Abstract
During the Paleoproterozoic Era, the Brazilian cratons experienced orogenic events that modified the archean basement and sedimentary successions. In the southern São Francisco Craton, it can be recognized evidence of an orogenic event that happened between Rhyacian and Orosirian periods. It is related to the closure of an oceanic basin at this time, which led to the collision between the Archean Divinópolis and Campo Belo metamorphic complexes. Graphite schist occurs close to the cities of Formiga and Itapecerica (Minas Gerais), located between these complexes. To contribute to the understanding of the origin and metamorphism of the graphite from Formiga, petrographic studies, X-ray diffraction (XRD) and Raman spectroscopy analyses have been done. XRD and Raman methods revealed that the temperatures recorded by graphite are around 460°C. However, Raman data showed that the crystallite sizes correspond to higher metamorphic grade conditions (amphibolite to granulite facies). Temperatures of 460°C are probably associated with hydrothermal processes along faults in post-collisional stage. The presence of todorokite, a mineral typical of deep-sea Mn nodules formed by microorganisms, in association with graphite from Formiga, suggests a biogenic origin for the graphite occurrence.

KEYWORDS: Southern São Francisco Craton; Raman spectroscopy; X-ray diffraction; graphite.

INTRODUCTION
Graphite and diamond are the polymorph occurrence of native carbon on the nature (Harlow 1998). Graphite has a growing economic value due to its modern technological use as graphene source (Simandl et al. 2015). Formed in several geological settings, graphite is most commonly found in metamorphic rocks, especially in orogenic belts. Graphite can be formed through maturation and metamorphism of biogenic carbonaceous material (CM); as precipitation from C-O-H fluids; mantle-derived; and through reduction of carbonates (Simandl et al. 2015).

There is a vast combination of variables like temperature, pressure, kinetics, composition of country rocks and presence or absence of fluids that can influence the formation of this mineral (Wintsch et al. 1981, Luque et al. 1998, Galvez et al. 2013). The graphite formed by biogenic CM undergoes a progressive and irreversible process called graphitization (Buseck and Beyssac 2014). It occurs in temperature and pressure of burial metamorphism, and decreases the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios, transforming disordered and non-crystalline CM in crystalline graphite (Kwiecińska and Petersen 2004) (Fig. 1). The process of graphitization does not depend on the metamorphic pressure, although it is influenced by the oxygen fugacity and metamorphic temperature (Tagiri and Oba 1986). There are two forms to quantify the metamorphic temperature associated to the graphitization of biogenic CM:
• by Raman spectroscopy geothermometry, from low (~330°C) to high-grade metamorphism (~600°C) (Beyssac et al. 2002);
• by X-ray diffraction (XRD) geothermometry, for metamorphism above 600°C (Wada et al. 1994).

An efficient method to analyse the origin of CM is to evaluate its isotopic composition, inasmuch as Buseck and Beyssac (2014) indicate that this kind of deposit preserves the δ13C between -35 and -20‰ biologic signature. A variety of minerals can be formed in this condition, as is the case of todorokite ((Mn, Mg, Ca, Ba, Na, K)2 Mn5O12.3H2O), which is formed by the accumulation of Mn-oxides (Lowenstam 1981), and can be used as evidence of biogenic activity on seafloor (Burns et al. 1983).

Graphite schist occurs at southern São Francisco Craton, in the Itapecerica Supracrustal Sequence, associated with the collision between the Archean Divinópolis and Campo Belo metamorphic complexes. In Itapecerica (Minas Gerais, Brazil), Miranda et al. (2019) characterized two different forms of graphite. They presented δ13C between -21.23 and -27.89‰, indicating biogenic source, and high-grade metamorphism associated with a syn-collisional stage, with average temperature around 729°C (metamorphic graphite), and hydrothermalism associated with post-collisional stage, around 611°C (recrystallized graphite).

In order to complement the study of Miranda et al. (2019), this paper aims to characterize the origin, crystallinity and metamorphism temperature of graphite from an area near the city of Formiga (MG), a city located about 40 km west of Itapecerica (MG) (Fig. 2), using XRD and Raman spectroscopy. The results are compared to previous studies to corroborate to the understanding of the tectonic model proposed for the Rhyacian-Orosirian orogeny in the southern São Francisco Craton.

GEOLICAL SETTING

The São Francisco Craton (SFC) is a tectonic domain (Almeida 1977) (Fig. 2) surrounded by Neoproterozoic orogens. Its southern sector is composed by Archean crust, with age between 3.5 and 2.6 Ga, that is formed mostly by granite-gneisses rocks (Farina et al. 2015) and greenstone belts (Rio das Velhas Supergroup) constituted by mafic-ultramafic, intermediate-felsic volcanic and volcanoclastic rocks (Noce et al. 1998) with terrigenous sediments (Dorr 1969, Baltazar and Zucchetti 2007).

The basement comprises the Campo Belo, Divinópolis, Bonfim and Belo Horizonte metamorphic complexes (Fig. 2).
(Machado Filho et al. 1983, Teixeira et al. 1996). The supra-
crustal sequence is formed by the Minas Supergroup, which
is characterized by clastic-chemical metasedimentary rocks
from the Paleoproterozoic (minimum deposition around 2.0
Ga), including the banded iron formations of the Quadrilátero
Ferrífero (Machado et al. 1996, Moreira et al. 2016), and also
the Bambuí Group, formed by pelitic-carbonate sedimen-
tary rocks with Neoproterozoic age (Alkmim and Martins-
Neto, 2001).

The Mineiro Belt (Noce et al. 1998, Ávila et al. 2014, Teixeira
et al. 2015) was formed by accretionary orogeny and occurred
between Rhyacian and Orosirian, which resulted in extensive
reworking of regions placed at the margins of the southern
SFC (Noce et al. 2007). Chaves et al. (2015) suggested the
existence of a Paleoproterozoic event in the Itapecerica region
based on chemical ages found in monazites in sillimanite-cord-
erite-garnet-biotite gneiss (graphite-rich khondalitic rocks),
which was confirmed by Carvalho et al. (2017), that found
isotopic ages from zircons of 2.05–2.03 Ga (U-Pb) in the inte-
rior of the basement.

Occurrences of graphite with $\delta^{13}C$ between -21.23 and
-27.89‰, indicating biogenic origin, (Miranda et al. 2019) are
reported in this area, where Itapecerica Supracrustal Sequence
has been described (Campello et al. 2015, Chaves et al. 2015,
Teixeira et al. 2017). The studied area is located near the city
of Formiga, where the graphite schist occurs between the
Divinópolis and Campo Belo complexes (Fig. 2).

**METHODS AND RESULTS**

Three samples were collected at the Formiga area
(20°26’40.4"S, 40°30’04.3"W). Samples LR44A and LR44C
were chipped from an abandoned trench (Fig. 3A) and sample
LR44B was chipped about 5 m away. Both collection spots are
formed by fine grained graphite schist composed of quartz, graph-
ite and mica, with presence of vertical foliation. In the trench
it is possible to notice the presence of quartz veins oblique to
the foliation that contain manganese minerals and occur filling
fractures. The host rock presents some recrystallization in the
contact with the veins. Samples LR44A and LR44B (Fig. 3B)
are graphite schist with vertical foliation, while sample LR44C
(Fig. 3C) was taken from an associated quartz vein (Fig. 3D),
with manganese minerals, oriented N40E/75NW. The visual
proportion between graphite and manganese mineral in this
sample is 4:1. Each sample was between 10 and 20 cm long
and weighed approximately 0.5 kg.

![Figure 3. Graphite schist sampling site. (A) Front view of trench; (B) place where samples LR44A and LR44B were collected; (C) sample
LR44C, collected from quartz vein with presence of todorokite and manganite; (D) quartz vein where sample LR44C was collected.](image)
Petrography

Thin sections of the collected samples were prepared and examined under transmitted and reflected light microscopy at the Centro de Pesquisa (Research Centre) Professor Manoel Teixeira da Costa of Institute of Geosciences of the Universidade Federal de Minas Gerais (CPMTC-IGC-UFMG), at Belo Horizonte, MG, Brazil.

The studied rocks are fine grained and have granolepidoblastic texture (Fig. 4). They are composed of quartz (50%), graphite (35%) and phengite (15%). Quartz is the dominant mineral in the composition and occurs in anhedral fractured grains. The second main component is graphite, presented in aggregates (LR44A) and in layers parallel with foliation (LR44B). Phengite marks the foliation in both samples, but occurs in larger crystals in sample LR44B than in sample LR44A. The foliation is more evident in sample LR44B than it is in sample LR44A.

X-ray diffraction

The XRD analyses of graphite were performed in the X-ray Laboratory at CPMTC-IGC-UFMG. The mineral was previously isolated from other minerals of the graphite schist by brushing the graphite-rich portion of the rock, followed by graphite flotation in aqueous environment and drying of the floated grains. PANalytical XPert PRO diffraction instrument with theta-theta geometry was used to record the XRD data, using a Cu Kα X-ray source (40 kV and 45 mA). The step size and scan step settings were 0.02°, 2θ and 0.5 s. The high accuracy of the lattice parameter was guaranteed using Rietveld methods (Young 1993) to fit the diffraction data, with starting parameters close to realistic values and equally applied to both samples LR44A and LR44B. Figure 5 shows the XRD results of sample LR44C, composed of todorokite and manganite instead of graphite. The XRD data from the graphite schist samples are organized in Table 1 and their respective diffractogram are presented in Figure 6.

To estimate the crystal size along stacking direction \( L_{c(002)} \), we used the Equation 1 provided by Baiju et al. (2005).

\[
L_{c(002)} = k \lambda / \beta_{c(002)} \cos \theta
\]  

(1)

In this equation, \( k \) means the shape constant (0.9), \( \lambda \) is the X-ray wavelength in angstroms (1.5406), \( \beta_{c(002)} \) represents the full width at half maximum of the peak in radian and \( \theta \) correspond to the angle of diffraction in radians. The graphitization degree (GD) has been calculated using the Equation 2 from Tagiri (1981), were \( d_{(002)} \) is the interplanar spacing:

\[
GD = \left( \frac{d_{(002)} - 3.7}{\log(L_{c(002)}/1000)} \right) \times 100
\]  

(2)

Moreover, the Equation 3 from Wada et al. (1994) has been used to calculate the metamorphism temperature:

\[
T(°C) = 3.2 \times GD + 280
\]  

(3)

The average temperature found for samples LR44A and LR44B were 442°C and 449°C respectively.

The graphs in Figure 7 show correlations that could be done with the results obtained from the XRD data. Figure 7A presents the relationship between interplanar spacing \( (d_{(002)}) \) and crystallite size \( (L_{c(002)}) \), that, in accordance with Tagiri and Oba (1986), can give information about the GD. Both samples LR44A and LR44B were classified as graphite as opposed to fully ordered graphite. The two samples presented similar XRD temperatures and are randomly arranged in the line that correlated GD with metamorphic temperature in the Figure 7B.
Table 1. X-ray diffraction data from LR44A and LR44B, graphite schist samples, in which d(002) represents interplanar spacing, FWHM is the full width at half maximum of the G-band, Lc(002) is the crystal size along stacking direction, GD is the graphitization degree and T is the metamorphic temperature.

| Sample  | 2θ  | d(002) (Å) | sd ±   | FWHM (2θ) | Lc(002) (Å) | sd ±  | GD  | T(°C) | sd ± |
|---------|-----|------------|--------|-----------|-------------|-------|-----|-------|------|
| LR44A1  | 26.533 | 3.357 | 0.005 | 0.347 | 236 | 25 | 55 | 455 | 23 |
| LR44A2  | 26.411 | 3.372 | 0.01 | 0.402 | 203 | 21 | 47 | 432 | 22 |
| LR44A3  | 26.666 | 3.340 | 0.005 | 0.441 | 185 | 19 | 49 | 437 | 22 |
| LR44A4  | 26.446 | 3.368 | 0.01 | 0.366 | 223 | 23 | 51 | 443 | 22 |
| LR44B1  | 26.556 | 3.354 | 0.005 | 0.330 | 247 | 26 | 57 | 462 | 23 |
| LR44B2  | 26.494 | 3.362 | 0.01 | 0.392 | 208 | 22 | 49 | 439 | 22 |
| LR44B3  | 26.578 | 3.351 | 0.005 | 0.467 | 175 | 18 | 46 | 427 | 21 |
| LR44B4  | 26.413 | 3.374 | 0.01 | 0.297 | 275 | 29 | 58 | 466 | 23 |

sd: standard deviation.
The area ratio is calculated as described by Beyssac et al. (2002) using the first-order peaks at ~1,350 cm⁻¹ (D1 band), ~1,580 cm⁻¹ (G band), and ~1,610 cm⁻¹ (D2 band), by the Equation 4:

\[ R_2 = \frac{D1}{G + D1 + D2} \]  

The results, showed in Figure 11, revealed that both samples present graphite. In Figure 11A both samples are plotted in upper amphibolite facies, while in Figure 11B they are classified as granulite. The reason why this divergence occurs is explored in the discussion section.

**DISCUSSION**

To characterize the graphite schist from Formiga, we correlate X-ray diffraction and Raman spectroscopy from samples LR44A and LR44B. The Table 3 compares metamorphic temperatures acquired from both methods that yielded temperatures around 460°C. According to Lünsdorf (2015), Raman analyses are reliable for temperatures between 330 and 600°C, so Raman data presented here are reliable. This temperature disagrees with the high metamorphic degree expected for the area (Chaves et al. 2015). However, it agrees with the results found by Miranda et al. (2019) for hydrothermal recrystallized graphite.

![Diffractograms of samples 44A and 44B showing graphite patterns. All peaks are from graphite.](image)

![Interplanar spacing (d(002)) versus crystallite size (Lc(002))](image)

![Graphitization degree versus X-ray diffraction data temperature](image)
Table 2. Raman spectroscopy data with values obtained by the IFORS method (Lünsdorf and Lünsdorf 2016) from graphite schist samples LR44A and LR44B. G HWHM represents the width at half maximum of the G-band in cm⁻¹, R2 is the area ratio and T is the metamorphic temperature in °C.

| Sample   | G HWHM | Center   | R2         | T °C | sd ± |
|----------|--------|----------|------------|------|------|
| LR44Aa1p1 | 7.94   | 1,581.58 | 0.00       | 0.00 | 521  |
| LR44Aa1p2 | 7.87   | 1,581.58 | 0.00       | 0.067| 496  |
| LR44Aa1p3 | 7.78   | 1,581.58 | 0.00       | 0.070| 410  |
| LR44Aa1p4 | 8.33   | 1,581.58 | 0.00       | 0.120| 492  |
| LR44Aa1p5 | 8.91   | 1,581.58 | 0.00       | 0.066| 465  |
| LR44Aa2p3 | 8.06   | 1,581.58 | 0.00       | 0.000| 488  |
| LR44Aa3p1 | 7.90   | 1,581.58 | 0.00       | 0.047| 499  |
| LR44Aa3p2 | 8.08   | 1,584.06 | 0.00       | 0.140| 497  |
| LR44Aa3p3 | 7.67   | 1,581.58 | 0.00       | 0.000| 494  |
| LR44Aa4p1 | 7.71   | 1,581.58 | 0.00       | 0.000| 476  |
| LR44Aa4p3 | 7.78   | 1,579.09 | 0.00       | 0.127| 479  |
| LR44Aa5p1 | 7.79   | 1,581.58 | 0.00       | 0.119| 501  |
| LR44Aa5p2 | 7.85   | 1,581.58 | 0.00       | 0.057| 499  |
| LR44Aa5p3 | 8.00   | 1,574.12 | 0.00       | 0.118| 487  |
| LR44Ba1p1 | 8.89   | 1,581.58 | 0.00       | 0.000| 502  |
| LR44Ba1p2 | 8.90   | 1,583.28 | 0.00       | 0.216| 492  |
| LR44Ba1p3 | 8.78   | 1,580.79 | 0.00       | 0.050| 498  |
| LR44Ba1p4 | 9.58   | 1,582.45 | 1.44       | 0.044| 491  |
| LR44Ba2p1 | 8.12   | 1,580.79 | 0.00       | 0.056| 502  |
| LR44Ba2p2 | 8.17   | 1,575.81 | 0.00       | 0.060| 493  |
| LR44Ba2p3 | 8.46   | 1,583.28 | 0.00       | 0.035| 505  |
| LR44Ba2p4 | 8.94   | 1,578.30 | 0.00       | 0.081| 481  |
| LR44Ba3p3 | 8.01   | 1,580.79 | 0.00       | 0.000| 500  |
| LR44Ba4p1 | 9.09   | 1,583.28 | 0.00       | 0.144| 496  |
| LR44Ba4p2 | 9.82   | 1,583.28 | 0.00       | 0.063| 492  |
| LR44Ba4p3 | 8.51   | 1,588.78 | 0.00       | 0.088| 499  |
| LR44Ba5p1 | 8.36   | 1,588.78 | 0.00       | 0.039| 491  |
| LR44Ba5p2 | 9.32   | 1,588.78 | 0.00       | 0.052| 491  |

sd: standard deviation.

Figure 8. Photomicrographs of graphite powder (extracted from sample LR44A) taken in plane polarized light. (A) Selected fields for analyses represented with squares; (B) a random powder chosen for Raman analyses, in which each cross represents a spot of analyse.
The XRD data (Tab. 1) was plotted in graphs to analyze the GD accordantly to its crystallinity. Figure 7A correlates interplanar spacing (d_{(002)} A) and crystallite size (L_{c(002)} A), and, as suggested by Tagiri and Oba (1986), shows that both samples are classified as graphite between the fields of disordered graphite and fully ordered graphite. This corresponds to the temperatures which were found in this work, as graphite becomes fully ordered around 600°C (Beyssac et al. 2002, Lünsdorf 2015). The GD and XRD data temperature (T) are plotted using the equation for graphitization in pelitic rocks (Wada et al. 1994), and data from samples LR44A and LR44B behave similarly, leading to the conclusion that they both have been metamorphized under the same conditions.

The data acquired by Raman spectroscopy (Tab. 2) gave quite controversial results when plotted in graphs that classify the metamorphic facies as proposed by Rantitsch et al. (2016). Figure 11A correlates the interplanar spacing d_{(002)} and half width at half maximum of the G-band (G HWHM) and classifies the sample LR44B as related to the amphibolite facies while the sample LR44A to the upper amphibolite facies. Figure 11B shows the correlation between d_{(002)} and area ratio (R2 from Beyssac et al. 2002) in which both samples are classified as related to the granulite facies. This result was expected assuming the metamorphism considered for the area (Chaves et al. 2015), but it disagrees with the temperatures found by both methods. Also, the samples are classified

Figure 9. Raman spectra of analyses made on sample 44A presenting graphite pattern. Some samples show some interference due to the contamination of phengite.
Figure 10. Raman spectra of analyses made on sample 44B presenting graphite pattern. Some samples show some interference due to the contamination of phengite.

Figure 11. (A) d(002) versus half width at half maximum of the G-band (G HWHM) (Beyssac et al. 2002, Kwiecińska and Petersen 2004, Rantitsch et al. 2016). Sample LR44A is classified as upper amphibolite facies and LR44B as amphibolite facies; (B) d(002) versus area ratio (R2) (Kwiecińska and Petersen 2004, Rantitsch et al. 2016). Both samples are classified as granulite facies.
as graphite (Kwiecińska and Petersen 2004) in both graphs presented in Figure 11.

An explanation for why the temperatures found by the XRD and Raman methods (Tab. 1), for both graphite schist samples, disagrees with the syn-collisional metamorphism (Chaves et al. 2015), and the classifications based on crystallinity (Rantitsch et al. 2016), revealed in Figure 11, could be associated with a post-collisional stage. In this phase, the reactivation of old faults creates open space for fluid percolation (Carvalho et al. 2017, Miranda et al. 2019). It is possible to observe quartz veins apparently related with this event (Fig. 3D). According to Miranda et al. (2019), hydrothermal process can decrease the crystallite size, placing the samples into high-grade metamorphic fields, even when they were metamorphized in much lower temperatures, that is, around 460°C. In their analyses, samples from hydrothermal recrystallized graphites had results similar to those presented here. They are classified as amphibolite facies in the correlation of Figure 8A and granulite facies in the correlation of Figure 11B, exactly as it happens to the samples analysed here.

The graphite schist from the Itapecerica region, which is adjacent to the present area of study, has biogenic origin (Miranda et al. 2019). As in Formiga area, todorokite (Mn-oxide mineral typical of deep-sea Mn nodules formed by microorganisms, as suggested by Lowenstam 1981) is also present. Given the geological and mineralogical similarities between the two areas, it is possible to assume that the graphite schist from Formiga also has biogenic origin. This carbonaceous material would have been deposited in an oceanic basin between the Campo Belo and Divinópolis complexes in the pre-collisional stage. During the Rhyacian-Orosirian orogeny, graphite schist would be metamorphosed under granulite facies conditions and faults were formed. In post-collisional stage, the faults would have been reactivated turning into pathways to fluids which changed the graphite structure, decreased its crystallite size and changed the temperature signature to around 460°C.

**CONCLUSION**

The graphite schist from Formiga presented temperature around 460°C by the XRD and Raman analyses. The hydrothermalism associated with a post-collisional event explains the decrease in the crystallite size of the graphite mineral and its low temperature, while temperature typical of granulite facies was expected. The occurrence of todorokite in quartz veins and the presence of graphite with δ13C between -21.23 and -27.89‰ in the adjacent area (Miranda et al. 2019) suggest a biogenic origin for the carbonaceous material that resulted in the graphite schist from Formiga.

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L.R. and A.C. made the field work together. L.R. made the petrographic analyses, thermometric treatment of Raman and diffraction data, edited the Figures and Tables and wrote the manuscript. A.C. provided the X-ray diffraction data and improved and completed the manuscript. S.R. provided the Raman data.

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**REFERENCES**

Alkmim F.F., Martins-Neto M.A. 2001. A Bacia Intracratônica do São Francisco: Arcabouço estrutural e cenários evolutivos. In: Martins-Neto M.A., Pinto C.P. (Eds.), Bacia de São Francisco. Belo Horizonte: SBG-MG, p. 9-30.

Alkmim F.F., Teixeira W. 2017. The Paleoproterozoic Mineiro Belt and the Quadrilátero Ferrífero. In: Heilbron M., Alkmim F., Cordani U.G. (Eds.), The São Francisco Craton and its margins, Eastern Brazil. Regional Geology Reviews. Switzerland: Springer, p. 71-94.

Almeida F.F.M. 1977. O Cratón do São Francisco. Revista Brasileira de Geociências, 7(4):349-364.

Ávila C.A., Teixeira W., Bongiolo E.M., Dussin I.A., Vieira T.A.T. 2014. Rhyacian evolution of subvolcanic and metasedimentary rocks of the southern segment of the Mineiro belt, São Francisco Craton, Brazil. Precambrian Research, 243:221-251. https://doi.org/10.1016/j.precamres.2013.12.028
