

UNIVERSIDADE FEDERAL DE MINAS GERAIS
Instituto de Geociências
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**METAMORPHISM AND GRAPHITIZATION IN CLÁUDIO SUTURE ZONE
(MINAS GERAIS): IMPLICATIONS FOR THE PALEOPROTEROZOIC
COLLISION OF CRUSTAL BLOCKS IN SOUTHERN SÃO FRANCISCO CRATON**

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Versão Final

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Metamorfismo e grafitização na Zona de Sutura de Cláudio (Minas Gerais): implicações sobre a colisão paleoproterozóica de blocos crustais no sul do Cráton do São Francisco

RAPHAEL MARTINS COELHO

Tese submetida à Banca Examinadora designada pelo Colegiado, como requisito para obtenção do grau de Doutor em GEOLOGIA, área de concentração GEOLOGIA REGIONAL, pelo Programa de Pós-graduação em Geologia do Instituto de Geociências da Universidade Federal de Minas Gerais.

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RESUMO

A porção sul do Cráton do São Francisco (CSF) abriga algumas das maiores minas de grafita do Brasil, localizadas na cidade de Itapecerica. Nas proximidades, foram encontradas ocorrências de grafita dentro da estrutura de escala regional conhecida como zona de cisalhamento de Cláudio (ZCC), possivelmente com relação geológica às das minas de Itapecerica. A ZCC corresponde a uma sutura geológica dextral NE-SW que separa os complexos metamórficos arqueanos Campo Belo/Bonfim e Divinópolis. Dentre outras rochas, a ZCC guarda sillimanita-cordierita-granada-biotita gnaisses (também conhecidos como paragneisses khondalíticos) associados a rochas metassedimentares ricas em grafita. As condições de temperatura (T) e pressão (P) do pico metamórfico dos khondalitos são 850-950 °C e 10-11 kbar, registradas pela reação de quebra da biotita, $Bt + Sil + Qz \pm Pl \rightarrow Grt + Kfs + Melt$. As condições de T e P do estágio pós-pico são 750–830 °C e 4,5–5,3 kbar, registradas pela reação de consumo de melt, $Grt + Sil + Melt \rightarrow Crd + Bt + \text{óxido de Fe}$. A geocronologia U-Th-Pb em monazita revela uma idade média de 2011 ± 20 Ma para o pico metamórfico e uma idade média de 1910 ± 20 Ma para o estágio pós-pico. O conjunto de dados obtido neste trabalho é muito semelhante em termos de evolução P e T ao Complexo Wulashan do Cráton do Norte da China (CNC). As rochas khondalíticas da ZCC e do Complexo de Wulashan foram submetidas a um metamorfismo de fácies granulito e percorreram trajetória P-T-t de sentido horário acompanhada de fusão parcial quando o CSF e CNC estiveram, provavelmente, conectados durante o Paleoproterozoico. Os dados de espectroscopia Raman e difração de raios X (DRX) mostraram que, em média, os cristais de grafita da zona de cisalhamento de Cláudio possuem alta cristalinidade e são semelhantes aos das minas de Itapecerica. A temperatura média encontrada pelo método de DRX (702 °C) neste estudo está próxima às amostras de alto grau de metamorfismo nas minas de Itapecerica previamente estudadas. No entanto, esta temperatura ainda está abaixo dos ~900 °C registrados pelos khondalitos locais. A hipótese para isso seria que a grafita desenvolveu alta cristalinidade, mas foi modificada durante a evolução do metamorfismo, ou durante a fase pós-colisional de percolação do fluido. Assim, os parâmetros de cristalinidade modificados levaram 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 Arqueanos e Paleoproterozóicos que formaram o supercontinente Columbia e localmente marcam a colisão paleoproterozoica dos complexos metamórficos arqueanos Campo Belo/Bonfim e Divinópolis.

Palavras-chave: Zona de cisalhamento de Cláudio; grafita; Khondalitos; metamorfismo de alto grau; pseudoseções; geocronologia U-Th-Pb; Crátons do São Francisco e do Norte da China.

ABSTRACT

The southern São Francisco Craton (SFC) hosts some of the largest graphite mines in Brazil located in the city of Itapeçerica. 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 Itapeçerica mines. The CSZ corresponds to a dextral NE-SW geological suture that separates the Archean Campo Belo/Bonfim and Divinópolis metamorphic complexes. Among other rocks, the CSZ keeps sillimanite-cordierite-garnet-biotite gneisses (also known as khondalitic paragneisses) associated with graphite-rich metasedimentary rocks. The temperature (T) and pressure (P) conditions of the khondalite metamorphic peak are 850–950 °C and 10–11 kbar, recorded by the reaction of biotite breakdown $\text{Bt} + \text{Sil} + \text{Qz} \pm \text{Pl} \rightarrow \text{Grt} + \text{Kfs} + \text{Melt}$. The post-peak stage T and P conditions are 750–830 °C and 4.5–5.3 kbar, recognized by the melt consumption reaction $\text{Grt} + \text{Sil} + \text{Melt} \rightarrow \text{Crd} + \text{Bt} + \text{Fe-oxide}$. Monazite U-Th-Pb geochronology reveals an average age of 2011 ± 20 Ma for the metamorphic peak and an average age of 1910 ± 20 Ma for the post-peak stage. The dataset obtained in this work is very similar in terms of P and T evolution to the Wulashan Complex from the North China Craton (NCC). The khondalitic rocks of both CSZ and Wulashan Complex were subjected to a clockwise P-T-t path granulite facies metamorphism accompanied by partial melting events when SFC and NCC were probably connected during Paleoproterozoic. The Raman spectroscopy and X-ray diffraction (XRD) data showed that, on average, the graphite crystals of the CSZ have high crystallinity and are similar to those from Itapeçerica mines. The average temperature found by XRD (702 °C) in this study is close to the high-grade metamorphism samples in Itapeçerica mines previously studied. The graphitization processes undergone by the carbonaceous material (CM) proceeded with collisional stress until the fully ordered graphite stage, and the shearing stress in CSZ, associated 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-T values found by 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 T conditions around 900 °C previously described. 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 Itapeçerica. The source of the CM for the CSZ graphite occurrences possibly is primitive biogenic carbon as indicated by previous study. The materialization of the ZCC during the Paleoproterozoic is a result of the collision between Archean Campo Belo/Bonfim and Divinópolis blocks. This collision is one of the many that promoted the formation of the Columbia supercontinent.

Keywords: Cláudio Shear zone; Graphite; Khondalites; High grade metamorphism; pseudosections; U-Th-Pb geochronology; São Francisco and North China cratons.

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INTRODUCTION

Suture zones are the record of the sites of obliteration of oceanic lithosphere by subduction and consequent welding of continental masses (Dewey, 1977). Throughout this process, the precursor basins undergo granulite-facies metamorphism and can be preserved as high-grade metapelitic rocks, usually containing sillimanite and garnet, known as khondalites (Dash, 1989).

The term khondalite was originally coined based on the distribution of this rock at the boundaries of the ancient “Khondistan” province or the country of the Khonds in central India. The petrologically descriptive term for this rock is garnet-sillimanite-graphite schist/gneiss. Walker (1902) proposed to call these rocks as khondalite, in honour of the Khonds, a hill tribe, in whose mountain jungles the rock is widely exposed. Although not formally recognized in the global nomenclature, the term khondalite has since then been widely used by geologist and petrologists for granulite facies aluminous metasedimentary rocks with sillimanite as an index mineral and with or without graphite.

Metapelitic rocks that have undergone low to high grade metamorphism occur in various orogenic belts of different ages. However, the term ‘khondalite belt’ is popular in literature only in a few cases, such as the Paleoproterozoic khondalite belt within the Inner Mongolia Suture Zone separating the Yinshan and Ordos Blocks in the North China Craton (Condie et al., 1992; Zhao et al., 2005; Santosh, 2010) and the Late Neoproterozoic-Cambrian khondalite belt in southern Kerala, India (Chacko et al., 1987; Santosh et al., 2003; Santosh, 2020). Khondalites have also been reported from several other terranes including East Antarctica (Santosh and Yoshida, 1992), Sri Lanka (Dharmapriya et al., 2014), Eastern Ghats Belt in India (Dash et al., 1987), also Korean Peninsula (Santosh et al., 2018), and southern São Francisco craton (Coelho and Chaves, 2019; Miranda et al., 2021).

Such high grade metamorphic rocks occurring within collisional orogenic belts are potential targets for constraining how pressure (P) and temperature (T) conditions vary with time (t) in crustal blocks that were welded each other, and to elucidate the metamorphic events associated with their assembly (Kröner et al., 2014; Spencer et al., 2017; Santosh et al., 2015; Hernández-Uribe et al., 2020). Notable improvements to geochronological protocols and techniques in recent years have enabled a better understanding of the rates of deposition of sedimentary successions and the duration and ages of prograde, peak, and retrograde metamorphic events (Cocherie and Robert, 2008; Chew et al., 2014; Huang et al., 2019).

The mineral commonly used for geochronological investigation in metamorphic rocks is monazite (Spear and Pyle, 2002; Palin et al., 2015; Treloar et al., 2019; Tang et al., 2017). It exhibit variable external morphology and internal textural zonation that reflect discrete tectono-thermal events, as well as chemical alteration (Bowring and Williams, 1999; Amelin et al., 1999, 2000; Mojzsis et al., 2003; Wilde et al., 2001).

Graphite is the stable form of elemental carbon in the crustal conditions of temperature and pressure. Commonly graphite comes from organic matter (derived from the biological activity) that had been 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 (figure 1). That process is known as graphitization (Buseck and Beyssac, 2014).

The advance in technological uses for carbon such as graphene, fullerene, carbon nanotubes, and anode to lithium ion batteries for electric cars has resulted in a demand increase for natural high crystalline graphite.

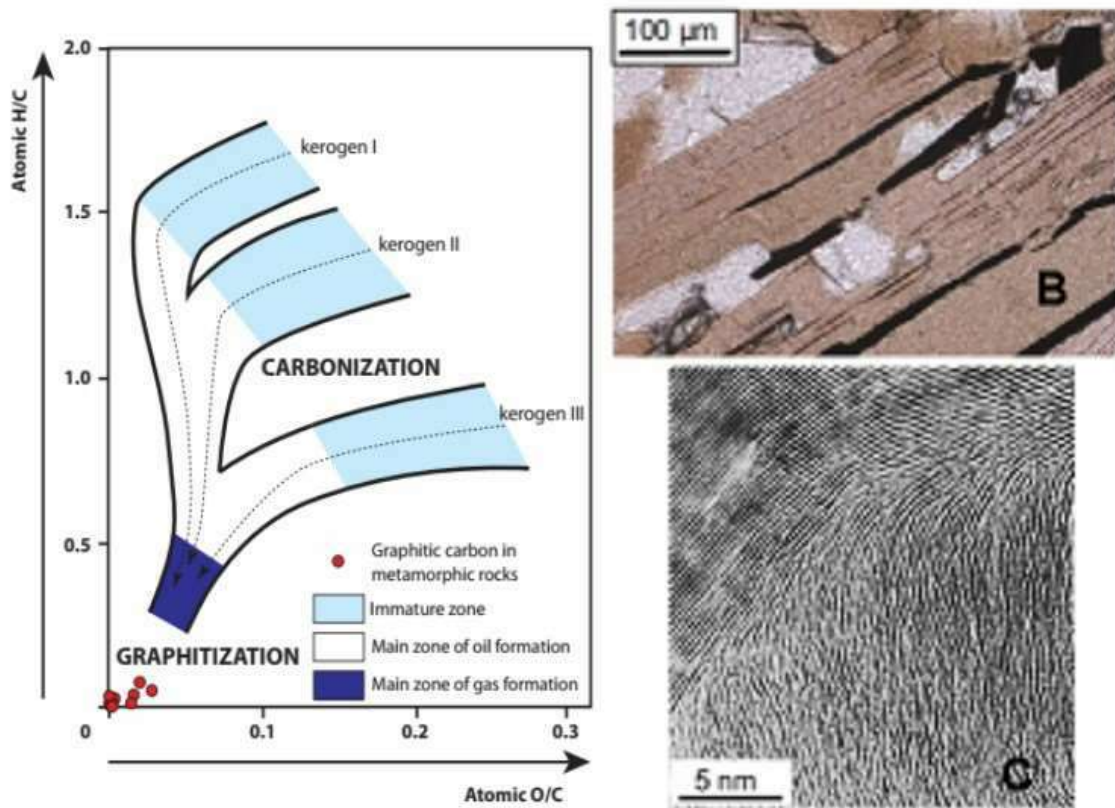


Figure 1: A - Van Krevelen diagram showing the chemical path of the three classes of kerogen during the carbonization process and the compositional data of graphitic carbon from metamorphic rocks. The organic matter of type I, II, and III kerogens is derived, respectively, from lake algae, marine microorganisms, and terrestrial plants. Kerogen III corresponds to coal. B - Biotite shale containing graphite lamellae, in black, seen under uncrossed polarizers under a petrographic microscope. C - Graphite image in the transmission electron microscope (Buseck & Beyssac, 2014).

The São Francisco Craton (SFC) is in the central part of a South American continental paleoplate consolidated at the end of the Paleoproterozoic (Almeida et al., 1981). It is subdivided into several Archean to Paleoproterozoic blocks bounded by major ca. 2.0 Ga suture zones (Teixeira et al., 1991; Barbosa et al., 2004; Oliveira et al., 2010). The southern sector of the SFC, delimited by Neoproterozoic orogenic belts, such as the Araçuaí Belt (Pedrosa-Soares et al., 2001) to the east and the Brasília Belt (Pimentel et al., 2011) to the west (Figure 2A), hosts some of the largest graphite mines in Brazil.

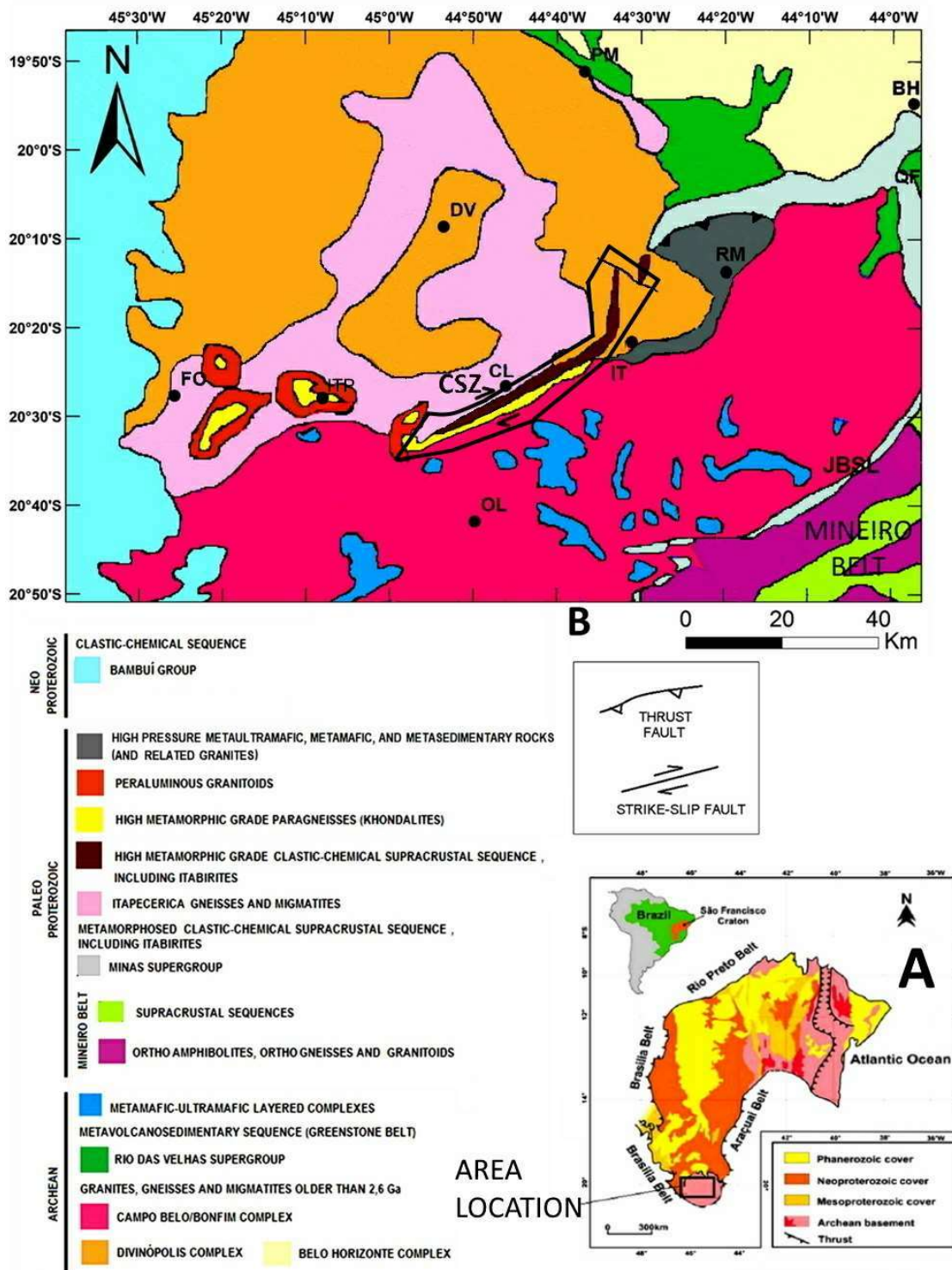


Figure 2: A - The São Francisco Craton. B - Simplified geological map of the Southern São Francisco craton. QF – Quadrilátero Ferrífero, JBSL – Jeceaba-Bom Sucesso lineament, CSZ – Cláudio shear zone. Cities: BH – Belo Horizonte, PM – Pará de Minas, ITP – Itapeçerica DV – Divinópolis, RM – Rio Manso, IT – Itaguara, FO – Formiga, CL – Cláudio, OL – Oliveira. (modified from Chaves et al.,2019). The black polygon shows the studied area.

Separating the Archean Campo Belo/Bonfim and Divinópolis metamorphic complexes in southern SFC, there is a prominent NE-SW-trending structure called Cláudio Shear Zone (CSZ), a geological suture (Figures 2B), as evidenced by the high deformation strain with dextral strike-slip motion (Oliveira, 2004; Teixeira et al., 2017). Metamorphosed ultramafic rocks (metaperidotite, talc-serpentine-chlorite-amphibole schist), amphibolite, garnet-sillimanite schist and 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., 2017).

After Teixeira (2017), the tectonic framework of the SFC has many similarities with that of the North China Craton, where the Paleoproterozoic accretionary orogenies also involved processes of amalgamation/collision of the Archean blocks. Statherian and Tonian mafic dykes can be found in both cratons, suggesting a connection between them during Proterozoic.

The purpose of this study is to examine the metamorphic evolution of khondalitic rocks and respective anatectic melts from the CSZ, located in the southern São Francisco craton, and determine, by X-ray diffraction (XRD) and Raman spectroscopy, the thermometry of the graphite occurrences close to the city of Cláudio that occur within the CSZ. This study is presented as two articles:

Article I presents the integration of petrological features, quantitative phase equilibria modelling (P–T pseudosections), monazite U–Th–Pb geochronology, the P–T–t path of khondalitic rocks and respective anatectic melts, and associated tectonic processes that occurred during a time when SFC was probably connected to North China craton.

Article II presents the thermometry data obtained by XRD and Raman spectroscopy in graphite sampled within the CSZ and compares the obtained results with the graphite data of Miranda et al. (2019) for the Itapeçerica mines close to the CSZ.

ARTICLE I - Pressure-temperature-time path of Paleoproterozoic khondalites from Cláudio shear zone (southern São Francisco craton, Brazil): Links with khondalite belt of the North China craton

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Abstract

The dextral Cláudio shear zone (CSZ) corresponds to a NE-SW geological suture that separates the Archean Campo Belo/Bonfim and Divinópolis metamorphic complexes in southern São Francisco craton (SFC). The CSZ comprises sillimanite-cordierite-garnet-biotite gneisses (also known as khondalitic paragneisses) associated with graphite-rich metasedimentary rocks. The temperature and pressure conditions of khondalite metamorphic peak are 850–950 °C and 10–11 kbar, recorded by the reaction of biotite breakdown $Bt + Sil + Qz \pm Pl \rightarrow Grt + Kfs + Melt$. The post-peak stage temperature and pressure conditions are 750–830 °C and 4.5–5.3 kbar, recognized by the melt consumption reaction $Grt + Sil + Melt \rightarrow Crd + Bt + Fe\text{-oxide}$. Monazite U-Th-Pb geochronology reveals an average age of 2011 ± 20 Ma for the metamorphic peak and an average age of 1910 ± 20 Ma for the post-peak stage. The dataset obtained in this work is very similar in terms of P and T evolution to the Wulashan Complex from North China Craton (NCC). The khondalitic rocks of both CSZ and Wulashan Complex were subjected to a clockwise P-T-t path granulite facies metamorphism accompanied by partial melting events when SFC and NCC were probably connected during Paleoproterozoic.

Keywords

Khondalite; High grade metamorphism; pseudosections; U-Th-Pb geochronology; São Francisco and North China cratons.

Introduction

Khondalites are high grade metapelitic rocks usually containing sillimanite and garnet (Dash, 1989). From a geodynamic perspective, khondalite belts represent precursor basins that underwent granulite-facies metamorphism due to subduction-collision phenomena, which culminated with the amalgamation of continental fragments. Some of the best examples occur in the North China Craton (NCC), such as ultrahigh temperature (UHT) mafic granulites and associated khondalites, which can also host important 1.95 Ga graphite mineralization (Teixeira et al., 2017).

Clockwise pressure-temperature-time (P-T-t) paths involving decompression following metamorphic peak of granulite facies khondalitic rocks have been established in some cratons (e.g. North China, Xia et al., 2006; Cai et al., 2016) based on their mineral assemblages, textures, structures, and P-T pseudosections, and have been used to provide constraints for the overall geotectonic evolution of the respective regions.

This study examined the metamorphic evolution of khondalitic rocks and respective anatectic melts from the Cláudio shear zone (CSZ), located in the southern São Francisco craton (SFC - Brazil), by integrating petrological features with quantitative phase equilibria modeling (P-T pseudosections) and monazite U-Th-Pb geochronology to comprehensively decipher their P-T-t path and associated tectonic processes that occurred during a time when SFC was connected to North China craton.

Geological Setting

The São Francisco Craton (SFC) is in the central part of a South American continental paleoplate consolidated at the end of the Paleoproterozoic (Almeida et al., 1981). It is subdivided into several Archean to Paleoproterozoic blocks bounded by major ca. 2.0 Ga suture zones (Teixeira et al., 1991; Barbosa et al., 2004; Oliveira et al., 2010). The southern part of the SFC is delimited by Neoproterozoic orogenic belts, such as the Araçuai Belt (Pedrosa-Soares et al., 2001) to the east and the Brasília Belt (Pimentel et al., 2011) to the west (Figure 1A).

The 3.2-2.6 Ga Archean core of the southern SFC is composed mainly of granite-gneisses terranes (Teixeira et al., 1996) and greenstone belts (Figures 1B, 1C), such as the Rio das Velhas Supergroup, which include associations of mafic to ultramafic rocks, intermediate to

felsic volcanic with volcanoclastic rocks and clastic sediments (Dorr, 1969; Baltazar and Zucchetti, 2007). The Minas Supergroup is younger and comprises clastic and chemical metasedimentary units, including the banded iron formations of the Quadrilátero Ferrífero mining district (Figure 1B), with a minimum deposition age of ~ 2.0 Ga (Machado et al., 1996). The Minas Supergroup extends to the SW of the Quadrilátero Ferrífero, as portrayed by the correlative strata along the Jeceaba-Bom Sucesso lineament (Neri et al., 2013).

The Rhyacian-Orosirian cycle, previously named “Transamazonian” (2.2-1.9 Ga), is recognized in several parts of the SFC and represents a significant period of crustal growth in the South American continent (Teixeira et al., 1996). In the southern SFC, this event, recently renamed as Minas accretionary orogeny by Teixeira et al. (2015), is related to the accretion of juvenile crust that formed the Mineiro Belt (Noce et al., 1998; Ávila et al., 2014) and was responsible for extensive reworking of terranes located at the margins of the craton (Noce et al., 2007).

A prominent NE-SW-trending structure called Cláudio Shear Zone (CSZ) is a geological suture that separates the Archean Campo Belo/Bonfim and Divinópolis metamorphic complexes in southern SFC (Figures 1B, 1C), as evidenced by the high deformation strain with dextral strike-slip motion (Oliveira, 2004; Teixeira et al., 2017). Metamorphosed ultramafic rocks (metaperidotite, talc-serpentine-chlorite-amphibole schist), amphibolite, garnet-sillimanite schist and 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 milonitic 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., 2017). According to Oliveira (2004), crustal reworking along the CSZ produced partial melting, generating the Kinawa migmatite, in which zircon with U-Pb age of 2048 ± 25 and 2034 ± 32 Ma (Carvalho et al., 2017) has been formed. These ages define a high-grade zircon-producing 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). Mafic dyke swarms of several ages (Figure 1B) are also recognized in the southern SFC (Chaves, 2013).

After Teixeira (2017), the tectonic framework of the SFC has many similarities with that of the North China Craton, where the Paleoproterozoic accretionary orogenies also involved processes of amalgamation/collision of the Archean blocks. Statherian and Tonian mafic dykes can be found in both cratons, suggesting a connection between them during Proterozoic.

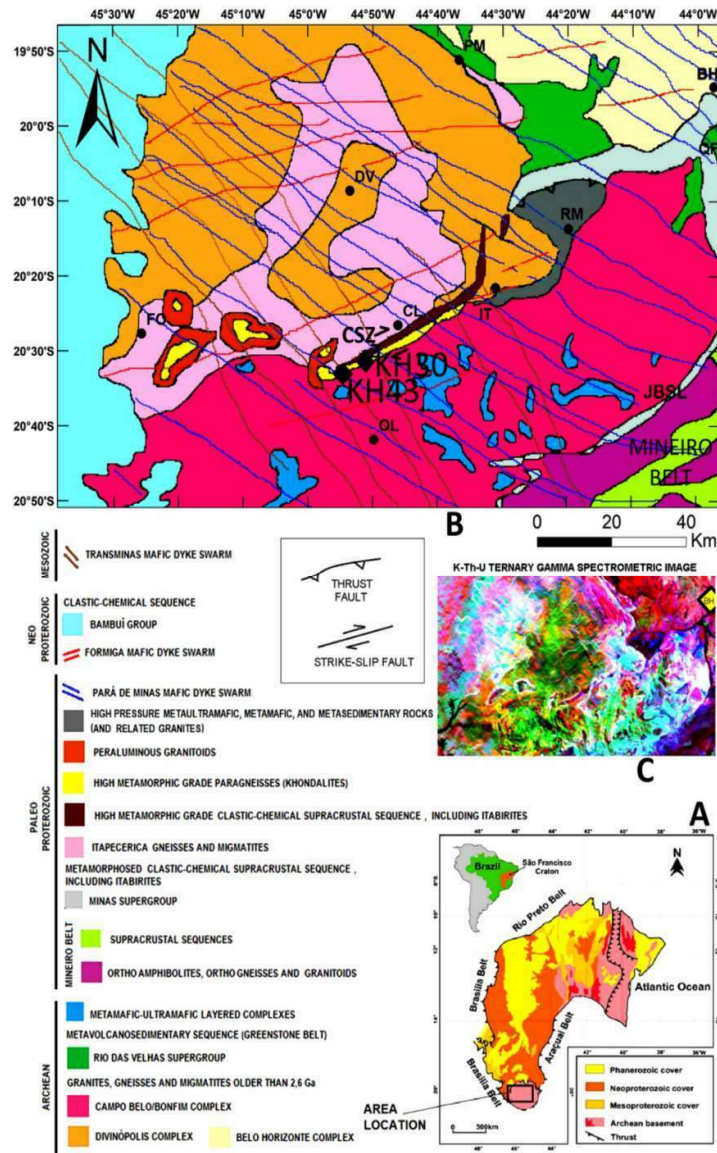


Figure 1: Studied area with sampling points as lozenges, A - The São Francisco Craton. B - Geological map of the southern São Francisco craton. QF – Quadrilátero Ferrífero, JBSL – Jeceaba-Bom Sucesso lineament, CSZ – Cláudio shear zone. Cities: BH – Belo Horizonte, PM – Pará de Minas, DV – Divinópolis, RM – Rio Manso, IT – Itaguara, FO – Formiga, CL – Cláudio, OL – Oliveira. C - K-Th-U ternary gamma spectrometric image of the Southern São Francisco craton (CPRM-CODEMIG, 2014).

Materials and methods

After field work and sample collecting in the Cláudio region two representative samples of khondalite rocks were chosen (Figure 1B), the KH30 sample with incipient partial melting features (Figure 2A) and the KH43 sample corresponding to a paleosome (Figure 2B and 2C). Polished thin sections were fashioned to petrographic, microanalytical and geochronological investigations. The abbreviations for names of rock-forming minerals used in this paper are from Whitney and Evans (2010).

The Theriak-Domino software (deCapitani & Petrakakis, 2010) with tcds55 database was used to produce pseudosections using bulk rock compositions. The bulk rock compositions were obtained at SGS Geosol Laboratory. After tungsten grinding the material was melted with lithium metaborate and diluted nitric digestion. The major elements were analyzed by ICP-OES (Optical Emission Spectrometry with Inductively Coupled Plasma). Detection limits were generally around 0.01% for higher oxides. The accuracy is in the range of 1-2% from the relative standard deviation. The loss on ignition occurred by mass difference after heating at 1000 °C. To the software calculations all Fe was considered as FeO and the water content was determined by calculating the lower limit of the H₂O that a given assemblage contains at 5 kbar (White et. al., 2004).

After micropetrography done in an Olympus BX41-P microscope, the chosen minerals (garnet, biotite, plagioclase and cordierite) were analyzed with a JXA-8900 JEOL electron microprobe (EMP), at Microanalysis Laboratory of the Microscopy Center at Federal University of Minas Gerais (LMA-CM-UFMG), by using wavelength dispersive X-ray spectroscopy (WDS). Operating conditions were 15 kV accelerating voltage and 20 nA sample current. Oxide and silicate standards were used for calibration. Counting times were 10-20 s on the peak and 5-10 s on the background. Three spectrometers were used simultaneously. A ZAF correction procedure was applied. The electron beam was focused to the minimum size (2 micrometers). Mineral imaging has been done by using backscattered electron technique.

Regarding microanalysis for geochronological purposes, the compositions of different monazite grains were determined using the same JEOL EMP of the LMA-CM-UFMG.

Quantitative WDS analytical parameters used during monazite analyses are shown in Table 1. A ZAF correction procedure was applied.

Table 1: Microprobe quantitative WDS analytical parameters used during monazite analyses.

Accelerating voltage = 25Kv							
Current intensity = 50nA							
Electron beam diameter = 2 micrometers							
Counting time (seconds)				Background offset			
Element	X-ray	Crystal	Peak	Background	Bg L	Bg U	Analytical standard
Y	La	TAP	20	10	1.12	0.84	Y-Al garnet
Dy	Lb	LIF	20	10	0.84	0.00	DyPO ₄
P	Ka	PETJ	10	5	0.70	0.70	Monazite
Si	Ka	TAP	10	5	1.38	0.84	ThSiO ₄
Gd	Lb	LIF	20	10	0.84	0.98	GdPO ₄
Pb	Mb	PETJ	200	100	1.64	0.64	PbCrO ₄
Th	Ma	PETJ	20	10	1.95	0.84	ThSiO ₄
Sm	Lb	LIF	20	10	0.55	0.53	REE2
U	Mb	PETJ	150	75	0.00	2.00	UO ₂
Ca	Ka	PETJ	10	5	0.84	0.70	Ca ₂ P ₂ O ₇
Nd	Lb	LIF	20	10	0.84	0.84	NdPO ₄
La	La	PETJ	10	5	0.84	0.84	Monazite
Pr	Lb	LIF	20	10	0.84	0.66	PrPO ₄
Ce	La	LIF	10	5	0.84	1.12	Monazite

Overlaps of X-ray peaks between Y and Pb have not been corrected because there was no measurement in PbMa (Lead M alpha), but only in PbMb (Lead M beta). However, to avoid errors in the obtained ages, the interference of ThMz (Thorium M gamma) on the measured UMb (Uranium M beta) had to be corrected, following Scherrer et al., (2000) in adaptation to the conditions of the LMA-CM-UFGM, as follows (Chaves et al., 2013):

$$U \text{ corrected} = U \text{ measured} - (0.006365 \times \text{Th measured}).$$

Microprobe chemical U-Th-Pb ages and associated errors were obtained using EPMA Dating software (Pommier et al., 2004) and the average ages were taken through Isoplot/Ex software (Ludwig, 2003). The age equation used is:

$$\begin{aligned} \text{Pb} = & \{ \text{Th} \times [\exp(\lambda_{232}T)-1] \times (M_{208}/M_{232}) \} + \{ \text{Uc} \times [\exp(\lambda_{238}T)-1] \times (M_{206}/M_{238}) \times 0.9928 \} \\ & + \{ \text{Uc} \times [\exp(\lambda_{235}T)-1] \times (M_{207}/M_{235}) \times 0.0072 \} , \end{aligned}$$

Where $^{238}\text{U}/(^{235}\text{U}+^{238}\text{U}) = 0.9928$ and $^{235}\text{U}/(^{235}\text{U}+^{238}\text{U}) = 0.0072$. Uc (U corrected), Th and Pb are concentrations in ppm; T is the age in Ma; M_{206} , M_{207} , M_{208} , M_{235} , M_{238} , M_{232} are the atomic masses of ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{235}U , ^{238}U , ^{232}Th ; $\lambda_{232} = 0.49475 \times 10^{-4} \text{ Ma}^{-1}$; $\lambda_{238} = 1.55125 \times 10^{-4} \text{ Ma}^{-1}$; $\lambda_{235} = 9.8485 \times 10^{-4} \text{ Ma}^{-1}$ (Pommier et al., 2004).

Results

Petrography

Excepting for the anatectic content, the analyzed samples of Sill-Crd-Gr-Bt gneisses are very similar to each other (Figure 2). They are fine-grained rocks with garnet, cordierite, plagioclase quartz and sillimanite. Ilmenite, magnetite, monazite, and zircon are accessory minerals. Those rocks are strongly foliated, marked by biotite and sillimanite orientation (Figure 2B). Porphyroblasts of garnet exhibit poikiloblastic texture with quartz, plagioclase, and rare biotite and sillimanite inclusions (Figure 3A). The garnets show reaction like corroded rounded rims (Figure 3B) remarkably when is included in cordierite. Biotite shows at last two crystals types: the crystals included in garnet (Figure 3A) and the subhedral crystals in matrix (Figure 3A, 3B, 3C and 3D). The plagioclase crystals eventually show poikiloblastic texture with biotite and sillimanite as inclusions (Figure 3D). Cordierite poikiloblastic crystals are relatively large when compared to other minerals. They have plagioclase, quartz, biotite and fibrolitic sillimanite, and in some case, garnets as inclusions (Figure 3B). Some of cordierite crystals are pinitized (Figure 3C).

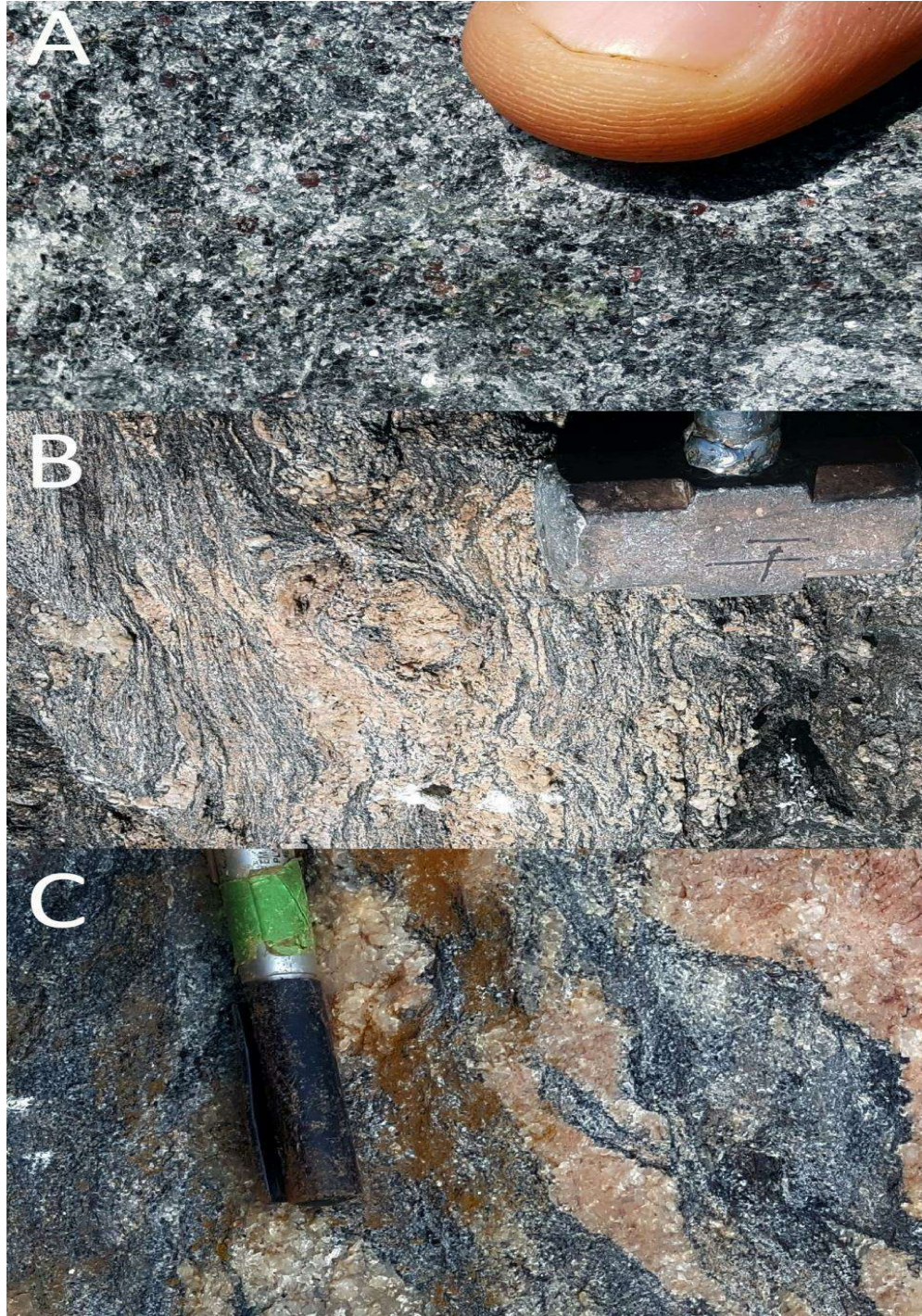


Figure 2: Khondalitic rocks from Cláudio shear zone, A-KH30 sample showing the main mineral content with no evidence of partial melting, B- KH43 foliated sample showing neosome and paleosome. C- Detail of paleosome and granitic neosome from KH43 sample.

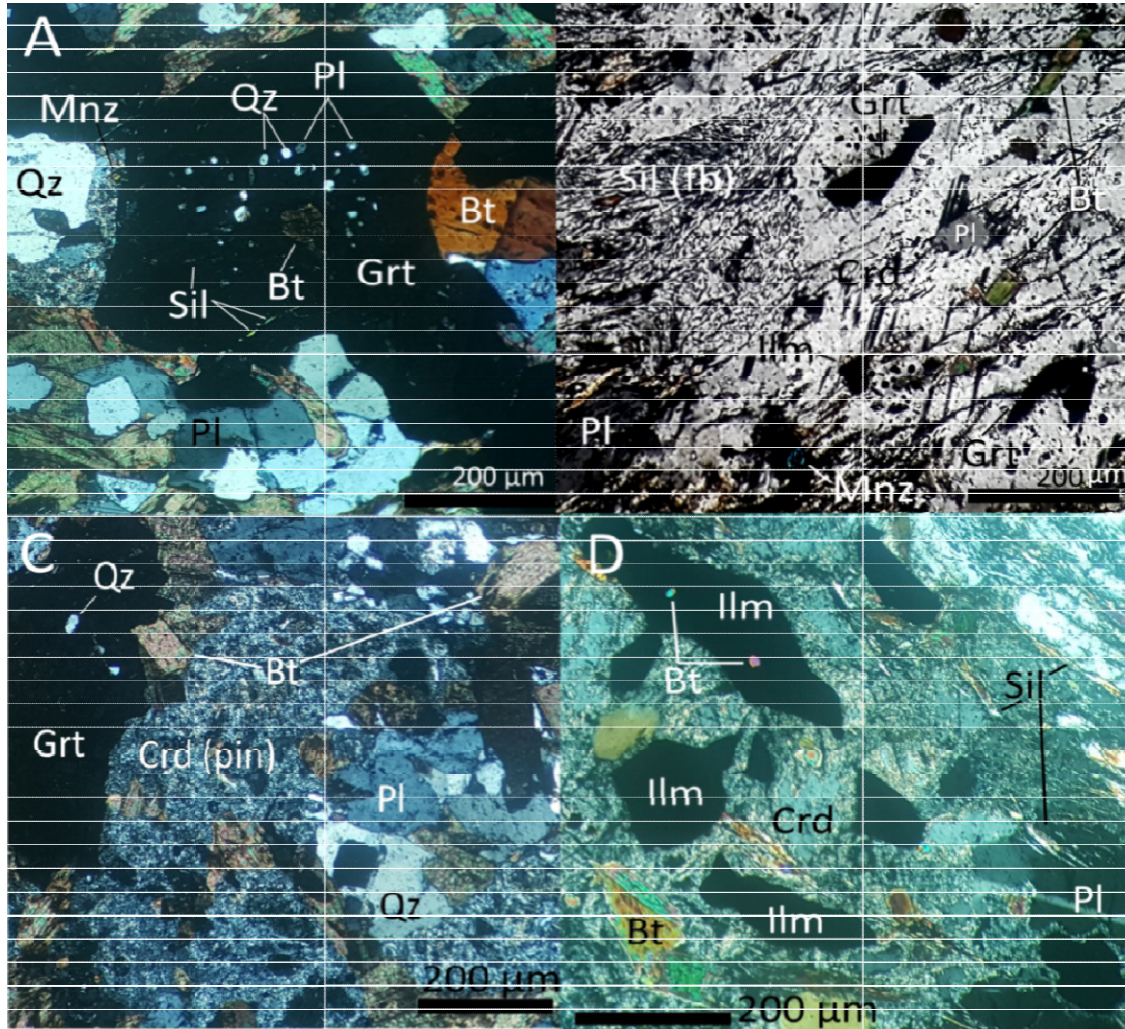
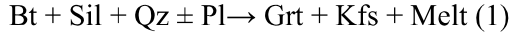


Figure 3: Representative photomicrographs under cross-polarized light, showing mineral assemblages and microstructures of the studied rocks. A - poikiloblastic garnet with biotite, quartz, plagioclase and sillimanite as inclusions B - Large cordierite crystal with garnet inclusion showing reaction like corrodé rim and fibrolitic sillimanite; C - Pinitized poikiloblastic cordierite with corrodé edges biotite crystals as inclusions and subedric biotite crystals; D - Ilmenite and sillimanite crystals in large cordierite crystal, the ilmenite have biotite inclusions.

Metamorphic reactions

The petrographic observation leads to infer a multistage metamorphism process with a peak stage and a post-peak stage. The garnet was formed in the peak stage and continued to grow by consuming sillimanite, biotite, and plagioclase due to the following biotite-melting dehydration reaction (Patiño Douce and Johnston, 1991):



The reaction 1 is coherent with the observed biotite inclusions in poikiloblastic garnet (Figure 3A). The post-peak stage is recorded by cordierite-producing at low pressure and melt-consuming reaction (Jiao et al., 2013a; Cai et al., 2014):



This reaction can explain the growing of large cordierite crystals, the corroded garnet crystals and the large ilmenite crystals as observed in figures 3B and 3D.

Mineral Chemistry

Garnet

Garnet porphyroblasts from samples KH30 and KH43 are essentially almandine (69-74 Mol%) with X_{Mg} [$\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$] values ranging from 0.20 to 0.25 (table 2).

Table 2: Representative electron microprobe analyses of garnet.

Sample Location	KH30 C	KH30 C	KH43 C	KH43 C
SiO ₂	37.78	37.19	37.45	37.49
TiO ₂	0.05	0.02	0.07	0.06
Al ₂ O ₃	22.05	22.03	22.32	22.32
Cr ₂ O ₃	0.03	0.05	0.02	0.02
FeO	30.75	32.83	31.35	31.45
MnO	1.28	1.44	1.39	1.43
MgO	6.15	4.90	5.96	5.93
CaO	0.98	0.91	1.01	0.87
Na ₂ O	0.00	0.02	0.03	0.03
Total	99.23	99.72	99.70	99.69
Si	2.98	2.96	2.95	2.95
Al	2.98	2.96	2.95	2.08
Ti	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00
Fe ³⁺	0.00	0.00	0.00	0.00
Fe ²⁺	2.08	2.23	2.11	2.12
Mn	0.09	0.10	0.09	0.10
Mg	0.72	0.58	0.70	0.70
Ni	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00
Ca	0.08	0.08	0.09	0.07
Total	8.00	8.02	8.02	8.02
X_{Mg}	0.25	0.20	0.25	0.25
$z(\text{gr})$	0.029	0.027	0.030	0.025
Alm	0.69	0.74	0.70	0.70
Grs	0.03	0.03	0.03	0.03
Prp	0.25	0.20	0.24	0.24
Sps	0.03	0.03	0.03	0.03

Note: Cations to 12 oxygen. C= core. $X_{\text{Mg}} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$. $z(\text{grt}) = \text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe}^{2+})$.

Biotite

Biotite from KH30 sample has X_{Mg} $[\text{Mg}/(\text{Mg}+\text{Fe}^{2+})]$ values ranging from 0.55 to 0.57 and is characterized by moderate TiO_2 (3.36-3.75 wt%) and low MnO (up to 0.06 wt%). Biotite from KH43 sample has higher X_{Mg} ranging from 0.67 to 0.71 and characterized by low TiO_2 (1.32-2.48 wt%) and high MnO (0.36 to 0.65 wt%) (table 3).

Table 3: Representative electron microprobe analyses of biotite.

Sample	KH30	KH30	KH30	KH30	KH43	KH43
Location	C	C	C	C	C	C
SiO_2	35.91	34.58	35.30	36.51	37.13	36.99
TiO_2	3.75	3.65	3.56	3.36	1.32	2.48
Al_2O_3	17.65	17.66	17.66	17.38	18.82	18.51
Cr_2O_3	0.14	0.17	0.14	0.15	0.07	0.02
FeO	15.82	16.51	15.73	16.62	11.40	12.22
MnO	0.00	0.05	0.06	0.03	0.36	0.65
MgO	11.83	11.83	11.54	11.57	15.69	14.11
CaO	0.01	0.03	0.01	0.05	0.03	0.04
Na_2O	0.13	0.15	0.31	0.27	0.25	0.30
K_2O	9.41	9.48	9.63	9.69	9.03	9.38
BaO	0.19	0.12	0.26	0.10	0.07	0.00
Total	94.83	94.23	94.19	95.71	94.17	94.71
Si	2.71	2.64	2.69	2.74	2.74	2.74
Al	1.57	1.59	1.59	1.54	1.64	1.62
Ti	0.21	0.21	0.20	0.19	0.07	0.14
Fe	1.00	1.06	1.00	1.04	0.70	0.76
Mn	0.00	0.00	0.00	0.00	0.02	0.04
Mg	1.33	1.35	1.31	1.29	1.73	1.56
Ca	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.02	0.02	0.05	0.04	0.04	0.04
K	0.90	0.92	0.94	0.93	0.85	0.89
Ba	0.01	0.00	0.01	0.00	0.00	0.00
Cr	0.01	0.01	0.01	0.01	0.00	0.00
Total	7.75	7.82	7.80	7.78	7.81	7.78
X_{Mg}	0.57	0.56	0.57	0.55	0.71	0.67

Note: Cations to 11 oxygen. X_{Mg} $[\text{Mg}/(\text{Mg}+\text{Fe}^{2+})]$ C= core

Cordierite

The analyzed cordierite in KH30 and KH43 samples are very similar each other with high X_{Mg} , from 0.81 to 0.84 (table 4).

Table 4: Representative electron microprobe analyses of cordierite.

Sample Location	KH30 M	KH30 M	KH43 M	KH43 Gr in	KH43 Gr in
SiO ₂	49.60	49.03	49.87	51.53	51.13
TiO ₂	0.00	0.04	0.01	0.00	0.03
Al ₂ O ₃	31.98	32.01	31.97	32.82	32.25
Cr ₂ O ₃	0.00	0.02	0.00	0.00	0.00
FeO	3.65	3.74	3.86	4.03	4.26
MnO	0.92	1.06	1.10	1.16	1.41
MgO	10.85	10.62	10.40	10.48	10.11
CaO	0.00	0.03	0.03	0.03	0.02
Na ₂ O	0.11	0.13	0.14	0.17	0.14
K ₂ O	0.00	0.03	0.00	0.01	0.00
Total	97.24	96.70	97.38	100.22	99.37
Si	5.08	5.05	5.10	5.12	5.13
Ti	0.00	0.00	0.00	0.00	0.00
Al	3.86	3.89	3.85	3.84	3.82
Fe ²⁺	0.31	0.32	0.33	0.33	0.36
Mn	0.08	0.09	0.10	0.10	0.12
Mg	1.66	1.63	1.59	1.55	1.51
Ca	0.00	0.00	0.00	0.00	0.00
Na	0.02	0.03	0.03	0.03	0.03
K	0.00	0.00	0.00	0.00	0.00
Total	11.00	11.02	10.99	10.98	10.97
X_{Mg}	0.84	0.84	0.83	0.82	0.81

Note: Cations to 18 oxygen X_{Mg} [$\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$]. M: matrix. Gr in: garnet inclusion.

Plagioclase

The plagioclase is mainly oligoclase (24-30% An, table 5).

Table 5: Representative electron microprobe analyses of plagioclase.

Sample	KH30	KH30	KH30	KH30	KH30	KH43	KH43	KH43	KH43	KH43
Location	C	C	C	C	C	C	C	C	C	C
SiO ₂	62.64	62.40	62.14	63.07	62.88	63.58	62.99	63.86	62.42	62.84
TiO ₂	0.00	0.00	0.01	0.01	0.04	0.04	0.00	0.02	0.10	0.00
Al ₂ O ₃	23.35	23.43	23.88	23.22	23.06	22.54	22.81	22.48	22.66	23.16
Cr ₂ O ₃	0.02	0.01	0.00	0.03	0.02	0.00	0.00	0.00	0.00	0.00
FeO	0.01	0.05	0.03	0.04	0.01	0.16	0.11	0.14	0.68	0.14
MnO	0.01	0.00	0.00	0.00	0.02	0.06	0.02	0.00	0.10	0.00
MgO	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.74	0.01
CaO	5.83	5.64	5.50	5.81	5.67	4.95	4.88	5.17	4.62	5.45
BaO	0.00	0.14	0.00	0.21	0.30	0.00	0.00	0.00	0.32	0.00
Na ₂ O	7.28	7.23	7.77	7.48	7.60	8.04	8.17	8.04	7.96	7.89
K ₂ O	0.27	0.24	0.28	0.28	0.22	0.10	0.09	0.09	0.31	0.08
Total	99.40	99.14	99.62	100.1	99.83	99.46	99.08	99.82	99.91	99.57
Si	2.82	2.82	2.78	2.824	2.82	2.85	2.83	2.86	2.79	2.82
Ti	0.00	0.00	0.00	0.000	0.00	0.00	0.00	0.00	0.00	0.00
Al	1.24	1.25	1.26	1.23	1.22	1.19	1.21	1.19	1.19	1.22
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ²⁺	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.03	0.01
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00
Ca	0.28	0.27	0.26	0.28	0.27	0.24	0.24	0.25	0.22	0.26
Ba	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
Na	0.64	0.63	0.67	0.65	0.66	0.70	0.71	0.70	0.69	0.69
K	0.02	0.01	0.02	0.07	0.01	0.01	0.01	0.01	0.02	0.00
Total	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
An	0.30	0.30	0.28	0.30	0.29	0.25	0.25	0.26	0.24	0.28
Ab	0.68	0.69	0.71	0.69	0.70	0.74	0.75	0.73	0.74	0.72
Or	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.00
Ca(pl)	0.30	0.30	0.28	0.30	0.29	0.25	0.25	0.26	0.24	0.28

Note: Cations to 8 oxygen; C= core; Ca(pl)= Ca/(Ca + Na + K)

Phase equilibria modelling

Table 6 shows the bulk rock chemical compositions used in fashioning pseudosections. The KH43 sample shows an enrichment in Fe, Mg, Mn, Al and Ti and is depleted in Si, Ca and Na as expected in a paleosome. Table 7 shows the bulk rock compositions converted to Theriak-

Domino input file, the used oxides were SiO₂, TiO₂, Al₂O₃, FeO, MnO, MgO, CaO, Na₂O and K₂O.

Table 6: Bulk rock compositions used for mineral equilibria modelling (LOI = lost on ignition).

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
KH30	64.08	0.55	17.11	0.04	8.08	0.15	2.87	1.79	2.44	2.06	0.07	1.00	100.2
KH43	44.73	1.06	25.93	0.06	15.12	0.59	5.16	1.05	1.79	2.19	0.07	1.56	99.31

Table 7: Theriak-Domino input file

Sample	SI	AL	TI	MN	FE	MG	CA	NA	K	H	O
KH30	58.1	18.3	0.38	0.12	6.32	3.89	1.74	4.30	2.38	4.55	?*
KH43	40.8	27.9	0.73	0.46	11.4	7.02	1.02	3.16	2.55	4.87	?*

*? for the oxygen amount instructs the program to assign exactly the stoichiometric oxygene atoms to the other elements.

KH30 sample pseudosection

In the P–T pseudosection (Figure 4), biotite is stable until 850 °C. The K-feldspar is stable above ~800 °C and coexists with biotite in the interval of 800 to 850 °C. Orthopyroxene is stable up to 6 kbar at temperatures above 940 °C. Plagioclase exists throughout all the range of modeled variables. Cordierite is stable at pressures below 6 kbar. Sillimanite is not stable between 5 and 6 kbar and above 800 °C inside this pressure interval. The ilmenite seems to be pressure dependent and stable below 7.5 kbar. Rutile is stable above this pressure.

Figure 4: KH30 sample pseudosection.

Concerning the sample KH30, the P-T of 10–11 kbar and 900–950 °C are the khondalite metamorphic peak conditions. The post-peak P-T conditions are 4.5–5 kbar and 750–800 °C.

KH43 sample pseudosection

The P–T pseudosection (Figure 5), biotite is stable until 890 °C. The K-feldspar is stable above ~800 °C and coexists with biotite in the interval of 800 to 890 °C. Orthopyroxene is stable up to 6 kbar at temperatures above 940 °C. Plagioclase exists throughout the range of modeled variables. Cordierite is stable at pressures below 6 kbar. Sillimanite is not stable at 5 kbar and 800 °C to 6 kbar and temperatures above 900°C. The ilmenite seems to be pressure dependent being stable below 7 kbar and rutile is stable above this pressure. Corundum is stable above 7.5 kbar and ~870 °C and hercynite below 7.5 kbar at the same temperature range.

Figure 5: KH43 sample pseudosection

Regarding the sample KH43, the P-T of 9.5–10.5 kbar and 850–870°C are the khondalite metamorphic peak conditions. The post-peak P-T conditions are 4.5–5.3 kbar and 750–830 °C.

Monazite U-Th-Pb geochronology

The WDS images of the investigated monazite crystals (Figure 6) show slightly distinct Y domains. The monazite microanalyses data presented in the table 8 show that all analyzed crystals are very similar to each other, despite the low Y in monazite inside garnet crystals. The monazites are classified as monazite-(Ce) with variable amounts of ThO₂ ranging from 2.302 to 5.020 wt%, UO₂ ranging from 0.518 to 0.912 wt% and PbO ranging from 0.350 to

0.690 wt%. The spot ages (and their respective errors) of the investigated monazites are shown in the table 9.

Despite the apparent homogeneity shown in the compositional map Y (Figure 6C, 6F and 6I), two distinct average ages were produced, defined by the absence of intercept between them and their respective errors, of 2011 ± 20 Ma and 1910 ± 20 Ma (Figure 7).

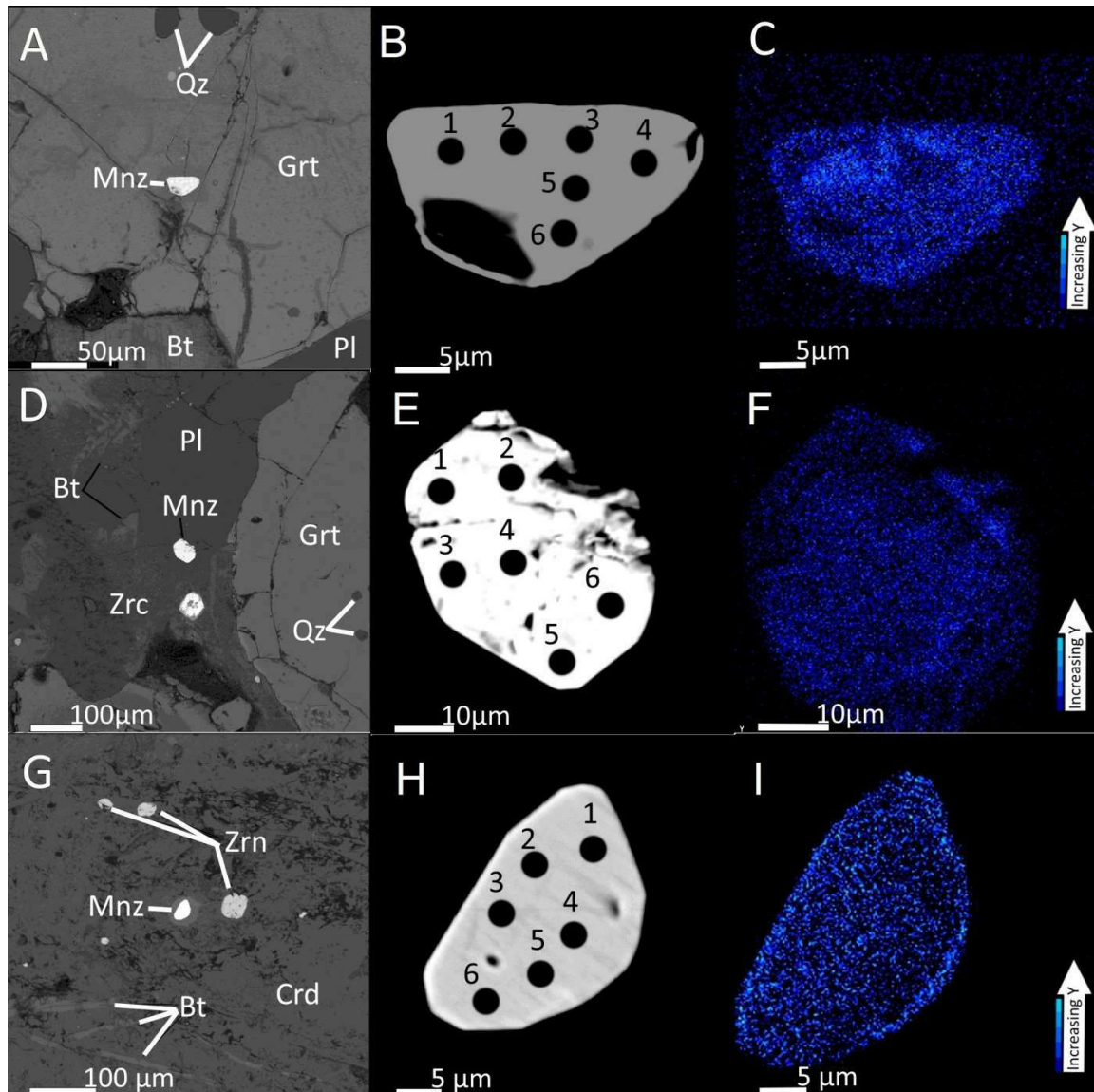


Figure 6: A-BSE image of monazite inside garnet from KH30 sample. B- Detailed BSE image with the analyzed spots. C- WDS Y map. D-BSE image of monazite in rock matrix from KH30 sample. E- Detailed BSE image with the analyzed spots. F- WDS Y map. G- BSE image of monazite in rock matrix from KH43 sample. H- Detailed BSE image with the analyzed spots. I- WDS Y map.

Table 8: Chemical composition of the monazite crystals.

Sample	KH30-Grt 1	KH30-Grt 2	KH30-Grt 3	KH30-Grt 4	KH30-Grt 5	KH30-Grt 6
P ₂ O ₅	30.182	30.621	29.468	28.760	29.724	29.726
SiO ₂	0.804	0.762	0.917	0.970	1.120	0.941
ThO ₂	2.527	2.894	4.008	4.986	4.683	4.466
UO ₂	0.552	0.575	0.769	0.872	0.957	0.912
Y ₂ O ₃	0.724	0.806	0.184	0.441	0.318	0.359
La ₂ O ₃	13.843	13.382	14.031	13.417	13.532	13.342
Ce ₂ O ₃	32.613	32.224	32.577	31.755	31.037	31.613
Pr ₂ O ₃	3.206	3.166	3.105	3.104	2.979	3.128
Nd ₂ O ₃	9.740	9.480	9.500	8.934	9.007	9.166
Sm ₂ O ₃	2.461	2.620	2.364	2.308	2.234	2.326
Gd ₂ O ₃	1.473	1.612	1.165	1.256	1.223	1.449
Dy ₂ O ₃	0.447	0.325	0.150	0.252	0.265	0.260
CaO	0.697	0.704	1.004	1.289	1.338	1.275
PbO	0.401	0.421	0.595	0.690	0.686	0.687
Total	99.670	99.592	99.837	99.034	99.103	99.650
Sample	KH30-M 1	KH30-M 2	KH30-M 3	KH30-M 4	KH30-M 5	KH30-M 6
P ₂ O ₅	30.462	29.075	29.051	29.856	29.016	29.705
SiO ₂	0.520	0.539	0.496	0.323	0.392	0.477
ThO ₂	3.383	5.020	5.196	2.302	4.261	4.239
UO ₂	0.529	0.534	0.569	0.521	0.719	0.625
Y ₂ O ₃	0.195	0.430	0.464	0.383	0.262	0.108
La ₂ O ₃	13.966	13.930	13.890	14.625	13.651	13.988
Ce ₂ O ₃	32.781	31.439	31.163	33.406	32.564	32.580
Pr ₂ O ₃	3.155	3.071	3.164	3.209	3.141	3.121
Nd ₂ O ₃	9.397	9.423	9.243	10.002	9.883	9.586
Sm ₂ O ₃	2.387	2.331	2.537	2.539	2.512	2.352
Gd ₂ O ₃	1.178	1.485	1.420	1.436	1.409	1.010
Dy ₂ O ₃	0.133	0.269	0.214	0.169	0.186	0.103
CaO	0.891	1.073	1.119	0.599	1.102	1.005
PbO	0.441	0.574	0.641	0.350	0.609	0.580
Total	99.418	99.193	99.167	99.720	99.707	99.479
Sample	KH43-M 1	KH43-M2	KH43-M3	KH43-M4	KH43-M5	KH43-M6
P ₂ O ₅	30.690	29.844	29.797	29.965	29.912	30.211
SiO ₂	0.588	0.447	0.503	0.402	0.651	0.484
ThO ₂	4.814	4.217	4.328	4.309	3.953	4.488
UO ₂	0.603	0.676	0.679	0.518	0.683	0.590
Y ₂ O ₃	2.866	3.248	2.941	2.686	2.982	2.795
La ₂ O ₃	11.947	11.684	11.757	11.793	11.823	11.930
Ce ₂ O ₃	29.003	29.901	29.990	29.914	29.986	29.456
Pr ₂ O ₃	2.946	2.953	2.886	2.964	3.062	2.820
Nd ₂ O ₃	9.028	8.780	9.051	9.458	9.673	9.852
Sm ₂ O ₃	2.441	2.517	2.462	2.372	2.370	2.195
Gd ₂ O ₃	1.955	2.051	1.938	1.884	1.938	1.836
Dy ₂ O ₃	0.821	0.789	0.783	0.702	0.888	0.786
CaO	1.741	1.590	1.629	1.529	1.580	1.647
PbO	0.623	0.557	0.621	0.548	0.544	0.555
Total	100.066	99.254	99.365	99.044	100.045	99.645

Note: M: monazite in rock matrix Grt: monazite inside garnet

Table 9: Ages and U, Th and Pb contents (and respective errors) of monazite crystals. MPb is the average Pb atomic mass.

Sample	Age Ma	Error Age Ma	U ppm	Error U %	Th ppm	Error Th %	Pb ppm	Error Pb %	MPb
KH30-Grt 1	1996	83	4725	2.1	2220	1	3722	2.7	207.1
KH30-Grt 2	1920	76	4907	2.0	2543	1	3908	2.6	207.2
KH30-Grt 3	1980	59	6555	1.5	3522	1	5523	1.8	207.2
KH30-Grt 4	1925	52	7408	1.3	4381	1	6405	1.6	207.2
KH30-Grt 5	1911	51	8174	1.2	4115	1	6368	1.6	207.2
KH30-Grt 6	1995	53	7789	1.3	3924	1	6377	1.6	207.2
KH30-M 1	1898	73	4474	2.2	2973	1	4094	2.4	207.3
KH30-M 2	1892	60	4426	2.3	4411	1	5328	1.9	207.5
KH30-M 3	2010	59	4725	2.1	4566	1	5950	1.7	207.4
KH30-M 4	1896	87	4464	2.2	2023	1	3249	3.1	207.1
KH30-M 5	2006	60	6100	1.6	3744	1	5653	1.8	207.3
KH30-M 6	2019	63	5272	1.9	3725	1	5384	1.9	207.3
KH43-M 1	2020	61	5046	2.0	4230	1	5783	1.7	207.4
KH43-M 2	1904	61	5723	1.7	3705	1	5171	1.9	207.3
KH43-M 3	2063	61	5743	1.7	3803	1	5765	1.7	207.3
KH43-M 4	2013	67	4325	2.3	3786	1	5087	2.0	207.4
KH43-M 5	1924	62	5800	1.7	3473	1	5050	2.0	207.2
KH43-M 6	1913	62	4950	2.0	3944	1	5152	1.9	207.4

Note: M: monazite in rock matrix; Grt: monazite inside garnet

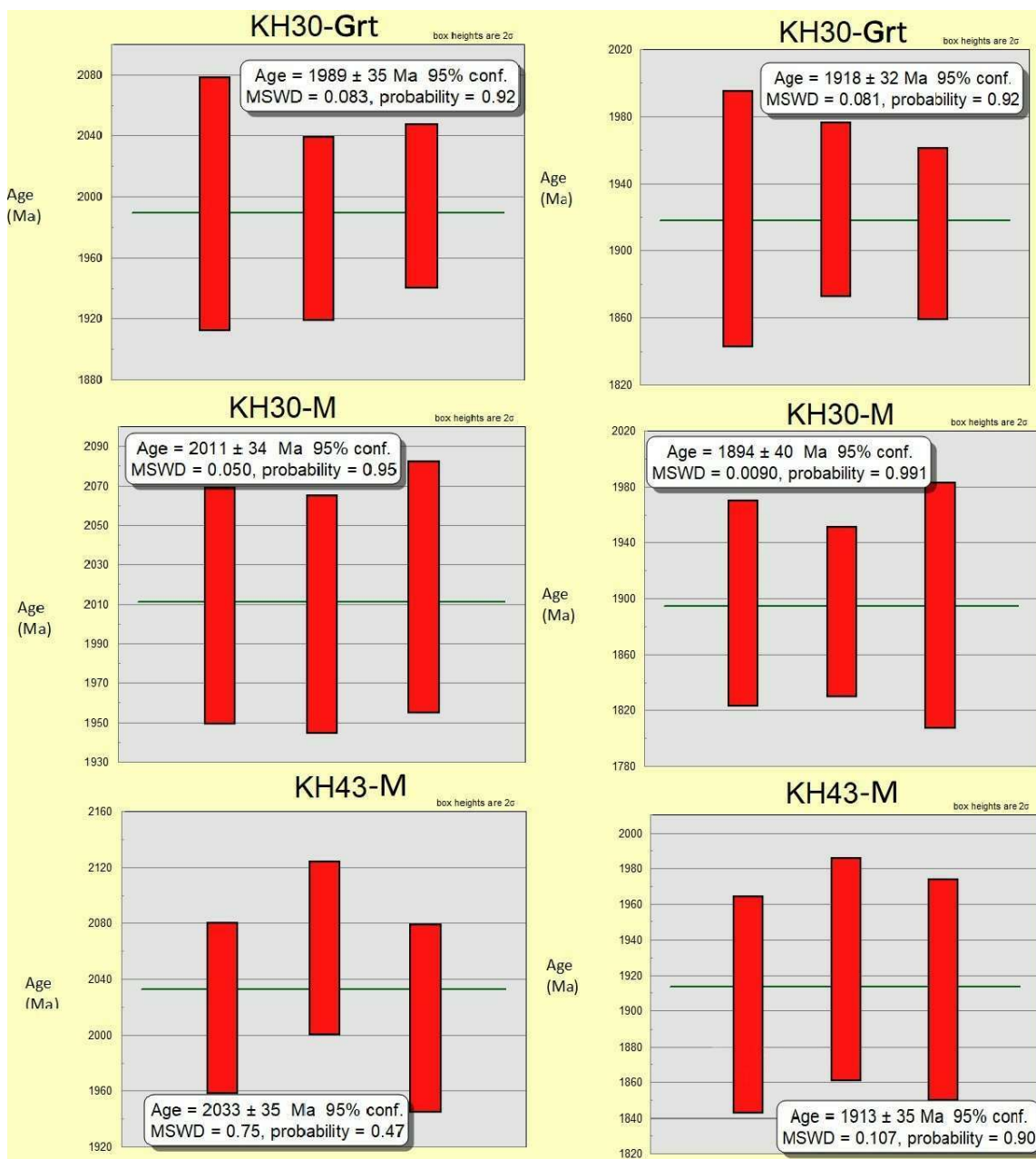


Figure 7: Average ages of studied monazite crystals. Grt- monazite inside garnet; M - Monazite in rock matrix.

Discussion

Pseudosections

The P–T pseudosections for the khondalites show similar topology (Figures 4 and 5), which are in good agreement with the sequence of mineral reactions deduced from the petrography. Isopleths of $Z(\text{grt}) = \text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe}^{2+})$ for garnet and $\text{Ca}(\text{pl}) = \text{Ca}/(\text{Ca} + \text{Na} + \text{K})$ for matrix plagioclase have been contoured to determine the peak P–T conditions (Figure 8). The inferred high pressure peak assemblage, based on reaction 1 of consumption of biotite (mineral unstable at peak conditions) and garnet growth, is $\text{Kfs} + \text{Pl} + \text{Grt} + \text{Sill} + \text{Qz} + \text{Rt} + \text{liquid}$, predicted to be stable at P–T conditions of 10–11 kbar and 900–950 °C for KH30 sample. The inferred peak temperature for the KH43 sample is lower than KH30 sample. This lowering of temperature was considered by virtue of the corundum, mineral predicted to be stable in the same peak conditions of KH30 sample, not being observed in the petrographic study. Thus the inferred high-pressure peak assemblage is $\text{Kfs} + \text{Pl} + \text{Grt} + \text{Bt} + \text{Sil} + \text{Rt} + \text{liquid}$ and the P–T conditions are 9.5–10.5 kbar and 850–870°C for the KH43 sample (Figure 8).

After peak conditions, there was decompression until 6 kbar. The isopleths of $\text{XMg}(\text{Bt}) = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ for biotite and $\text{XMg}(\text{Crd}) = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ for cordierite have been contoured to determine the post-peak P–T conditions based on the equation 2 of consumption of garnet and melt under pressures below 6 kbar to form cordierite and biotite (Figure 8). The inferred post-peak assemblage of $\text{Pl} + \text{Grt} + \text{Bt} + \text{Ilm} + \text{Crd} + \text{Qz} + \text{Sil}$ is predicted to be stable at P–T conditions of 750–800 °C and 4.5–5 kbar for KH30 and 750–830 °C and 4.5–5.3 kbar for sample KH43. Thus a clockwise P–T path is inferred for the KH30 and KH43 samples. As the orthopyroxene was not observed in petrography the inferred path must pass avoiding this stability field. P–T evolution of the khondalite gneisses is shown in figure 8.

Geochronology

According to Williams et al., (2007), compositional domains in monazite crystals can reveal different U–Th–Pb ages, which are associated with distinct metamorphic events. The 2011 ± 20 Ma average age is inferred as the metamorphic peak, which overprinted any other pre peak ages. The 1910 ± 20 Ma average age is inferred as a post peak and cooling stage due to decompression that affected the internal structure of the monazite, recording this late event.

Catlos et al., (2005) argue that monazite is able to record the timing of extensional events. These inferences are recorded in figure 8.

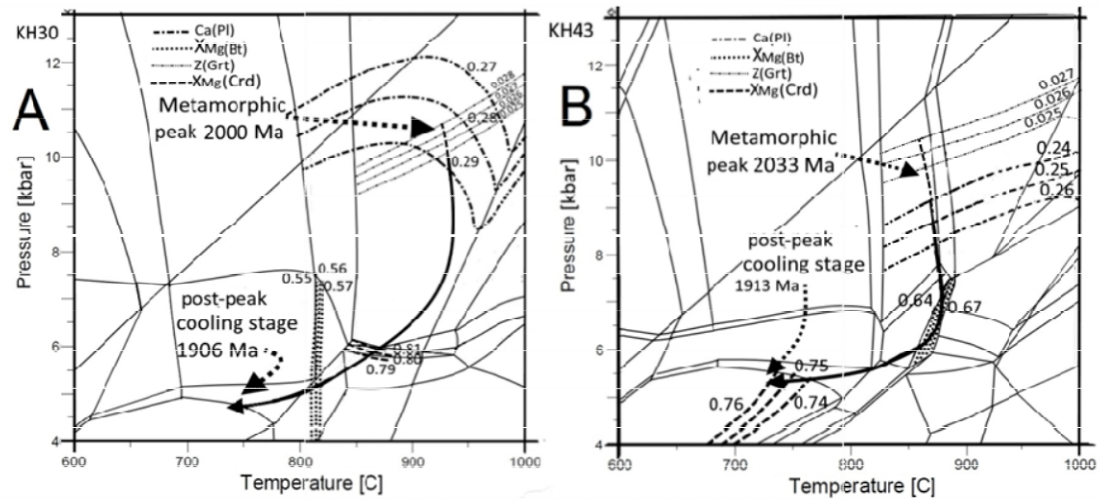


Figure 8: Simplified pseudosections with inferred P-T paths and inferred age events. A- KH30 sample; B - KH43 sample. Isopleths for garnet, $z(grt) = Ca/(Ca + Mg + Fe^{2+})$, plagioclase, $Ca(pl) = Ca/(Ca + Na + K)$, $X_{Mg}(Bt) = Mg/(Mg+Fe^{2+})$, $X_{Mg}(Crd) = Mg/(Mg+Fe^{2+})$.

Tectonic evolution

Khondalite protolith represents the sediments of a Paleoproterozoic basin, which was open before 2.1 Ga. That basin was progressively closed and its rocks reached the metamorphic peak at ~2.0 Ga. In that stage the metasedimentary rocks were converted into khondalites and graphite-rich rocks during the collisional stage. Post-collisional regional processes occurred during the orogenic collapse, leading to decompression that was registered in the studied monazite crystals at ~1.9 Ga. This geological evolution is summarized in figure 9.

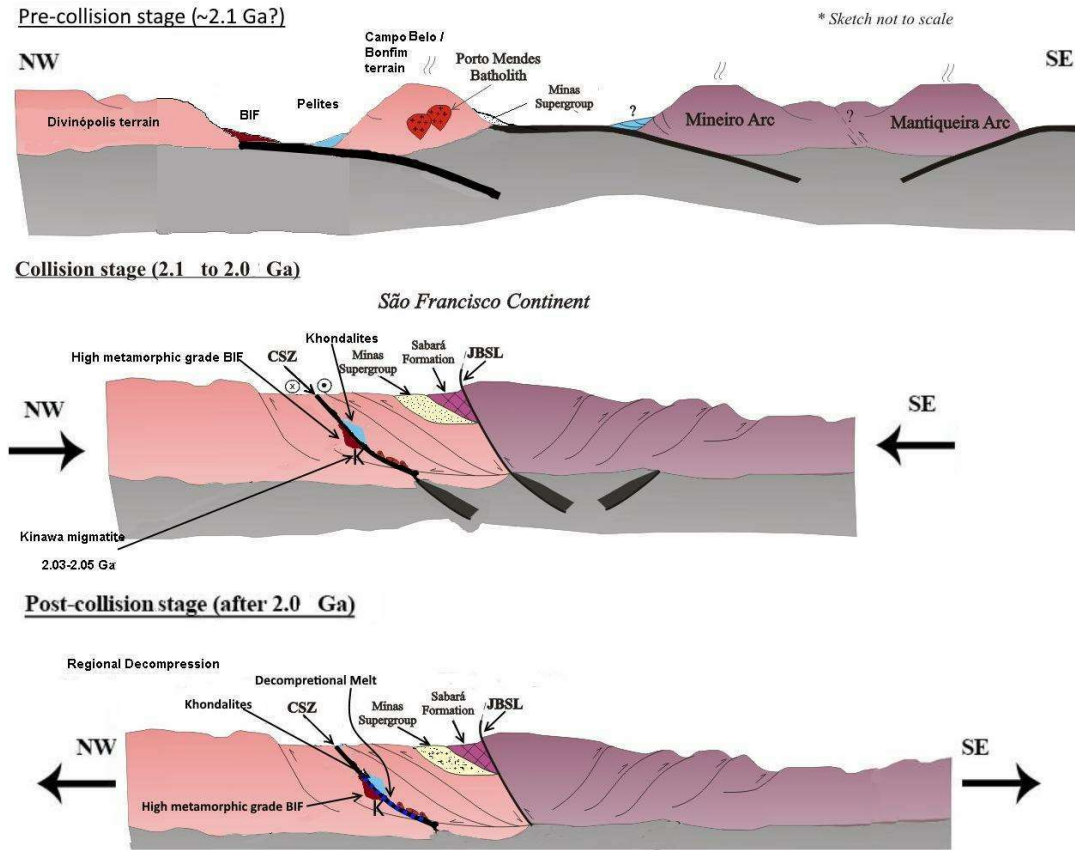


Figure 9: Geological modeling for the tectonic evolution of CSZ (modified from Carvalho et al., 2017).

Globally, Late Paleoproterozoic orogenic belts (including khondalite rocks) are conspicuous around the world, such as in Baltica, Laurentia, Amazonia, Siberia, Australia, Africa and North China. From a paleotectonic perspective, the pervasive collisional dynamics have been associated with the history of the Columbia (Nuna) supercontinent (Meert, 2012). Graphite can be synorogenic in collisional settings, such as the Late Paleoproterozoic deposits in North China craton, which were generated through the conversion of organic matter in ancient sediments that were subjected to granulite-facies conditions (Yang et al., 2014).

The khondalitic rocks studied in this work are very similar in terms of age and P and T evolution with that of ~1.95 Ga khondalitic rocks of the Wulashan Complex from North China Craton investigated by Cai et al., (2016). Based on paleomagnetic data, Xu et al., (2017) proposed a 1.8 Ga paleogeographic reconstruction that connects the São Francisco/Congo and North China cratons. In figure 10 this reconstruction is presented with a possible khondalite belt zone comprising both cratons.

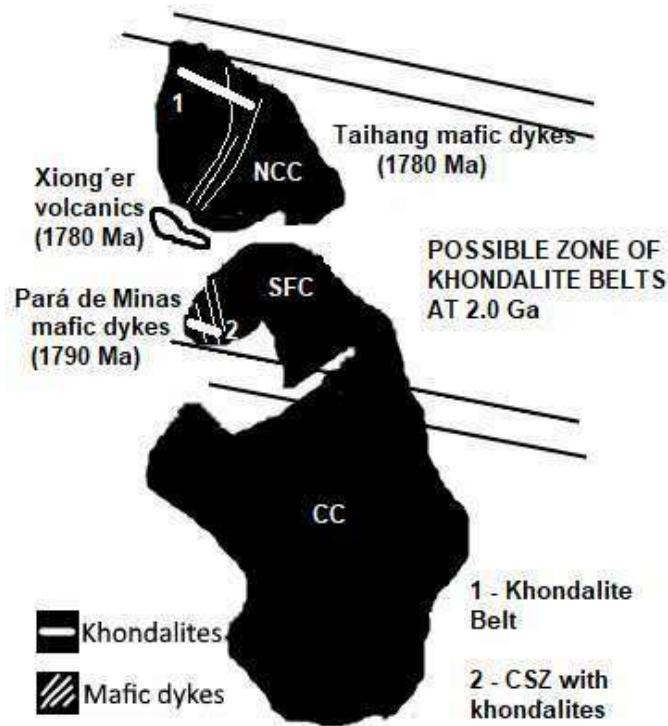


Figure 10: Paleomagnetically based 1.8 Ga paleogeographic reconstruction of Xu et al. (2017 and references therein), with the possible zone of khondalite belts at 2.0 Ga. NCC – North China craton, SFC – São Francisco craton, CC – Congo craton.

Conclusions

The metamorphic setting of the CSZ khondalitic paragneisses is characterized by a metamorphic peak of 900–950 °C and 10–11 kbar, recorded by the reaction of biotite breakdown $Bt + Sil + Qz \pm Pl \rightarrow Grt + Kfs + Melt$. The post peak stage temperature and pressure conditions are 750–830 °C and 4.5–5.3 kbar, recognized by the melt consumption reaction $Grt + Sil + Melt \rightarrow Crd + Bt + Fe\text{-oxide}$. Monazite U-Th-Pb geochronology reveals an age of 2011 ± 20 Ma for the metamorphic peak and an age of 1910 ± 20 Ma for the post peak stage. The dataset obtained in this work is very similar in terms of P and T evolution to the Wulashan Complex from North China Craton (NCC). The khondalitic rocks of both CSZ and Wulashan Complex were subjected to a clockwise P-T-t path granulite facies metamorphism accompanied by partial melting events when SFC and NCC were probably connected during Paleoproterozoic.

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ARTICLE II - 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 Itaipicera. 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 Itaipicera. The average temperature found (702 °C) in this study is close to the samples from Itaipicera. 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 Itapeceirica 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, thermometry, X-ray diffraction.

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 and 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 and Bo-Jun 1985; Tagiri and Oba 1986; Pasteris and Wopenka 1991; Wopenka and Pasteris 1993; Wada et al. 1994; Yui et al. 1996; Nishimura et al. 2000; Beyssac et al. 2002b, 2004; Buseck and 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 Neoarchean granite-greenstone terrains, Palaeoproterozoic clastic-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, Divinópolis 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 terrain 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 cutted 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).

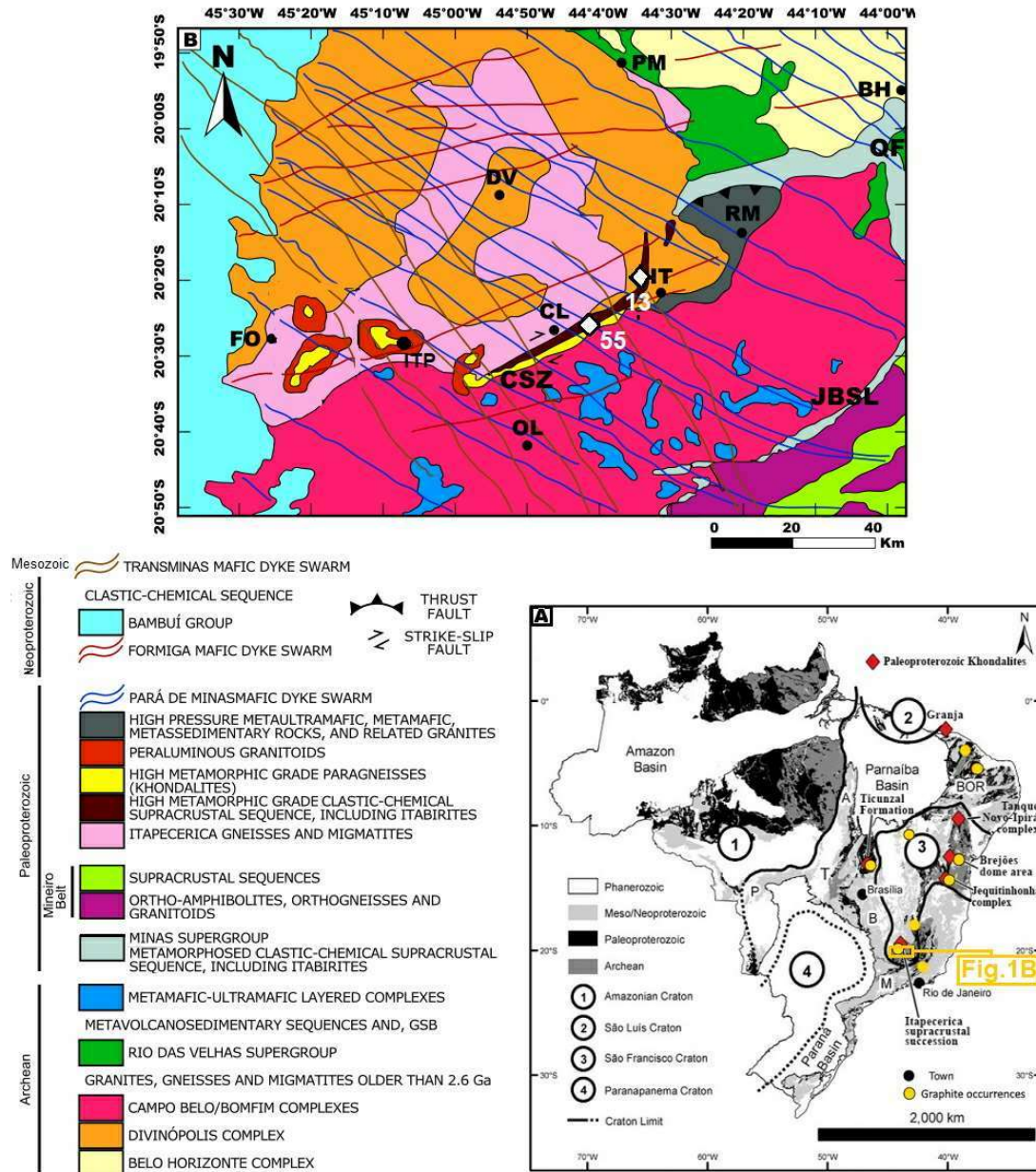


Figure 1: A – Graphite occurrences in Brazilian shield. BOR – Borborema Structural Province. M – Mantiqueira Structural Province. T – Tocantins Structural Province. P – Paraguai Belt. A–Araguaia Belt. B –Brasília Belt. Modified from Fuck et al. (2014), Klein et al. (2018). B – Geological map of the Southern São Francisco craton, studied area with sampling points as lozenges. QF – Quadrilátero Ferrífero, JBSL – Jeceaba-Bom Sucesso lineament, CSZ – Cláudio shear zone. Cities: BH – Belo Horizonte, PM – Pará de Minas, DV – Divinópolis, RM – Rio Manso, IT – Itaguara, FO – Formiga, CL – Cláudio, OL – Oliveira, ITP – Itapequerica (modified from Chaves et al. 2019).

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 (metaperidotite, talc-serpentine-chlorite-amphibole schist), amphibolite, garnet-sillimanite 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 by Coelho and 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 hosts 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 granolepidoblastic 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 $\delta^{13}\text{C}$ range between -21.23 and -27.89 ‰, indicating that the source of the graphite was a primitive biogenic 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.

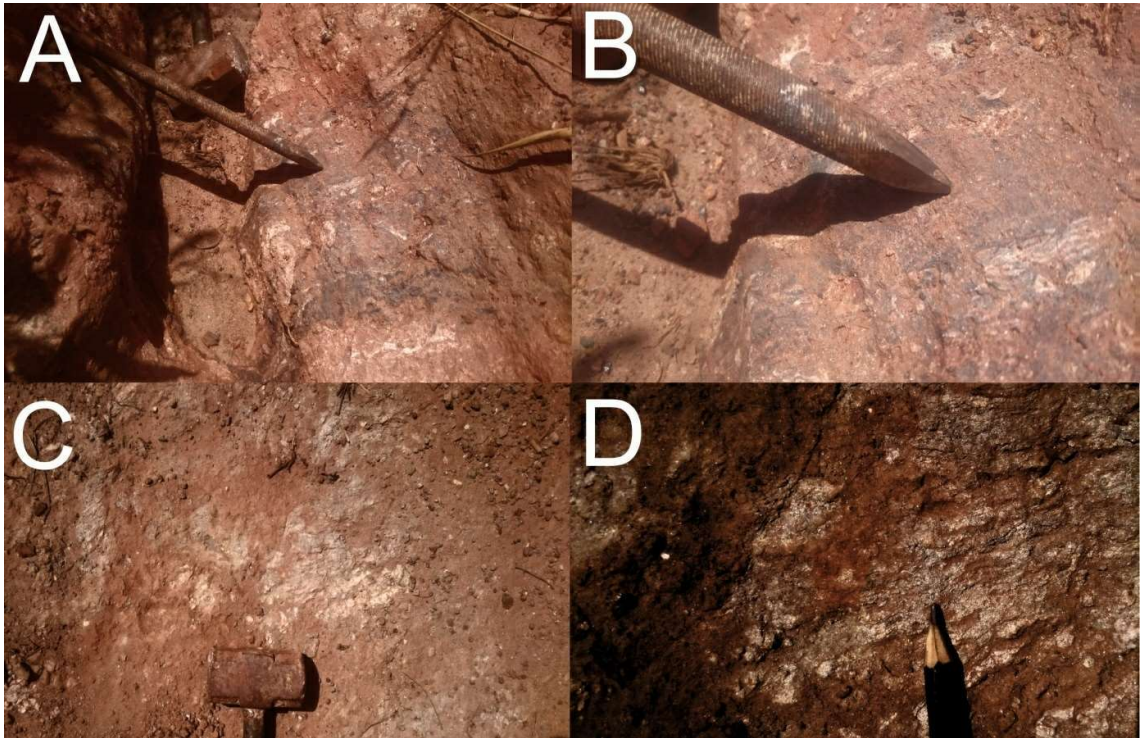


Figure 2: Graphite schist outcrops from CSZ. A - Sampling point 13; B - Detailed view of the outcrop; C Sampling point 55; D - Detailed view of the outcrop.

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).

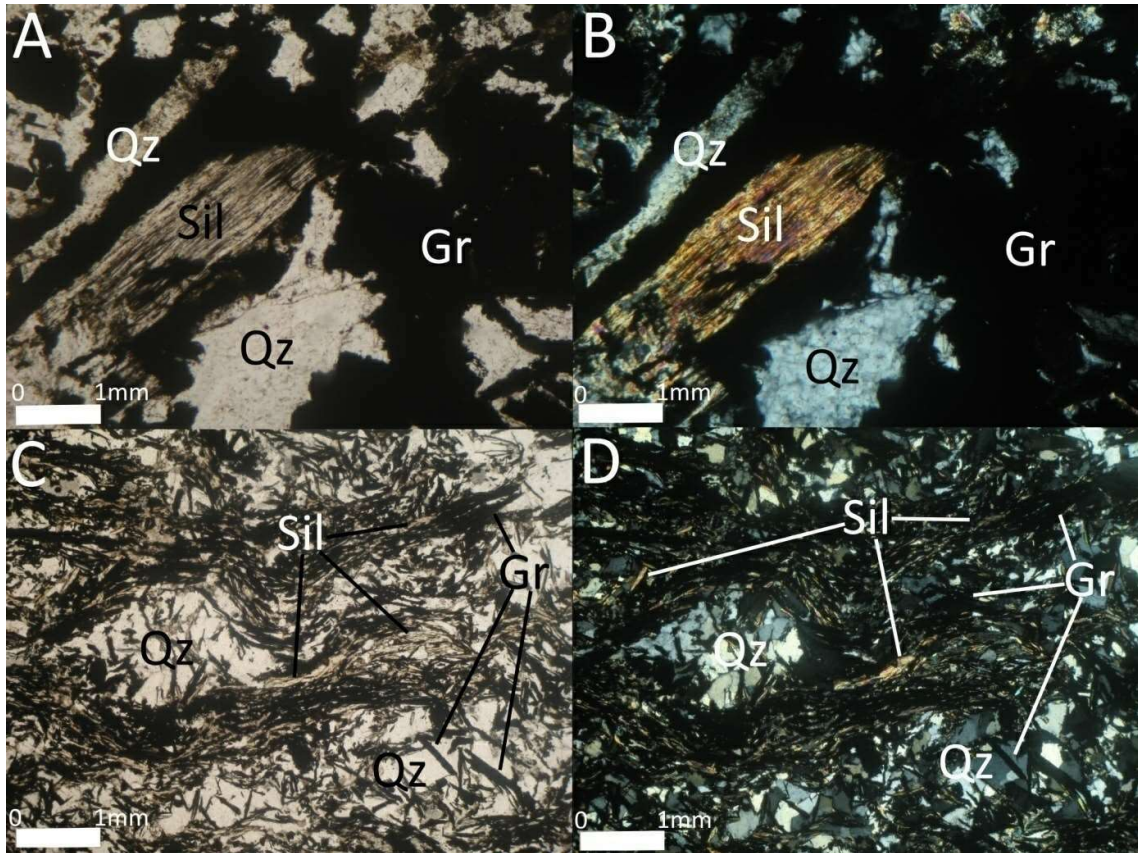


Figure 3: Photomicrographs illustrating graphite textures: A and B are from sample 13 and C and D from sample 55 showing the scattered aspect of the graphite inside schist (A and C under plane polarized light - PPL and B and D under crossed polarized light-XPL) Mineral abbreviations according to Whitney and 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 schists 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 PANalyticalX'Pert PRO diffraction instrument with theta-theta geometry, using a Cu K α X-ray source (40 kV and 45 mA). The diffraction data were collected with a step size of 0.02° 2 θ 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):

$$Lc(002) = k\lambda/\beta(002)\cos\theta$$

where k is the shape constant (0.9), $\beta(002)$ 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):

$$GD = \{[d(002) - 3.7]/[\text{Log}(Lc(002)/1000)]\} \times 100$$

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

$$T(^{\circ}\text{C}) = 3.2 \times GD + 280.$$

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

Table 1: Graphite XRD diffraction data

Sample	2 θ	$d_{(002)}$ Å	sd $\pm$	FWHM (2 θ)	$L_c(002)$ Å	sd $\pm$	GD	T (°C)	sd $\pm$
13a	26.633	3.347	0.005	0.157	519	52	124	676	34
13b	26.605	3.351	0.005	0.138	592	59	154	772	39
13c	26.498	3.361	0.01	0.144	567	57	138	720	36
13d	26.620	3.346	0.005	0.168	508	51	120	665	33
55a	26.669	3.343	0.005	0.177	461	46	106	620	31
55b	26.656	3.344	0.005	0.138	593	59	157	781	39
55c	26.620	3.346	0.005	0.168	486	49	113	642	32
55d	26.668	3.340	0.005	0.144	567	57	146	747	37

(sd: standard deviation)

The binary plot of $L_c(002)$ vs. $d(002)$ (Tagiri and Oba 1986) shows that the samples are predominant fully ordered graphite fields (figure 4A). The plot of GD versus T (°C) (figure 4B) shows the samples aligned with the trend of Ryoke pelites of Wada et al. (1994).

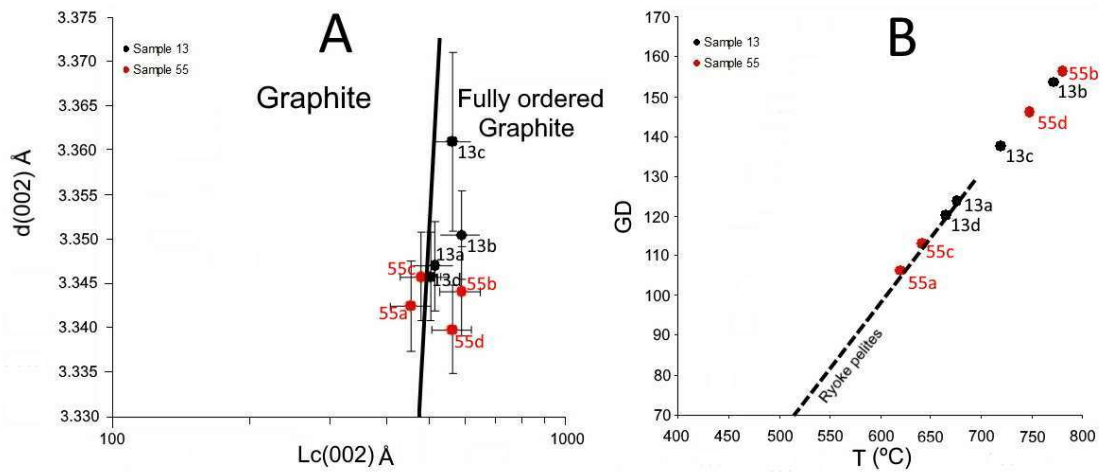


Figure 4: A - Interplanar spacing $d_{(002)}$ versus crystallite size $L_c(002)$ (Tagiri and Oba 1986). B - Graphitization degree (GD) versus XRD data temperature compared to the linear relationship for Ryoke pelites of Wada et al. (1994).

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, $\lambda = 532.2$ nm). Raman spectra were collected with 50 $\times$ 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 $\sim 1350\text{ cm}^{-1}$ (D1 band), $\sim 1500\text{ cm}^{-1}$ (D3 band), $\sim 1580\text{ cm}^{-1}$ (G band), and $\sim 1610\text{ cm}^{-1}$ (D2 band) (Figure 5C). The Raman spectroscopy data was evaluated by IFORS method (Lünsdorf and 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 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 and Lünsdorf 2016).

Table 2 shows the results of Raman spectroscopy, R2 ratio, and the temperature calculations by the IFORS method (Lünsdorf and Lünsdorf 2016) which revealed temperatures between 542 and 605 °C.

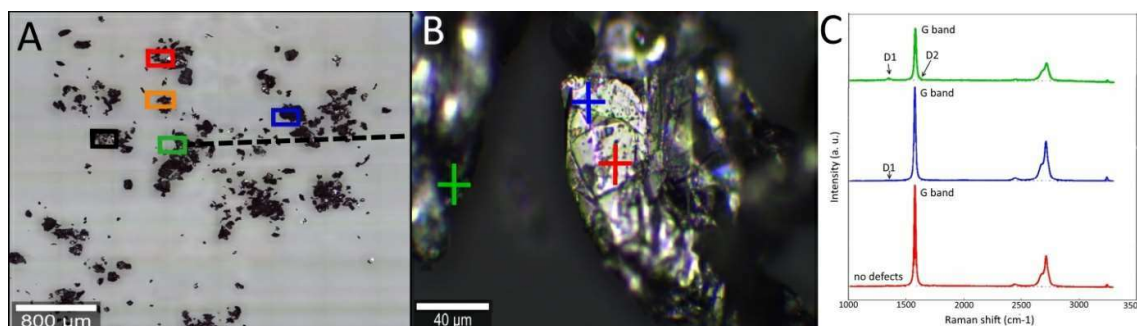


Figure 5: A - View of a sample in the microscope with five major fields: red; green; orange; blue and black. Photomicrograph taken in PPL. B - Zoom of the blue major field with three spots of analysis red; green; blue. Photomicrograph taken in PPL. C - Raman spectra of the spots.

Table 2: Raman spectroscopy data of graphite with values obtained by the IFORS method (Lünsdorf and Lünsdorf, 2016).

Sample	D1-1350 cm-1					D3-1500 cm-1					D2-1610 cm-1					G-1580 cm-1					R2	sd ±	T (°C)	sd ±				
	HWHM	sd±	Center	sd ±	Area	sd ±	HWHM	sd±	Center	sd ±	Area	sd ±	HWHM	sd±	Center	sd ±	Area	sd ±	HWHM	sd±					Center	sd ±	Area	sd ±
13-red-p1	21.62	0.00	1348.97	0	107.72	0.19	48.70	0.55	1507.67	0	51.30	0.50	2.97	0.07	1597.41	0	4.23	0.25	8.73	0.00	1580.79	0.00	1481.82	0.65	0.07	0.00	589	37
13-red-p2	21.50	0.01	1350.64	0	168.50	0.26	75.95	0.96	1501.03	0	124.7	2.66	4.71	0.02	1621.51	0	9.51	0.12	8.10	0.00	1580.79	0.00	1625.20	0.42	0.09	0.00	590	37
13-red-p3	20.87	0.02	1348.97	0	213.40	0.90	10.13	0.03	1364.76	0	33.51	0.59	5.90	0.01	1621.51	0	19.40	0.04	8.44	0.00	1580.79	0.00	1990.35	0.41	0.10	0.00	591	37
13-orange-p1	21.50	0.02	1350.64	0	96.43	0.25	22.25	0.15	1501.03	0	21.80	0.48	5.14	0.03	1619.84	0	6.17	0.03	8.10	0.00	1579.96	0.00	1826.03	0.27	0.05	0.00	596	37
13-green-p3	21.58	0.01	1348.14	0	96.64	0.08	-	-	-	-	-	-	-	-	-	-	-	-	8.60	0.01	1579.13	0.00	1806.45	0.50	0.05	0.00	570	37
13-black-p1	20.47	0.05	1348.97	0	23.27	0.31	8.86	0.17	1497.70	0	9.97	0.68	6.08	0.09	1598.24	0	14.06	3.36	7.89	0.01	1580.79	0.00	1817.25	3.97	0.01	0.00	605	37
13-black-p2	25.16	0.10	1351.74	0.5	31.41	0.82	15.35	0.33	1501.03	0	17.58	0.48	1.14	0.01	1594.09	0	1.07	0.04	7.98	0.00	1579.96	0.00	1712.42	0.41	0.02	0.00	603	37
13-black-p3	17.56	0.01	1349.80	0	51.68	0.04	-	-	-	-	-	-	-	-	-	-	-	-	8.89	0.01	1579.96	0.00	1101.39	0.41	0.04	0.00	587	37
13-blue-p1	19.79	0.12	1349.80	0	22.25	0.20	43.33	2.51	1514.88	1.73	51.48	4.31	4.95	0.54	1597.41	0	17.66	5.26	7.86	0.02	1579.96	0.00	1763.54	14.07	0.01	0.00	604	37
13-blue-p2	20.96	0.04	1348.97	0	147.99	1.00	16.48	2.09	1497.15	0.48	18.59	1.26	6.75	0.08	1619.84	0	15.90	0.36	8.79	0.00	1579.13	0.00	2031.21	4.78	0.07	0.00	589	37
13-blue-p3	62.89	3.84	1356.45	0.8	83.12	9.03	56.72	0.25	1506.57	0.48	54.75	1.77	5.69	0.29	1599.71	0	18.37	1.79	8.21	0.03	1580.79	0.00	1844.10	20.11	0.04	0.00	598	37
55- red-p1	25.96	0.01	1334.018	0	185.32	2.12	35.56	3.22	1490.23	4.70	42.39	6.16	11.42	0.94	1592.98	0.96	34.96	1.11	8.13	2.01	1565.01	0.00	1406.35	12.0	0.08	0.00	581	37
55- orange-p1	24.80	0.01	1342.33	0	209.16	0.92	-	-	-	-	-	-	3.74	0.02	1616.52	0	5.56	0.03	8.59	0.02	1574.15	0.00	903.38	2.92	0.19	0.00	576	37
55- orange-p2	45.12	0.10	1323.22	0	242.98	6.33	-	-	-	-	-	-	13.99	0.02	1617.35	0	32.72	0.25	8.02	0.00	1572.48	0.00	929.98	0.29	0.20	0.00	577	37
55- orange-p4	24.27	0.10	1340.67	0	95.70	0.72	-	-	-	-	-	-	50.75	1.01	1598.79	1.27	174.88	44.66	8.89	0.05	1573.31	0.00	445.80	3.61	0.13	0.00	542	37
55- orange-p3	24.06	0.39	1339.00	0	138.57	6.05	-	-	-	-	-	-	23.36	2.53	1603.78	4.80	70.93	63.28	9.74	0.26	1569.99	0.00	659.11	28.46	0.16	0.00	556	37
55- green-p2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8.32	0.01	1568.33	0.00	541.33	0.23	0.00	0.00	563	37
55- green-p3	25.25	0.07	1337.34	0	82.20	0.45	-	-	-	-	-	-	-	-	-	-	-	-	9.25	0.02	1575.53	0.00	475.28	1.17	0.15	0.00	555	37
55- green-p4	23.24	0.01	1339.83	0	266.45	0.09	-	-	-	-	-	-	-	-	-	-	-	-	11.28	0.00	1569.99	0.00	1420.32	0.55	0.16	0.00	555	37
55-black-p2	24.82	0.00	1341.50	0	160.41	0.03	-	-	-	-	-	-	7.95	0.072	1607.38	0	38.10	0.39	8.61	0.00	1569.16	0.00	1840.68	0.69	0.08	0.00	588	37
55-black-p3	26.52	0.07	1334.02	0	48.49	0.16	-	-	-	-	-	-	9.23	4.97	1594.92	5.82	12.10	7.82	6.36	4.12	1568.61	0.00	562.21	485.1	0.05	0.00	593	37
55- blue-p3	25.86	0.01	1340.67	0	262.04	0.48	-	-	-	-	-	-	8.27	0.048	1607.38	0	23.82	0.16	8.64	0.01	1569.99	0.00	1370.07	2.39	0.16	0.00	602	37

(sd: standard deviation)

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 and Petersen 2004; Rantitsch et al. 2016) are presented in the figures 6A and 6B.

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

Sample	XRD								Raman						
	n	d ₍₀₀₂₎ (Å)	sd	GD	std	T(°C)	sd	n	G HWHM (cm ⁻¹)	std	R2	sd	T(°C)	sd	
13	4	3.351	0.007	134	15	708	49	11	8.33	0.38	0.05	0.03	593	10	
55	4	3.343	0.003	130	25	697	79	11	8.77	1.21	0.12	0.06	572	19	

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 Itapekerica mines.

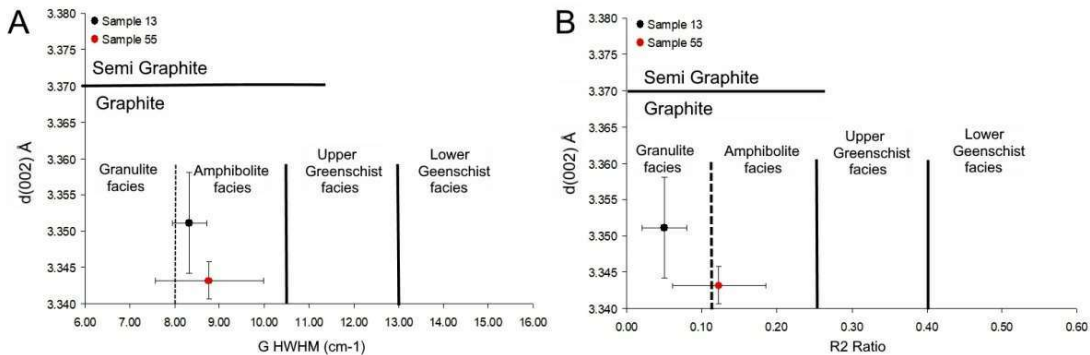


Figure 6: Graphite samples plotted in diagrams from Rantitsch et al. (2016). A - Half width at half maximum (HWHM) of the G-band versus $d(002)$ lattice distance (Graphite/Semi-graphite at – G HWHM ~ 13.0 and $d(002) \sim 3.370$). B - R2 ratio (Beyssac et al. 2002a; $D1/(G+D1+D2)$ area ratio) versus $d(002)$ lattice distance (Graphite/Semi-graphite at – R2 ~ 0.4 and $d(002) \sim 3.370$).

By comparing the temperatures (table 3) obtained from the Raman data (around 583 °C) and XRD data (around 702 °C), 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 600 °C, forming flake-type graphite. According to Beyssac et al. (2002a) and Lünsdorf (2015), around 600 °C 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 °C) of the high-grade metamorphism samples in Itapecerica mines studied by Miranda et al. (2019). However, when compared to the metamorphism temperatures around 900 °C described by Coelho and Chaves (2019) in the CSZ, the temperatures around 702 °C 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 °C described by Coelho and 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 Itaipicera and therefore has undergone a tectonic process analogous to that proposed by Miranda et al. (2019) to the graphite-rich sequences from Itaipicera. 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 and 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.

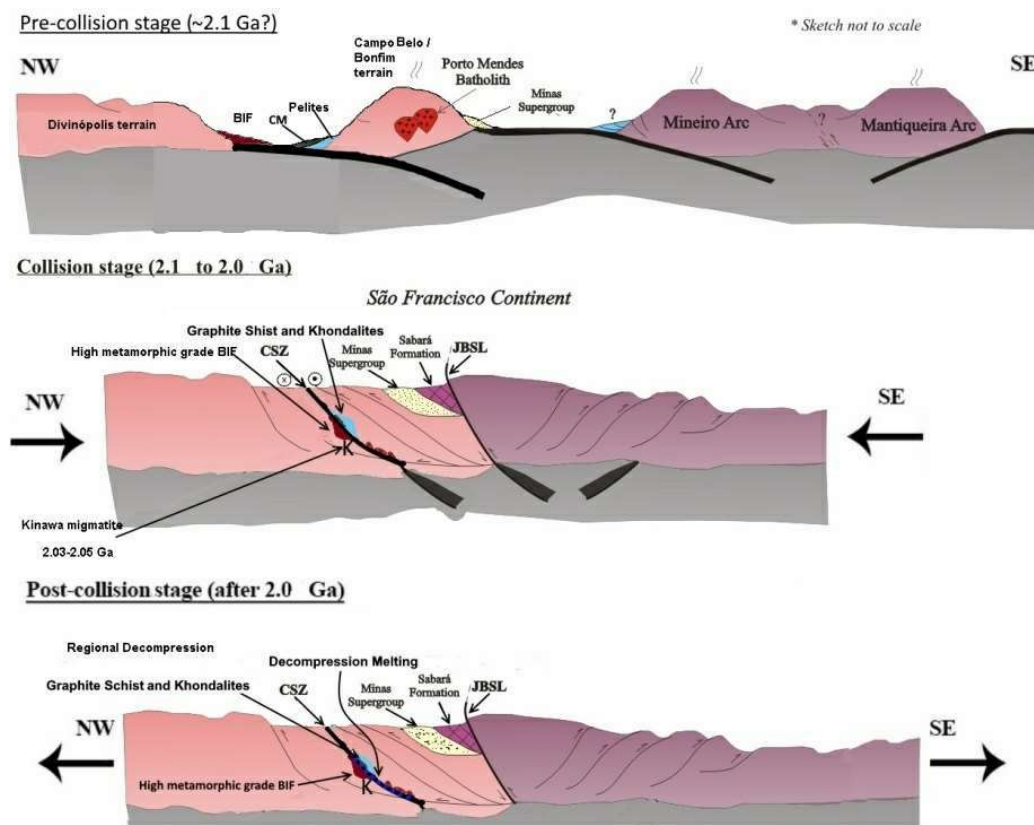


Figure 7: Geological modeling for the tectonic evolution of CSZ (modified from Carvalho et al. 2017).

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 (702 °C) in this study is close to the high-grade metamorphism samples in Itapeccerica mines studied by Miranda et al., (2019). The graphitization processes undergone 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 and 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 Itapeccerica. 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 $\delta^{13}\text{C}$ 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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FINAL COMMENTS

From a local geodynamic scenario, the graphite schists and the khondalites of the CSZ represent the metamorphism of the sediments of a possible Paleoproterozoic oceanic basin. 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 mines as suggested in Miranda et al. (2019).

Supported by the petrological data, the pseudosection analysis of the CSZ khondalitic paragneisses shows a setting characterized by a metamorphic peak of 900–950 °C and 10–11 kbar, recorded by the reaction of biotite breakdown $Bt + Sil + Qz \pm Pl \rightarrow Grt + Kfs + Melt$. The dataset acquired in the present study for the metamorphic peak establishes the CSZ metamorphic conditions as ultra-high temperature and close to high-pressure conditions as can be observed in figure 3. Such conditions are expected to be observed in Cláudio suture zone, where the rocks of the precursor basin were submitted to enormous temperatures and pressures during the paleoproterozoic collision between Archean Campo Belo-Bonfim and Divinópolis blocks that generate high strain structures and partial melting.

The high-T and P metamorphism data presented here for the CSZ khondalites seems to concur with the new dataset acquired to the adjacent Itaguara region, where the remnants of 2.2 Ga retroeclogites (Chaves and Porcher, 2020) in association with accretionary prism (Chaves et al. 2019), collisional peraluminous S-type granites of 2.0 Ga (Chaves and Coelho, 2020) and corundum of about 2.1 Ga - also a continental collision marker (Chaves and Dutra, 2020) – have been found. These finds support the proposition that in the Cláudio-Itaguara region there was oceanic crust subduction followed by continental collision in the Paleoproterozoic.

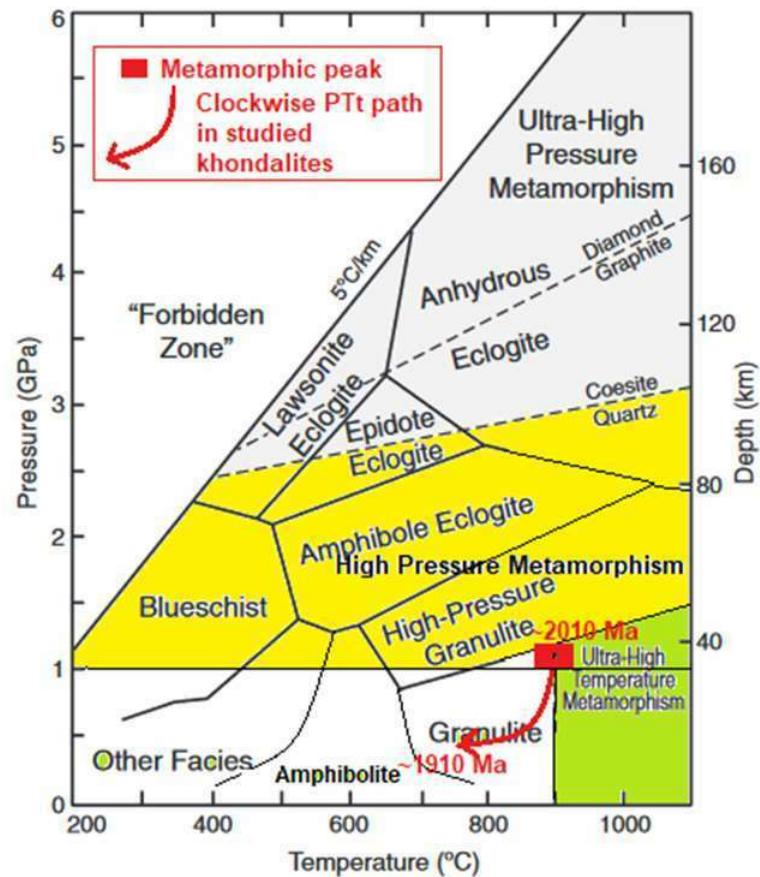


Figure 3: Classic metamorphic facies diagram with the khondalite P-T-t path plotted (Modified from Palin et al. 2020).

Monazite U-Th-Pb geochronology reveals an age of 2011 ± 20 Ma for the metamorphic peak and an age of 1910 ± 20 Ma for the post peak stage of the khondalites. That dataset is very similar in terms of P and T evolution to the Wulashan Complex from North China Craton (NCC). The khondalitic rocks of both CSZ and Wulashan Complex were subjected to a clockwise P-T-t path granulite facies metamorphism accompanied by partial melting events when SFC and NCC were probably connected during the amalgamation of the supercontinent Nuna (Columbia) during the Paleoproterozoic (Chaves, 2021 figure 4).

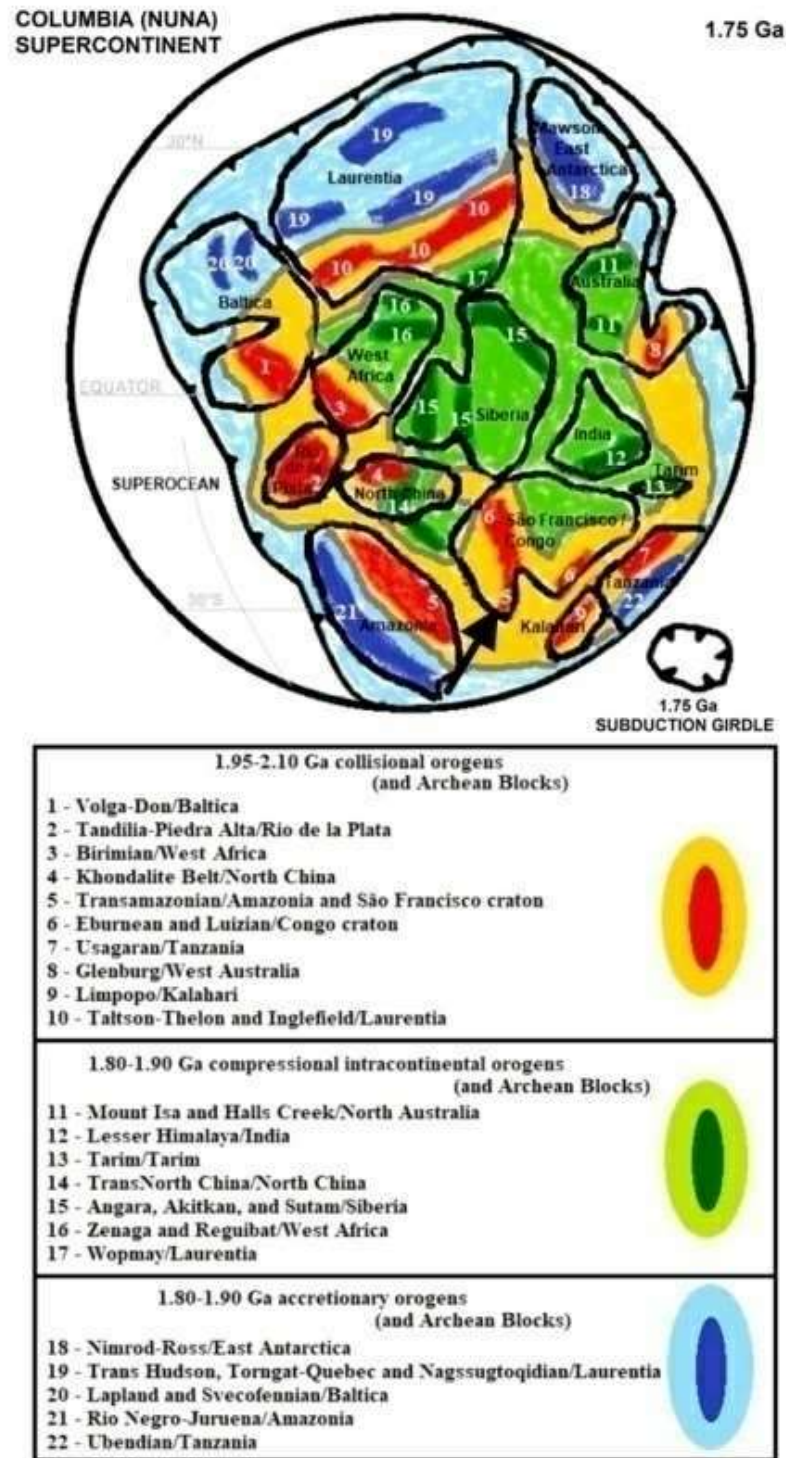


Figure 4: Distribution of concentric collisional (1.95–2.10 Ga), accretionary and compressional intracontinental (1.80–1.90 Ga) orogens and undiscriminating Archean blocks on 1.75 Ga Columbia (Nuna) reconstruction. The arrow indicates the orogenic system where the CSZ is inserted (Chaves, 2021 modified).

The temperature obtained by XRD and Raman spectra is the lower than the estimated in the pseudosections for the khondalite metamorphic peak. This observation could be explained by the following hypothesis: the graphitization processes undergone by the carbonaceous material (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 the expected temperature.

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 Itapeçerica. 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 $\delta^{13}\text{C}$ between -21.23 and -27.89 ‰.

P.S. Due to the new coronavirus pandemic, the ^{13}C carbon isotope data of the graphite samples from CSZ, which have been sent to UFPE did not arrive in a timely manner to be included in this work.

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