PALEOPROTEROZOIC GRAPHITIZATION IN THE CLÁUDIO SHEAR ZONE (SOUTHERN SÃO FRANCISCO CRATON - BRAZIL) INVESTIGATED BY RAMAN SPECTROSCOPY AND X-RAY DIFFRACTION

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ABSTRACT - The southern São Francisco craton hosts some of the largest graphite mines in Brazil, located in the city of Itapecerica. This paper addresses graphite crystals that occur within the regional structure known as the Cláudio shear zone in terms of thermometry. Raman spectroscopy and X-ray diffraction data showed that, on average, graphite crystals of the Cláudio shear zone have high crystallinity and are similar to those from mines in Itapecerica. The average temperature found (702 °C) in this study is close to the samples from Itapecerica. However, this temperature is still lower than the expected (~900 °C) from previous studies. The hypothesis for this would be that the graphite devolved high crystallinity, but was modified during the evolution of the metamorphism, or during the post-collisional stage fluid percolation. Thus, the modified crystallinity parameters lead to the relatively low-temperature values found. The proximity and similarity of geological framework suggest correlation between the precursor basins that formed the Itapecerica and the Cláudio shear zone graphite occurrences. From a global perspective, the closure of precursor basins and formation of the Cláudio shear zone are part of the collisions of Archean and Paleoproterozoic crustal blocks that formed the Columbia supercontinent.

Keywords: Graphite. High-grade metamorphism. Raman spectroscopy. Southern São Francisco craton. X-ray diffraction.

RESUMO - O sul do cráton do São Francisco abriga algumas das maiores minas de grafite do Brasil, localizadas na cidade de Itapecerica. Este artigo aborda cristais de grafite que ocorrem dentro da estrutura regional conhecida como zona de cisalhamento de Cláudio em termos de termometria. Dados de espectroscopia Raman e difração de raios X mostraram que, em média, os cristais de grafite da zona de cisalhamento de Cláudio possuem alta cristalinidade e são semelhantes aos das minas de Itapecerica. A temperatura média encontrada (702 °C) neste estudo está próxima das amostras de Itapecerica. No entanto, esta temperatura ainda está abaixo do esperado (~900 °C) de estudos anteriores. A hipótese para isso seria que o grafite degenerou alta cristalinidade, mas foi modificado durante a evolução do metamorfismo, ou durante o estágio pós-collisional de percolação do fluido. Assim, os parâmetros de cristalinidade modificados levam aos valores de temperatura relativamente baixos encontrados. A proximidade e similaridade do arcabouço geológico sugerem correlação entre as ocorrências das bacias precursoras que formaram a Itapecerica e a zona de cisalhamento de Cláudio. Do ponto de vista global, o fechamento de bacias precursoras e a formação da zona de cisalhamento Cláudio fazem parte das colisões de blocos crustais do Arqueano e do Paleoproterozoico que formaram o supercontinente Columbia.

Palavras-Chave: Grafita. Metamorfismo de alto grau. Espectroscopia Raman. Sul do cráton do São Francisco. Difração de raios X.

INTRODUCTION

Graphite ordinarily comes from organic matter (derived from the biological activity) that was deposited with sediments, when they subsequently undergo transformations at high temperatures and pressures during metamorphic processes over geological time. The combinations of conditions in the geological environment (pressure, temperature, kinetics, and fluid activity) lead to progressive transformation of disordered or partly ordered non crystalline carbonaceous material (CM) into pure carbon, end-member crystalline graphite. That process is known as graphitization (Buseck & Beyssac, 2014). According to Crespo et al. (2006), graphite
crystallinity can be described both along the stacking direction (c axis) of the carbon layers and along the a-b plane. In the first case, highly crystalline graphite has shorter spacing between adjacent layers of carbon atoms (the d002 spacing from which the c parameter is calculated). In addition, the continuity of the carbon layers along the stacking direction (the Lc crystallite size) is larger than for poorly crystalline graphite. In the second case, crystallinity refers to the continuity of carbon layers along the in-plane directions (defined by the La crystallite size).

The crystallinity, determined by X-ray diffraction (XRD) and Raman spectroscopy, has been used as a geothermometer due to the fact that, in natural environments, crystallinity has been proved to increase (smaller d002, larger Lc and La) with increasing metamorphic grade (Landis, 1971; Grew, 1974; Diessel et al., 1978; Kwiecinska, 1980; Buseck & Bo-Jun, 1985; Tagiri & Oba, 1986; Pasteris & Wopenka, 1991; Wopenka & Pasteris, 1993; Wada et al., 1994; Yui et al., 1996; Nishimura et al., 2000; Beyssac et al., 2002b, 2004; Buseck & Beyssac, 2014; Rantitsch et al., 2016).

Approximately 9% of graphite production worldwide is mined in Brazil (USGS, 2021), which has several occurrences of graphite generally associated with Paleoproterozoic khondalitic belts (figure 1A). The southern São Francisco craton (SFC) hosts some of the largest Brazilian graphite mines located in the city of Itapecerica (Figure 1A).

The origin and thermometry of the graphite in these mines were previously studied by Miranda et al. (2019). In the vicinity, occurrences of graphite within the regional scale structure known as the Cláudio shear zone (CSZ) have been found, possibly with geological relation to those of the Itapecerica mines (Figure 1B), still have not been studied regarding their origin and thermometry. The objective of this study is to determine, by XRD and Raman spectroscopy, the thermometry of the occurrences close to the city of Cláudio that occur within the CSZ and to compare the obtained results with the graphite data of Miranda et al. (2019) for the Itapecerica mines.

**GEOLOGICAL SETTING**

The southern sector of São Francisco Craton (Figure 1A) is composed of Meso- to Neoproterozoic granite-greenstone terrains, Palaeoproterozoic elastic-chemical metasedimentary rocks (including Itabirites of Quadrilátero Ferrífero (QF)) from Minas Supergroup, and Neoproterozoic pelitic-carbonatic sedimentary rocks from Bambuí Group (Teixeira et al., 2017a).

The Archaean core is composed by the complexes denominated Campo Belo-Bonfim, Divinopolis and Belo Horizonte that are TTG (tonalite-trondhjemite-granodiorite) suites associated to greenstone belts (3.20–2.90 Ga), granitoid plutons generated by partial melting of older material (2.79–2.70 Ga) (Teixeira et al., 2017a), mafic-ultramafic intrusions (Noce et al., 1998), and granitoid rocks emplaced later at 2.61 Ga (Farina et al., 2015). The main supracrustal units of the region are the Neoarchean greenstone belt sequence (Rio das Velhas Supergroup, 2.77–2.73 Ga) and the Early Palaeoproterozoic Minas Supergroup (Moreira et al., 2016; Teixeira et al., 2017a) (Figure 1B).

The Mineiro Belt (Noce et al., 1998; Ávila et al., 2014; Teixeira et al., 2015) is a large juvenile terrane formed by accretionary orogeny between Siderian and Orosirian periods, which resulted in an extensive reworking of regions placed at the margins of the southern SFC (Noce et al., 2007; Seixas et al., 2013; Teixeira et al., 2015; Barbosa et al., 2019; Moreira et al., 2020 and Lopes et al., 2020). The region is cut by several generations of mafic dike swarms (Chaves, 2013) from 1.7 Ga (Pará de Minas dike swarm) to 135 Ma (Transminas dyke swarm) (Figure 1B).

A distinct NE-SW trending structure known as Cláudio Shear Zone (CSZ - Figure 1B) is a geological suture that separates the Archean Campo Belo-Bonfim and Divinópolis metamorphic complexes in southern SFC (figure 1B), as evidenced by the high deformation strain with dextral strike-slip motion (Oliveira, 2004; Teixeira et al., 2017b). Metamorphosed ultramafic rocks (metapertidotite, talc-serpentine-chlorite-amphibole schist), amphibolite, garnet-sillimanites schist, graphite schist, quartzite, banded iron formation and sillimanite-cordierite-garnet-biotite gneiss (Oliveira, 2004) outcrop along the CSZ. The foliation within the CSZ mega-structure shows dips from medium to high angle and mylonitic feature in its inner region.

The sillimanite-cordierite-garnet-biotite gneisses, also known as khondalitic paragneisses, are associated with graphite schist, the graphite bearing host rocks in some local graphite mines (Chaves et al., 2015; Teixeira et al., 2017b; Miranda et al., 2019). The khondalitic paragneisses investigated

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Coelho & Chaves (2019) indicated metamorphic peak estimate temperatures about 900°C around 2011 Ma (age determined by chemical U-Th-Pb method in monazites). This age is close to U-Pb zircon ages described by Carvalho et al. (2017) in the Kinawa migmatite (2048 ± 25 and 2034 ± 32 Ma). These ages define a high-grade event in the interior part of the southern SFC Archean core along the CSZ during the granulite facies metamorphic peak and confirm the existence of a Paleoproterozoic event previously recognized only from monazite in khondalitic rocks near CSZ (Chaves et al., 2015).

According to Miranda et al. (2019) the town of Itapecerica host the second largest graphite mine in Brazil, located 20 km west of the CSZ. The Itapecerica graphite schist is composed of fine to medium grained graphite, quartz and sillimanite showing granoepidoblastic texture. Graphite is the main component and marks the rock foliation. Quartz is the second main component, with elongated (ribbons) crystals. Sillimanite occurs in variable proportions as fibrous or prismatic habit. The values of 813C range between -21.23 and -27.89 ‰, indicating that the source of the graphite was a primitive biogenetic carbon material. High-grade metamorphic graphite from Itapecerica shows average temperatures around 729 °C, indicating granulite to amphibolite facies formation conditions.
The graphite occurrences within the CSZ are layers of grayish-colored graphite schist with a few centimeter lengths (Figure 2) surrounded by large hydrothermal quartz veins. The graphite has a very fine grain and the layers rich in quartz generally have boudin- and sigmoid-like structures.

Figure 2 - Graphite schist outcrops from CSZ. A - Sampling point 13; B - Detailed view of the outcrop; C Sampling point 55; D - Detailed view of the outcrop.

The photomicrographs of the graphite schists show that graphite is fine-grained disseminated over the rock, forming aggregates intercalated with layers of quartz and sillimanite (Figure 3), which define the schistosity. The sillimanite crystals are less abundant, often with fibrous habit interspersed with graphite crystals in foliation. The effects of shear stress are well observable above the quartzose layers, such as the dynamic recrystallization of quartz grains, the ribbon quartz, and the anastomosed texture of the quartz layers (Figure 3).

Figure 3 - Photomicrographs illustrating graphite textures: A and B are from sample 13 and C and D from sample 55 showing the scattered aspect of the graphite inside schist (A and C under plane polarized light - PPL and B and D under crossed polarized light-XPL) Mineral abbreviations according to Whitney & Evans (2010): Gr: graphite; Sil: sillimanite; Qz: quartz.
METHODOLOGY AND RESULTS

Two samples of natural graphite from the Cláudio shear zone were collected (sample 13, coordinates 20° 20.480' S 44° 33.469' W; sample 55 coordinates 20° 26.443' S 44° 43.565' W) (sampling location in figure 1B). In Manoel Teixeira da Costa Research Center (CPMTC-IGC-UFMG) laboratories, the graphite schist samples were prepared for the XRD and for Raman spectroscopy. Due to the graphite shists of CSZ being friable, the samples were cautiously disaggregated in an agate mortar to avoid the interference of the grinding for the analysis (Crespo et al., 2006) and subsequently subjected to the flotation process to separate the graphite from the quartz-sillimanite fractions of the rock.

X-Ray Diffraction (XRD)

XRD analyses were performed at the Manoel Teixeira da Costa Research Center (CPMTC-IGC-UFMG, at Belo Horizonte-MG) X-ray Laboratory. XRD spectra were recorded with a PANalytical X’Pert PRO diffraction instrument with theta-theta geometry, using a Cu Kα X-ray source (40 kV and 45 mA). The diffraction data were collected with a step size of 0.02° 2θ and a scan step of 0.5 s.

To obtain lattice parameters of high accuracy, the diffraction data were fitted by Rietveld methods (Young, 1993). The starting parameters for the refinement were identical for each sample and chosen to be as close as possible to realistic values. Based on Tagiri (1981), the standard deviation of the error of d(002) is ~0.02 over 3.53 Å, ~0.01 between 3.53 and 3.36 Å, and ~0.005 between 3.36 and 3.35 Å. The experimental error of Lc(002) is about 4% below 30 Å and about 10% over 500 Å (Tagiri, 1981)

The crystal size (Lc(002)) along stacking direction is estimated from the follow equation (Baiju et al., 2005):

\[ Lc(002) = \frac{k\lambda}{\beta(002)\cos\theta} \]

where k is the shape constant (0.9), β(002) is the full width at half maximum of the peak in radian, λ is the X-ray wave length in angstroms (1.5406), and θ is the angle of diffraction in radians.

Further, the graphitization degree (GD) has been calculated from the equation (Tagiri, 1981):

\[ GD = \frac{[d(002) - 3.7]}{[\log(Lc(002)/1000)]} \times 100 \]

Additionally, the metamorphism temperature is calculated by the equation for pelitic rocks (Wada et al., 1994):

\[ T(ºC) = 3.2 \times GD + 280 \]

The results are shown in table 1 and graphitization temperatures are between 620 and 781°C.

Table 1 - Graphite XRD diffraction data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ</th>
<th>d(002) Å</th>
<th>sd ± FWHM (2θ)</th>
<th>Lc(002) Å</th>
<th>sd ± GD</th>
<th>T (ºC)</th>
<th>sd ±</th>
</tr>
</thead>
<tbody>
<tr>
<td>13a</td>
<td>26.633</td>
<td>3.347</td>
<td>0.005</td>
<td>0.157</td>
<td>519</td>
<td>52</td>
<td>124</td>
</tr>
<tr>
<td>13b</td>
<td>26.605</td>
<td>3.351</td>
<td>0.005</td>
<td>0.138</td>
<td>592</td>
<td>59</td>
<td>154</td>
</tr>
<tr>
<td>13c</td>
<td>26.498</td>
<td>3.361</td>
<td>0.01</td>
<td>0.144</td>
<td>567</td>
<td>57</td>
<td>138</td>
</tr>
<tr>
<td>13d</td>
<td>26.620</td>
<td>3.346</td>
<td>0.005</td>
<td>0.168</td>
<td>508</td>
<td>51</td>
<td>120</td>
</tr>
<tr>
<td>55a</td>
<td>26.669</td>
<td>3.343</td>
<td>0.005</td>
<td>0.177</td>
<td>461</td>
<td>46</td>
<td>106</td>
</tr>
<tr>
<td>55b</td>
<td>26.656</td>
<td>3.344</td>
<td>0.005</td>
<td>0.138</td>
<td>593</td>
<td>59</td>
<td>157</td>
</tr>
<tr>
<td>55c</td>
<td>26.620</td>
<td>3.346</td>
<td>0.005</td>
<td>0.168</td>
<td>486</td>
<td>49</td>
<td>113</td>
</tr>
<tr>
<td>55d</td>
<td>26.668</td>
<td>3.340</td>
<td>0.005</td>
<td>0.144</td>
<td>567</td>
<td>57</td>
<td>146</td>
</tr>
</tbody>
</table>

sd: standard deviation.

The binary plot of Lc(002) vs. d(002) (Tagiri & Oba, 1986) shows that the samples are predominantly fully ordered graphite fields (Figure 4A). The plot of GD versus T (ºC) (Figure 4B) shows the samples aligned with the trend of Ryoke pelites of Wada et al. (1994).

Raman Spectroscopy

The Raman data were obtained in the Technological Center of Nanomaterials (CT nano) at technological park of Belo Horizonte (MG) – BH Tec, using the same methodology proposed in Rantitsch et al. (2016) and the same equipment, a confocal microscope Alpha300R WITEC (Wissenschaftliche Instrumente und Technologie GmbH®, Ulm, Germany) equipped with a Nd-YAG laser with double frequency (2.49 mW, λ = 532.2 nm). Raman spectra were collected with 50× lens objective, where five scans in the 1000–3200 cm⁻¹ spectra (first order = 1000–2000 cm⁻¹; second order = 2200–3200 cm⁻¹) were performed with an acquisition time of 30 s. In each sample, five major fields (red,
green, blue, orange and black) were randomly selected (Figure 5A). Figure 5B shows the analyzed spots (red, green, blue). Figure 5C shows the Raman spectra of these spots. The analysis of the spectra focused on the first-order peaks at \approx 1350 \text{ cm}^{-1} (D1 band), \approx 1500 \text{ cm}^{-1} (D3 band), \approx 1580 \text{ cm}^{-1} (G band), and \approx 1610 \text{ cm}^{-1} (D2 band) (Figure 5C). The Raman spectroscopy data was evaluated by IFORS method (Lünsdorf & Lünsdorf, 2016).

The IFORS (Interactive Fitting of Raman Spectra) method arose to avoid the process of curve-fitting that is commonly biased by subjectivity, due to many programs requiring manual intervention, especially when baseline manipulation is necessary. It consists of software with an iterative algorithm that does an automated evaluation based on the randomized mutation of function parameters. The approach follows the idea that the Raman spectroscopy of carbonaceous material recorded consists of high-frequency signal components and low-frequency baseline components with added normal distributed noise. The signal components are described by pseudo-Voigt functions and the baseline component by a polynomial, which are modeled simultaneously (Lünsdorf & Lünsdorf, 2016). Table 2 shows the results of Raman spectroscopy, R2 ratio, and the temperature calculations by the IFORS method (Lünsdorf & Lünsdorf, 2016) which revealed temperatures between 542 and 605\degree C.

**DISCUSSIONS**

With the same approach of Rantitsch et al. (2016), which tried to correlate XRD and Raman data, the table 3 shows the mean values of these data. A significant correlation between the d(002) lattice distance and the width of the Raman G band (Figure 6A) and also the R2 ratio (D1/(G + D1 + D2) area ratio of Beyssac et al. (2002a) (Figure 6B) are verified. Metamorphic facies (Beyssac et al., 2002a; Rantitsch et al., 2016) and the semi-graphite/graphite separation (Kwiecińska & Petersen, 2004; Rantitsch et al., 2016) are presented in the figures 6A and 6B.
**Table 2** - Raman spectroscopy data of graphite with values obtained by the IFORS method (Lünsdorf & Lünsdorf, 2016).

<table>
<thead>
<tr>
<th>Sample</th>
<th>d(002) (Å)</th>
<th>GD (°C)</th>
<th>std</th>
<th>T(°C)</th>
<th>sd</th>
<th>n</th>
<th>G HWHM (cm⁻¹)</th>
<th>std</th>
<th>R²</th>
<th>sd</th>
<th>T(°C)</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>3.351</td>
<td>3.370</td>
<td>0.007</td>
<td>134</td>
<td>15</td>
<td>708</td>
<td>49</td>
<td>11</td>
<td>8.33</td>
<td>0.38</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>55</td>
<td>3.343</td>
<td>3.370</td>
<td>0.003</td>
<td>130</td>
<td>25</td>
<td>697</td>
<td>79</td>
<td>11</td>
<td>8.77</td>
<td>1.21</td>
<td>0.12</td>
<td>0.06</td>
</tr>
</tbody>
</table>

sd: standard deviation.

**Table 3** - Mean values of the results for XRD and Raman spectroscopy, “n” shows the number of analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>d(002) (Å)</th>
<th>std</th>
<th>GD</th>
<th>std</th>
<th>T(°C)</th>
<th>sd</th>
<th>n</th>
<th>G HWHM (cm⁻¹)</th>
<th>std</th>
<th>R²</th>
<th>sd</th>
<th>T(°C)</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>4</td>
<td>3.351</td>
<td>0.007</td>
<td>134</td>
<td>15</td>
<td>708</td>
<td>49</td>
<td>11</td>
<td>8.33</td>
<td>0.38</td>
<td>0.05</td>
<td>0.03</td>
<td>593</td>
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<tr>
<td>55</td>
<td>4</td>
<td>3.343</td>
<td>0.003</td>
<td>130</td>
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<td>697</td>
<td>79</td>
<td>11</td>
<td>8.77</td>
<td>1.21</td>
<td>0.12</td>
<td>0.06</td>
<td>572</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 6** - Graphite samples plotted in diagrams from Rantitsch et al. (2016). A - Half width at half maximum (HWHM) of the G-band versus d(002) lattice distance (Graphite/Semi-graphite at ~ G HWHM ~ 13.0 and d(002) ~ 3.370). B - R² ratio (Beyssac et al. 2002a; D1/(G+D1+D2) area ratio) versus d(002) lattice distance (Graphite/Semi-graphite at ~ R² ~ 0.4 and d(002) ~ 3.370).
Although G HWHM values (Figure 6A) put all samples in high amphibolite facies, the R2 ratio in figure 6B places the sample 13 in the granulite facies and the sample 55 in the high amphibolites facies. This indicates a good relation of the R2 parameter with the graphite formation temperature, as seen on Beyssac et al. (2002a), Lünsdorf (2015) and Rantitsch et al. (2016). The average data obtained by XRD and Raman spectroscopy in this study are very similar to the data presented by Miranda et al. (2019) for high-grade metamorphic graphite schist in the Itapecerica mines.

By comparing the temperatures (Table 3) obtained from the Raman data (around 583ºC) and XRD data (around 702 ºC), it becomes clear that the temperature obtained by the IFORS method does not correspond to the metamorphism in granulite facies estimated for the region. This is due to the fact that graphite reaches the maximum crystallinity at 600ºC, forming flake-type graphite. According to Beyssac et al. (2002a) and Lünsdorf (2015), around 600ºC all graphite becomes fully ordered and the IFORS method cannot calculate higher temperatures. Samples of high-grade metamorphic conditions in Baiju et al. (2005) support an extrapolation of temperatures above 700 °C on the equation for pelitic rocks of Wada et al. (1994).

The average temperatures found by XRD in this study (table 3), although slightly lower, are similar to the average temperatures (729 ºC) of the high-grade metamorphism samples in Itapecerica mines studied by Miranda et al. (2019).

However, when compared to the metamorphism temperatures around 900 ºC described by Coelho & Chaves (2019) in the CSZ, the temperatures around 702 ºC found by XRD in this study are much lower. The hypotheses that explain this observation are: the graphitization processes undergone by the CM proceeded with collisional stress until the fully ordered graphite stage, and then the shearing stress in CSZ (Crespo et al., 2006), together with the percolation of metamorphic fluids (represented by quartz veins), changed physically the graphite crystals thus modifying the crystallinity parameters and leading to the relatively low-temperature values found by the technique of XRD.

Or maybe the graphite within the CSZ had modified its crystallinity during decompression promoted by the post-collisional stage making it incompatible with expected for the temperature conditions around 900 ºC described by Coelho & Chaves (2019).

From a local geodynamic scenario, the graphite schists and the khondalites of the CSZ, associated with garnet-sillimanite quartzites, banded iron formations and ultramafic rocks, represent the metamorphism of the sediments of a possible Paleoproterozoic oceanic basin. Carvalho et al. (2017) have proposed a tectonic model in which the Archean block is the lower plate and the Mineiro belt is the upper plate that collided at 2.05 Ga, but not included the generation of Itapecerica graphite-rich metasedimentary sequence. Chaves et al. (2015) and Teixeira et al. (2017b) were the first to suggest the possibility of including this sequence in the tectonic discussion.

The paleobasin of CSZ is possibly related to those of the graphite mines of Itapecerica and therefore has undergone a tectonic process analogous to that proposed by Miranda et al. (2019) to the graphite-rich sequences from Itapecerica. According to Miranda et al. (2019) during the pre-collisional stage (2.35–2.08 Ga) the CM-rich sedimentary sequence was deposited on an oceanic basin (Miranda & Chaves, 2021 and references therein). Such sequence was involved during the collision stage (2.07–2.01 Ga) and the CM transformed into graphite under high-grade metamorphism. Figure 7 proposes a tectonic model modified from Carvalho et al. (2017) for the formation of the graphite occurrences within the CSZ around 2.05 Ga, involving the Paleoproterozoic Mineiro orogenic belt.

From a global perspective, the orogenic system highlighted by the CSZ corresponds to the closure of internal oceans and subsequent collision of Archean and Paleoproterozoic crustal blocks that promoted the formation of the supercontinent Columbia (Nuna) (Chaves, 2021 and references therein).

**CONCLUSIONS**

The Raman spectroscopy and XRD analyses showed data that, on average, are similar to those obtained by Miranda et al. (2019), demonstrating that the graphite at CSZ has high crystallinity. The average temperature found by XRD (702ºC) in this study is close to the high-grade metamorphism samples in Itapecerica mines studied by Miranda et al. (2019). The graphitization processes undergone.
CONCLUSIONS

by the CM proceeded with collisional stress until the fully ordered graphite stage, and then the shearing stress in CSZ, together with the percolation of metamorphic fluids (represented by quartz veins), changed physically the graphite crystals thus modifying the crystallinity parameters and leading to the relatively low-temperature values found by the technique of XRD. Or maybe the graphite within the CSZ had modified its crystallinity during decompression promoted by the post-collisional stage making it incompatible with expected for the temperature conditions around 900 °C described by Coelho & Chaves (2019) in the CSZ.

The proximity and the similar geological framework suggest that the precursor basin that formed the graphite occurrences of CSZ is correlated with the precursor basin that originated graphite from Itapecerica. Thus, the source of the CM for the CSZ graphite occurrences possibly is primitive biogenic carbon as Miranda et al. (2019) indicate by the analysis of $\delta^{13}C$ between -21.23 and -27.89 ‰. From a global perspective, the orogenic system highlighted by closure of precursor basins and formation of the CSZ is part of the collisions of Archean and Paleoproterozoic crustal blocks that promoted the formation of the Columbia supercontinent.

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