2 collector, the ^{85}Rb mass was analyzed in the L1 collector (see Supplementary Figure 1). The diagram presented in figure 8 shows the variation of the ^{85}Rb mass signal during the analysis on the mass spectrometer. However, the abundance of the ^{85}Rb mass decreased from 0.00029 Volts to 0.00015 Volts, indicating a decline in Rb concentration from the inner to the outer layer of the coral growth axis.
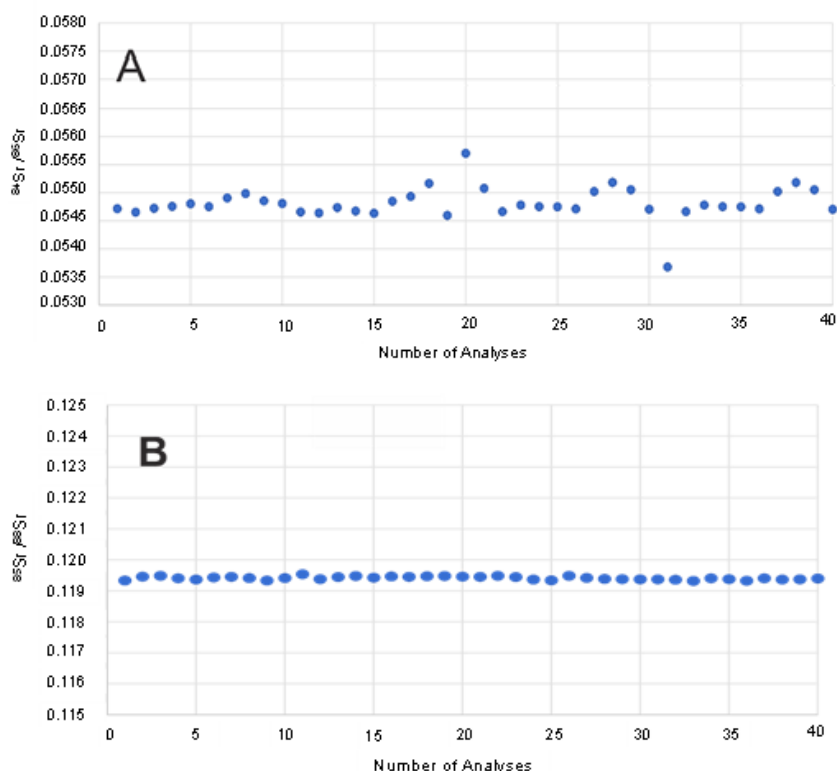

Figure 7 - Results for the profile of 40 craters along the coral growth axis of the ratios: A. $^{84}Sr/^{86}Sr$ and; B. $^{85}Sr/^{88}Rb$.
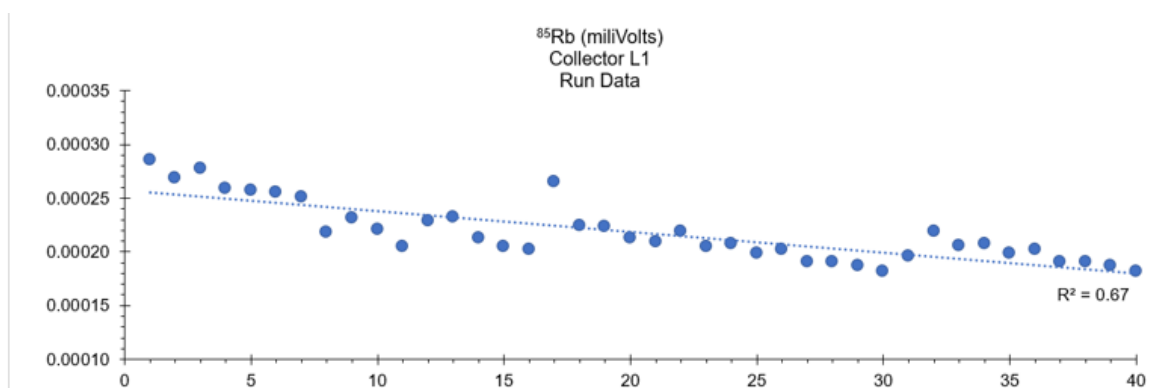
Figure 8 - Results of the abundance of the [85]Sr mass for the profile of 40 craters along the coral growth axis.

Rb and Sr concentrations

Decreasing Rb concentrations obtained in the sample (from the bottom to the top of the coral) lead to a decrease in the final $^{87}Sr/^{86}Sr$ ratio along the coral's growth axis.

Therefore, the conventional approach to Rb correction considering the Rb/Sr ratio of 1:50 can be considered adequate. This approach suggests that higher values of this ratio can generate inaccurate results in unknown samples.

This should be considered especially in the case of LA analyses, where a separation of Sr and Rb from the matrix cannot be performed before the analysis and in cases where significant amounts of Rb are expected.

In the analyzed sample of coral, the concentrations of Sr (ranging between 10,000 and 8,000 µg/g) and Rb (ranging from 0.024 to 0.015 µg/g) suggest a decrease in these elements along the growth of the coral skeleton.

In addition, the Rb/Sr ratio shows a small decrease in this ratio (between 0.0000025 and 0.0000018), indicating a greater incorporation of Sr relatively to Rb due to the replacement of Sr by Ca in the structure of the carbonate skeleton.

The Neptune MC yielded reliable isotopic data of Sr and Rb using the LA-ICP-MS system and applying a carefully calibration strategy to avoid intensities variations.

For this reason, we performed a rigid calibration to use adequate intensities to obtain concentration data.

DISCUSSION

A variety of reference values for normalization or correction of instrumental isotopic fractionation has been increasingly discussed in the literature (Jochum et al., 2019). It is also a major concern in Sr isotopic analyzes, where the diversity of reference values used and/or published increase constantly. In this investigation, the measurement data of a NIST SRM-987 solution were evaluated to define the main parameters of the mass spectrometer, such as: Ar flow in the plasma feed, Ar flow in the sample feed, ionization energy with power variation plasma frequency regulation (RF), as well as the energy used in the particle ionization.

Mass spectrometry protocol

The natural fractionation of the ^{88}Sr in relation to the ^{86}Sr can have significant impact on the $^{87}Sr/^{86}Sr$ ratio so that the correction of the internal instrumental isotopic fractionation needs to be performed. Therefore, the use of the $^{88}Sr/^{86}Sr$ ratio for correction should be strongly reconsidered when analyzing natural samples, since the deviations are significant in relation to the total uncertainties (of 0.71034 for the $^{88}Sr/^{86}Sr$ ratio; Halliday et al., 1995; Ohno & Hirata, 2007).

This study highlights the best procedures for the measurement of Sr isotope ratio by means of the LA-MC-ICP-MS and the challenges that this implies (Quitmyer et al., 1997; Ohno & Hirata, 2007). The best levels of accuracy obtained via LA-MC-ICP-MS are obtained with tens of Sr µg/g (Weber et al., 2020) and under ideal analytical conditions (e.g., high Sr concentrations and low Rb content). The approaches presented in this work offer promising possibilities to deal with the problems inherent in the measurement of Sr isotopic ratios by LA-MC-ICP-MS. The greatest challenges can certainly be attributed to the correction of instrumental isotopic fractionation and interferences. It was demonstrated that interferences are present in all investigated sample matrices (reference materials and unknown samples) and, consequently, they have significant influence on the Sr isotope ratios measured by LA-MC-ICP-MS. However, the importance of interferences depends strongly on the abundance of Sr mass in the sample. The contribution of

interferences based on high Sr concentrations can be determined and eliminated. Thus, the Sr isotope ratios obtained by LA-MC-ICP-MS in samples, such as corals can be significantly accurate, and, in addition, smaller amounts of sample are sufficient for isotopic analyzes.

The results reported in the literature of Sr isotopes were predominantly obtained by TIMS (Pitombo et al., 1998), whose fractionation correction technique is not compensated by the level of precision obtained. Thus, even with all the instrumental isotopic fractionation processes that occur in LA-MC-ICP-MS, the measurements are accurate, fast and inexpensive (Schöne et al., 2003). However, instrumental isotopic fractionation and interferences in Sr isotope ratio analyzes require clear and well-reported strategies comprising the analytical protocol, starting from sample preparation and measurement itself to data processing, including all corrections made, which are: (1) the blank; (2) correction of instrumental isotopic fractionation; (3) correction of Rb.

These strategies can differ strongly between different laboratories, instrumentations (that is, multicollector or monocollector ICP-MS, in addition to systems that include LA) and type of samples (especially considering the different matrices such as sulfides, carbonates and silicates, among others). The heterogeneity of the sample and the variations in the formation and stability of such interferences can, however, differ strongly between natural samples. Thus, the applicability of a measurement method of practical and quick use requires a data evaluation protocol where the applied corrections must be described in detail, whenever Sr isotope ratios are reported.

Sr isotopic change in corals

The "sclerochronology" includes studies on mollusks and corals as environmental and paleoenvironmental proxies (Grocke & Gillikin, 2008; Oppitz et al., 2015). These works demonstrated the relationship between the mollusk shells growth and environmental and climate change in different places around the world (McArthur et al., 2001; Lazareth et al., 2003; Takesue & Van Geen, 2004; Gillikin et al., 2005a). The "sclerochronology" studies aim to characterize the isotopic and geochemical composition of the environment through the geochemical record in carbonate biogenic structures. The organisms with carbonate structures can present a wide range of growth rates and can register daily changes (induced by local environmental variations), seasonal (inter-monthly variations), annual and long-term environmental changes and climatic oscillations (Shen et al., 1996; Gillikin et al., 2005b; Schöne et al., 2005; 2013).

Important factors, such as the temperature of sea water, its chemical composition, and the physiology of the organisms, seem to control the mineralogy of biogenic carbonates (Takesue & Van Geen, 2004). Skeletal carbonates are composed of aragonite, calcite with high magnesium content and calcite with a low magnesium content and, in some cases, with the mixture of these minerals. Calcite with low Mg content is more stable, that is, it generally retains its original low Mg, Na, Sr, Fe and Mn contents; calcite with a high Mg content is less stable (Rogers, 1990; Changa et al., 2004; Crespi, 2013; Ellot et al., 2018).

The results presented in this work for *M. braziliensis* are consistent with those presented by Gattuso et al. (1999) in corals from Peru. The coral used in this investigation have Sr concentrations ranging from 10,000 to 8,000 µg/g and Rb ranging from 0.024 to 0.015 µg/g and $^{87}Sr/^{86}Sr$ ratio from 0.70920 to 0.70627 (mean 0.70892 ± 0.00006; n = 40), showing a decrease from the inner to the outer layer of the coral.

The LA-ICP-MS technique applied along the growth axis of a coral sample of *M. braziliensis* allowed to analyze 100 µm craters, spaced in a very high spatial resolution, which is a great advantage since it allowed to identify changes in short time periods probably related to environmental changes of the marine environment during the growth of the coral. The application of stable isotopes and trace elements in corals has been reported in the literature, for instance, for *Montastrea annularis,* which may have growth rates of centimeters per month (Ellot et al., 2018). According to Ramos et al. (2004a) and Ellot et al. (2018) the compositional and isotopic variation of Rb and Sr in corals may also be the result of annual climatic variations during the growth of coral colonies.

The coral used in this investigation, sampled with 40 craters along its growth axis using laser ablation, showed a decrease in the $^{87}Sr/^{86}Sr$ ratio from the inner to the outer layer of the coral (from 0.70920 to 0.70627. The $^{84}Sr/^{86}Sr$ ratio, stable isotopes with constant abundances in nature, practically did not vary and had an average value of 0.0565 (Ingle et al., 2003) between the inner

and outer layers of the coral; this pattern was confirmed by the ^{85}Rb/^{88}Sr ratio (also with fixed value in nature) with an almost constant value around the average 0.192. In addition, the abundance of the ^{85}Rb mass varies from 0.00029 Volts to 0.00015 Volts, indicating a decrease in the concentration of this element along the coral growth axis and suggesting a decrease in the concentration of Rb in marine water surrounding area or a change in the growth rate of the coral as a result of water masses temperature variation due to oceanographic conditions. This hypothesis is confirmed by the concentration values of Sr (ranging from 10,000 to 8,000 µg/g) and Rb (ranging from 0.024 to 0.015 µg/g) that suggest a decrease in these elements over the growth time of the coral. This decline was probably influenced by the decrease of continental waters incursions (due to weather variability), which induced a decrease in the availability (concentration) of these elements in the study area.

The results obtained in this work indicate a variation in the availability of Sr and Rb in the marine water surrounding the coral or a change in the supply of particulate and/or dissolved material containing these elements in the environment, during the organism growth. Therefore, the application documented in this work can provide an important proxy for high spatial and temporal resolution, namely in corals (Anagnostou et al., 2011; Sifeddine et al., 2014). The carbonate structure of these organisms has high potential for paleoclimate reconstructions because they are present in all the oceans. The methodology applied allows the identification of changes at a detailed scale of temporal resolution. Corals are a useful tool for the study of environmental changes, because, besides being extremely sensitive, they record these changes in layers that overlap each year. And these peculiar characterristics make possible to study the variation in the quantity of chemical elements during the year, consequently inferring climatic changes that occurred in the area where the corals live or lived.

The fractionation of stable isotopes between coexisting phases (solid, liquid, gaseous) is fundamentally dependent on the temperature. Therefore, the measurement of this fractionation makes the stable isotopes as potential indicators of climatic variations. Therefore, studies with LA-ICP-MS are becoming important in the assessment of global climate changes. In addition, with the help of monitoring physical, chemical, and biological parameters, it is possible to identify the causes of environmental changes. In this way, they allow the identification of anthropogenic impacts, which can be controlled by environmental management actions.

CONCLUSION

This study demonstrates the suitability of the use of LA-MC-ICP-MS *in situ* for the identification of Sr isotope signatures spatially distributed in carbonate materials rich in Sr (>100 - 200 µg/g). The results reported in this work strongly support the effectiveness of the low deviation of isotopic ratios (^{84}Sr/^{86}Sr and ^{84}Sr/^{88}Sr) from the certified values, as well as for unknown samples. The low deviation of the ^{87}Sr/^{86}Sr ratios from the values determined via LA-MC-ICP-MS for the reference materials after the instrumental isotopic fractionation correction (via external correction with the use of reference material USGS MACS3), show that this technique is adequate and accurate.

Data improvements were performed on a selected set of unknown samples (coral) both for Sr isotopic ratios and to obtain Rb and Sr concentrations. The analytical uncertainty of Sr data by LA-MC-ICP-MS (this work) is comparable to studies carried out in other carbonate materials. The results of ablation techniques are reproducible within the analytical error, which implies that this technique produces robust results when applied to coral carbonates.

The results of the MC-ICP-MS measurements with a 193 nm laser show that the presented approach can be transferred to other laser ablation systems. The measurements of NIST-612 and USGS MACS3 are in good agreement with values reported in the literature. The performance of our reference material correction approach (bracketing) results in accurate values of the ^{87}Sr/^{86}Sr ratio of the RM and consequently of unknown analyzed samples. In general, the ^{87}Sr/^{86}Sr data of the applied reference materials, obtained with the laser ablation system, agree within the error and, therefore, are probably not affected by the differences in the matrix effects between the different configurations of the mass spectrometers. Therefore, the advancement in the understanding of the variability of the ^{87}Sr/^{86}Sr isotopic indicators obtained in this study contributes to the improvement of the use of the

coral *Mussismilia braziliensis* as an environmental and paleoenvironmental reconstruction tool an explanation for why the strontium isotopic composition of the coral decreased through time may be the ocean signature changed over the growth of the coral probably due the source of Sr that contributes to that part of the ocean change through time.

ACKNOWLEDGMENT

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