

PRESERVATION OF NEOARCHEAN VHMS MINERALIZATION DURING 2.08 Ga REGIONAL METAMORPHISM IN THE NORTHERN SÃO FRANCISCO CRATON: EVIDENCE FROM U–Pb TITANITE GEOCHRONOLOGY

*PRESERVAÇÃO DE MINERALIZAÇÃO VHMS NEOARQUEANA DURANTE METAMORFISMO
REGIONAL A 2,08 Ga NO NORTE DO CRÁTON DO SÃO FRANCISCO: EVIDÊNCIAS DE
GEOCRONOLOGIA U–Pb EM TITANITA*

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ABSTRACT – The Fazenda Coqueiro volcanic-hosted massive sulfide (VHMS) deposit, located in the Mundo Novo greenstone belt, northern São Francisco Craton, represents Neoarchean base-metal mineralization subsequently overprinted by Rhyacian-Orosirian regional metamorphism. Although the timing of mineralization has been previously constrained by Pb–Pb isotopic data, the extent to which this metamorphic event modified the primary isotopic and genetic signature of the mineral system remains unresolved. This study presents new U–Pb geochronological data from metamorphic titanite in the ore-hosting metavolcanic sequence to constrain the timing and effects of regional metamorphism. Titanite grains yield a concordant age of 2086 ± 58 Ma, interpreted as the timing of greenschist- to amphibolite-facies metamorphism. In contrast, previously established Pb–Pb ages of the sulfide mineralization preserve Neoarchean isotopic signatures, with no evidence of isotopic resetting. The persistence of Archean Pb isotopic compositions despite Rhyacian-Orosirian metamorphism implies limited Pb mobility during recrystallization and attests to the isotopic robustness of the primary mineral system. These results demonstrate clear temporal decoupling between Neoarchean mineralization and subsequent metamorphism, establishing the Fazenda Coqueiro deposit as a well-preserved Neoarchean ore system within a reworked Paleoproterozoic terrane. In this context, the findings also highlight the long-term preservation potential of primary metallogenic signatures in metamorphosed greenstone belts and carry significant implications for mineral exploration in ancient cratonic domains.
Keywords: VHMS. U–Pb titanite geochronology. Regional metamorphism. Isotopic preservation. São Francisco Craton.

RESUMO – O depósito de sulfeto maciço hospedado em rochas vulcânicas (VHMS) da Fazenda Coqueiro, localizado no *greenstone belt* Mundo Novo, norte do Cráton do São Francisco, representa uma mineralização neoarqueana de metais de base posteriormente sobreposta por metamorfismo regional riaciano-orosiriano. Embora a idade da mineralização tenha sido previamente estabelecida por dados isotópicos Pb–Pb, a extensão em que esse evento metamórfico modificou a assinatura isotópica e genética primária do sistema mineral permanece indefinida. Este estudo apresenta novos dados geocronológicos U–Pb obtidos em titanita metamórfica da sequência metavulcânica hospedeira, com o objetivo de definir a idade e avaliar os efeitos do metamorfismo regional. Os grãos de titanita forneceram idade concordante de 2086 ± 58 Ma, interpretada como a idade do metamorfismo em condições de fácies xisto-verde a anfibolito. Em contraste, as idades Pb–Pb previamente determinadas para a mineralização sulfetada preservam assinaturas isotópicas neoarqueanas, sem evidências de reequilíbrio isotópico. A persistência das composições isotópicas de Pb arqueanas, apesar do metamorfismo riaciano-orosiriano, implica mobilidade limitada de Pb durante a recristalização e atesta a robustez isotópica do sistema mineral primário. Esses resultados demonstram clara dissociação temporal entre a mineralização neoarqueana e o metamorfismo subsequente, estabelecendo o depósito Fazenda Coqueiro como um sistema mineral neoarqueano bem preservado em um terreno retrabalhado no Paleoproterozoico. Nesse contexto, os resultados também evidenciam o potencial de preservação a longo prazo de assinaturas metalogenéticas primárias em *greenstone belts* metamorfizados e apresentam implicações significativas para a exploração mineral em domínios cratônicos antigos.

Palavras-chave: VHMS. Geocronologia U–Pb em titanita. Metamorfismo regional. Preservação isotópica. Cráton do São Francisco.

INTRODUÇÃO

The Fazenda Coqueiro volcanic-hosted massive sulfide (VHMS) Zn-Pb deposit is hosted in the Mundo Novo greenstone belt (MNGB), northern São Francisco Craton, northeastern Brazil (Figures São Paulo, UNESP, *Geociências*, v. 45, n. 2, p. 269 - 282, 2026

1A, 1B and 1C). The Zn-Pb deposit represents Neoproterozoic submarine hydrothermal mineralization associated with volcanic-exhalative processes within the greenstone terrane (Spreafico et al., 2020).

Mineralization occurs within the western metabasalt of the middle volcanic sequence of the MNGB and is spatially associated with carbonate and sericite-chlorite alteration zones that control sulfide distribution (Spreafico, 2017). Geochronological data from felsic meta-volcanic rocks indicate a Neoproterozoic age for the

volcanic sequence of the MNGB (Spreafico et al., 2019), supporting a syngenetic relationship between volcanism and mineralization.

Despite its Archean origin, the Fazenda Coqueiro deposit was subsequently affected by a Rhyacian-Orosirian tectonothermal and metamorphic event during the Paleoproterozoic evolution of the northern São Francisco Craton, related to the development of the Contendas-Jacobina lineament (Leite, 2002; Barbosa & Sabaté, 2004; Barbosa, 2021).

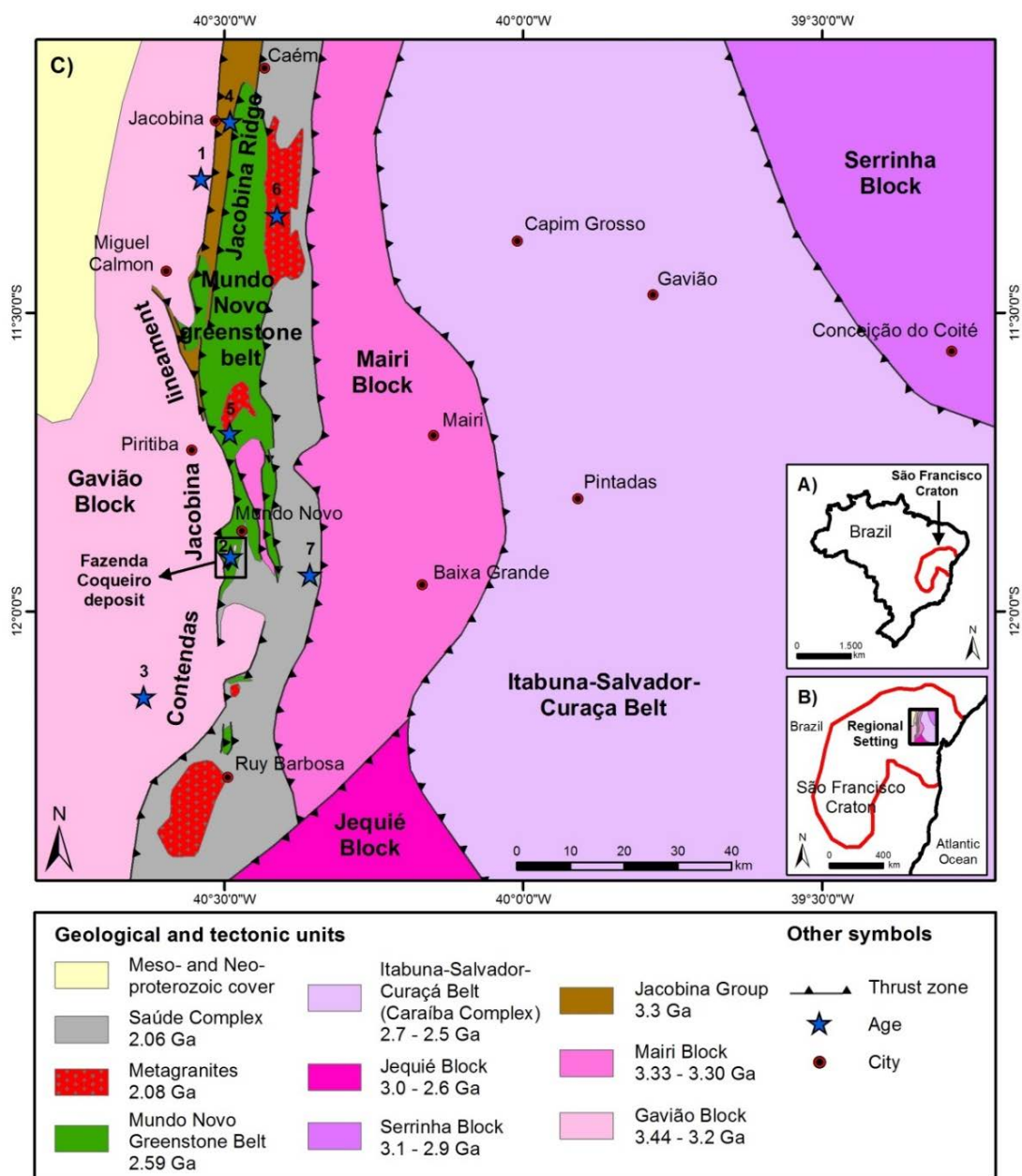


Figure 1 - A) Location of the São Francisco Craton in northeastern Brazil. B) Regional setting of the northern portion of the São Francisco Craton. C) Regional tectonic framework showing the MNGB and the Fazenda Coqueiro VHMS deposit (modified from Barbosa & Sabaté, 2004; Barbosa, 2021). Ages corresponding to the numbered locations on the map: 1- 3442 ± 2 Ma (U-Pb zircon, TTG; Mougeot, 1996); 2- 3303 ± 11 Ma (U-Pb zircon, metarhyolite from the Gavião Block; Zincone et al., 2016); 3- 3292 ± 3 Ma (U-Pb zircon, metagranite from the Gavião Block; Zincone et al., 2016); 4- $3500 - 3220$ Ma (U-Pb zircon, quartzite from the Jacobina Group; Teles et al., 2015); 5- 2595 ± 21 Ma (U-Pb zircon, metadacite from the MNGB; Spreafico et al., 2019); 6- 2080 ± 18 Ma (U-Pb monazite, Cachoeira Grande granite; Leite, 2002); 7- 2068 ± 12 Ma (U-Pb zircon, biotite schist from the Saúde Complex; Zincone et al., 2017).

This regional metamorphic overprint, reaching greenschist- to amphibolite-facies conditions, may have affected the deposit and partially obliterated primary volcanic and hydrothermal features.

In metamorphosed terranes, the extent to which later tectonothermal events modify primary isotopic systems remains a critical issue for metallogenic interpretation (Pomiès et al., 1998; Blichert-Toft et al., 2016; Tessalina et al., 2016). Although previous thermal ionization mass spectrometry (TIMS) Pb–Pb analyses of sulfides from the Fazenda Coqueiro deposit constrained the timing of Neoarchean mineralization (Spreafico et al., 2020), the degree to which Rhyacian–Orosirian metamorphism may have induced isotopic re-equilibration has not been fully assessed.

Titanite is a robust accessory mineral widely used to constrain the timing of metamorphic events due to its capacity to incorporate U and Th

during recrystallization or neocrystallization (Kohn, 2017; Olierook et al., 2019). U–Pb titanite geochronology therefore provides an effective approach to establish the timing of regional metamorphism and to evaluate potential decoupling between primary mineralization and subsequent tectonothermal overprinting.

Accordingly, this study presents new laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U–Pb ages obtained from metamorphic titanite in the ore-hosting metavolcanic sequence of the MNGB. Integration of these data with previously established Pb–Pb sulfide ages constrains the timing of Rhyacian–Orosirian metamorphism recorded in the Fazenda Coqueiro deposit, assesses the isotopic robustness of the Neoarchean mineral system, and evaluates the long-term preservation of primary metallogenic signatures in reworked Archean terranes.

GEOLOGICAL SETTING

The northern portion of the São Francisco Craton was formed through the amalgamation of five Archean blocks during Paleoproterozoic continent-continent collisions (Barbosa & Sabaté, 2004; Spreafico et al., 2019; Barbosa, 2021): the Gavião, Mairi, Serrinha, and Jequié blocks, together with the Itabuna-Salvador-Curaçá Belt (Figure 1C).

The Paleoproterozoic event involved the MNGB and the surrounding crust between the cratonic blocks, resulting in the development of the Contendas-Jacobina lineament. Uplift associated with this event may have promoted erosion and the formation of Rhyacian–Orosirian sedimentary basins, including the uppermost sequence of the MNGB.

The MNGB is bounded to the west by 3.4 Ga tonalite-trondhjemite-granodiorite (TTG) basement rocks and subordinate metagranites of the Gavião Block (Mougeot, 1996), and to the east and south by paragneisses of the Saúde Complex with maximum depositional ages between 2.20 and 2.06 Ga (Zincone et al., 2017; Figure 2).

To the north and northwest, the MNGB is in contact with quartzites of the Jacobina Group, deposited between 3.55 and 3.22 Ga (Teles et al., 2015), as well as with Paleoproterozoic granites.

The regional geological framework includes granulite (2.9 Ga) and multiple charnockite intrusions (2.7 and 2.6 Ga) in the Jequié Block (Wilson, 1987; Silva et al., 2002); tonalitic granulite (2.57 Ga) and enderbite (2.7 Ga) of the Itabuna-Salva-

dor-Curaçá Belt (Silva et al., 1997; Oliveira et al., 2010); and the Mairi (3.33 – 3.30 Ga) and Serrinha (3.1 – 2.9 Ga) blocks (Oliveira et al., 2002a, b; Rios et al., 2009; Sousa et al., 2018; Figure 1C and Table 1).

Although the Itabuna-Salvador-Curaçá Belt and the Serrinha Block are located far from the MNGB, they are important for understanding the broader tectonic evolution of the study area.

The eastern margin of the Gavião Block is in tectonic contact with the MNGB along a north-south-trending, west-vergent thrust zone (Figure 1C). It comprises TTG gneisses and migmatites with mafic enclaves (Barbosa et al., 2012a), as well as metagranites and metarhyolites (Zincone et al., 2016), which together form the basement of the MNGB.

Three TTG groups are recognized: two trondhjemitic units yielding U–Pb zircon ages of 3403 ± 5 Ma and 3158 ± 5 Ma obtained by sensitive high-resolution ion microprobe (SHRIMP; Barbosa, 1997; Leal, 1998), and a granodioritic group that includes the 3225 ± 10 Ma Aracatu granitoid (Barbosa et al., 2012a). Although the block is broadly dated at 3.4 Ga (Mougeot, 1996), metarhyolites (3303 ± 11 Ma) and metagranites such as the Boa Sorte granite (3291 ± 2.5 Ma) have also been reported (Zincone et al., 2016).

The Jacobina Group is tectonically juxtaposed against the MNGB along a north-south-trending, west-vergent thrust zone, with the Gavião Block forming the footwall (Figure 1C).

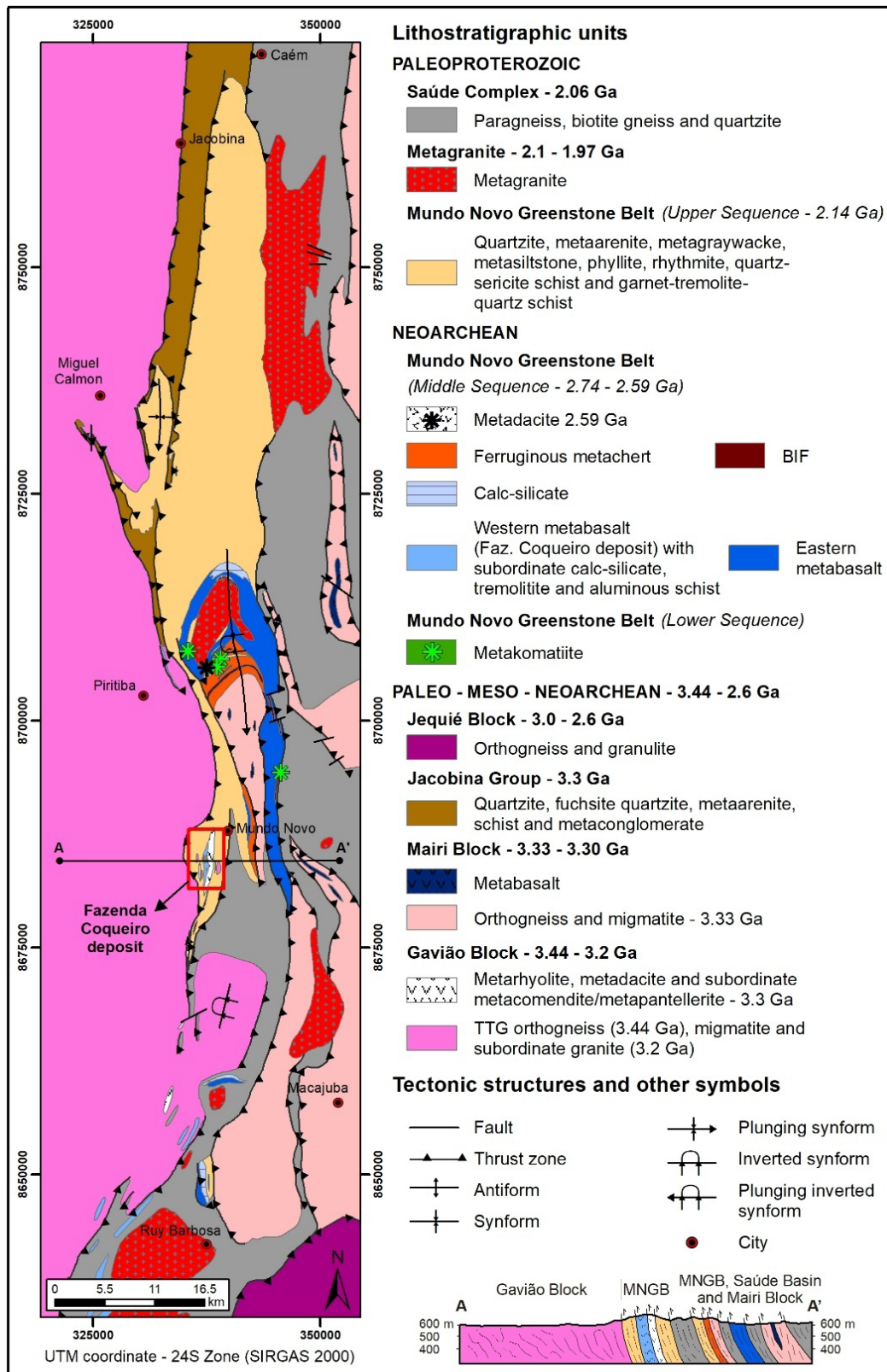


Figure 2 - Geological map of the MNGB and adjoining units. Modified from Spreafico et al. (2019, 2020).

It comprises metaconglomerates, quartzites, metaarenites, phyllites, chlorite schists, and quartz-sericite schists (Mascarenhas et al., 1998), and is interpreted as a passive-margin succession (Reis et al., 2021).

Detrital zircon data indicate deposition between 3500 Ma and 3220 Ma (Magee et al.,

2001; Teles, 2013; Teles et al., 2015; Barbuena et al., 2016). The Jacobina Ridge therefore represents an Archean supracrustal sequence with a maximum depositional age of 3.22 Ga, likely sourced from plutonic-volcanic rocks and TTG suites of the Gavião Block (Zincone et al., 2016).

Table 1 - Compilation of regional geochronological data from the MNGB and adjoining units.

Geological/tectonic unit	Lithotype	Age	Method	Mineral dated	Author
Saúde Complex	Biotite schist	2068 ± 12 Ma	U-Pb (LA-MC-ICP-MS)	Detrital zircon	Zincone et al. (2017)
Cachoeira Grande granite	Leucogranite	2080 ± 18 Ma	U-Pb (electron microprobe)	Monazite (crystallization age)	Leite (2002)
Uppermost sequence (MNGB)	Quartzite	2133 ± 14 Ma	U-Pb (LA-ICP-MS)	Detrital zircon	Barbuena et al. (2016)
Middle sequence (MNGB)	Metadacite	2595 ± 21 Ma	U-Pb (LA-ICP-MS)	Zircon (crystallization age)	Spreafico et al. (2019)
Middle sequence (MNGB)	Calc-silicate rock	2747 ± 16 Ma	Pb-Pb (TIMS)	Chalcopyrite	Spreafico et al. (2020)
Itabuna-Salvador-Curaçá Belt	Tonalitic granulite	2574 ± 6 Ma	U-Pb (SHRIMP)	Zircon (crystallization age)	Oliveira et al. (2010)
	Enderbite	2695 ± 12 Ma	U-Pb (SHRIMP)	Zircon (crystallization age)	Silva et al. (1997)
Jequié Block	Granulites	2715 ± 29 Ma	U-Pb (SHRIMP)	Zircon (crystallization age)	Silva et al. (2002)
	Charnockite	2900 ± 24 Ma	Rb-Sr (TIMS)	Whole-rock (crystallization age)	Wilson (1987)
Serrinha Block	Granitoid	2989 ± 11 Ma 3072 ± 2 Ma 3162 ± 26 Ma	U-Pb (SHRIMP)	Zircon (crystallization age)	Rios et al. (2009)
	Gneiss, migmatite	3152 ± 5 Ma	U-Pb (SHRIMP)	Zircon (crystallization age)	Oliveira et al. (2002a, b)
Jacobina Group	Quartzite	3500 - 3220 Ma	U-Pb (LA-MC-ICP-MS)	Detrital zircon	Magee et al. (2001), Teles (2013), Teles et al. (2015), Barbuena et al. (2016)
Mairi Block	Orthogneiss	3.33 - 3.30 Ga	U-Pb (LA-SF-ICP-MS)	Zircon (crystallization age)	Sousa et al. (2018)
Gavião Block	Metagranite	3291 ± 2.5 Ma	U-Pb (LA-ICP-MS)	Zircon (crystallization age)	Zincone et al. (2016)
	Metarhyolite	3303 ± 11 Ma	U-Pb (LA-ICP-MS)	Zircon (crystallization age)	Zincone et al. (2016)
	TTG	3442 ± 2 Ma	U-Pb (ID-TIMS)	Zircon (crystallization age)	Mougeot (1996)

The MNGB is divided into three stratigraphic sequences (Spreafico et al., 2019): (i) a lowermost ultramafic sequence; (ii) a middle sequence with a zircon age of 2595 ± 21 Ma, comprising western and eastern metabasalts, felsic rocks, and clastic and chemical metasedimentary rocks (Spreafico et al., 2019); and (iii) an uppermost sequence composed of siliciclastic metasedimentary rocks with a maximum zircon age of 2133 ± 14 Ma (Barbuena et al., 2016; Figure 2). Two progressive ductile Rhyacian-Orosirian deformational phases are described in the MNGB.

The D₁ phase is characterized by west-vergent isoclinal and recumbent folds that generated greenschist-facies metamorphic rocks. The D₂ phase involved refolding of sub-horizontal axial planes and eventually resulted in the develop-

ment of coaxial interference patterns and compressional to transpressional shear zones, which bounded MNGB lithotypes and generated greenschist- to amphibolite-facies metamorphism. The most prominent brittle structures are east-trending faults and fractures. Neoarchean volcanism in the MNGB (Spreafico et al., 2019) and Paleoproterozoic sedimentation at the top of the sequence (Barbuena et al., 2016), coeval with the Rhyacian-Orosirian tectonic event (Leite, 2002), represent the main geological, tectonic, and metamorphic events recorded in the study area.

Regarding the Fazenda Coqueiro deposit, drill hole programs conducted by Companhia Baiana de Pesquisa Mineral (CBPM) defined resources of 4,200,000 t in the massive sulfide body, with average grades of 6.12% Zn and 0.41% Pb

(Spreafico et al., 2020). Silver values of up to 28 g/t were obtained over a one-meter interval, whereas gold grades reach 2.75 g/t over a two-meter interval in association with the massive sulfides. A Cu-rich disseminated zone averages 0.75% Cu over a four-meter interval (Spreafico et al., 2020).

The Saúde Complex occurs east of the MNGB (Figure 1C) and is tectonically juxtaposed along west-vergent thrust zones associated with the Contendas-Jacobina lineament. It consists mainly of aluminous paragneisses and biotite gneisses, with subordinate quartzites, distributed along a north-south trend, particularly in the Mundo Novo region and eastern Jacobina Ridge (Mascarenhas et al., 1998; Leite et al., 2007; Reis et al., 2021;

Figure 1C). A maximum depositional age of 2.06 Ga (Zincone et al., 2017) indicates the development of a Rhyacian-Orosirian basin adjacent to the MNGB, which was later affected by high-grade metamorphism.

Paleoproterozoic granites occur along the Contendas-Jacobina lineament (Figure 1C; Leite, 2002). They are generally undeformed leucogranites composed of quartz, feldspar, biotite, and muscovite, locally containing garnet and sillimanite (Barbosa et al., 2012b). The Cachoeira Grande granite, located northeast of the MNGB, is a peraluminous leucogranite dated at 2080 ± 18 Ma (Leite, 2002), coeval with Rhyacian-Orosirian granitic intrusions within the MNGB.

ANALYTICAL TECHNIQUES

The study of the Fazenda Coqueiro deposit involved fieldwork and the geological description of cores from five drill holes (FCQ-06, FCQ-13, FCQ-16, FCQ-18, and FCQ-22) completed by CBPM in the 1990s (Figure 3), including petro-

graphic analyses of the western metabasalts. In addition, one metabasalt sample (RR-F6) was collected from drill hole FCQ-06 at approximately 100 m depth to constraint the timing of mineralization.

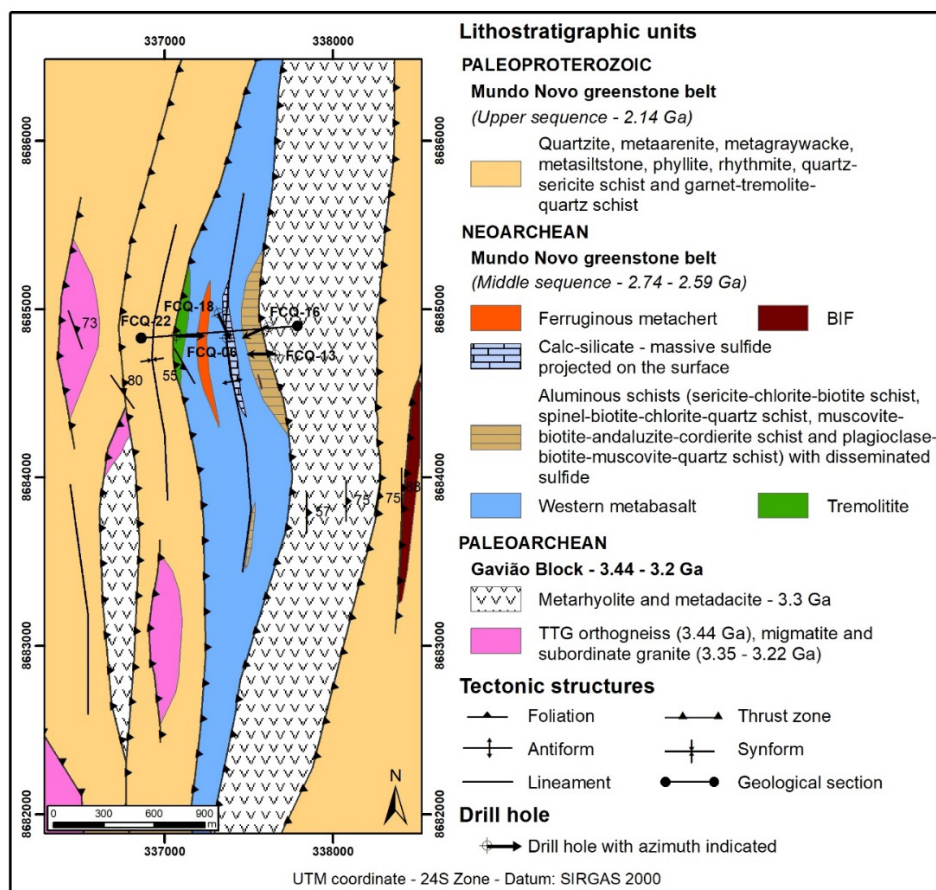


Figure 3 - Geological map of the Fazenda Coqueiro VHMS deposit showing drill hole locations from which samples were collected for U-Pb titanite geochronology and petrographic analyses.

Drill core data were compiled into a geological-structural cross section illustrating the Fazenda Coqueiro deposit and indicating the location of the sample selected for geochrono-

logical analysis. Petrographic investigations were carried out using a ZEISS Axio Scope.A1 microscope provided by CBPM to determine the mineralogical composition and microstructural

features of 17 metabasalt samples and their associated titanite grains. Mineral abbreviations used in petrographic images and throughout the manuscript follow the conventions of Kretz (1983) and Siivola & Schmid (2007).

U–Pb analyses of titanite were performed by LA-ICP-MS at the Isotope Geology Laboratory (LAGIS), Institute of Geosciences, State University of Campinas, Brazil. Titanite grains were separated using conventional crushing, density, and magnetic separation techniques, handpicked under a binocular microscope, mounted in epoxy resin, and polished to expose internal domains.

Cathodoluminescence imaging was used to identify inclusion-free and compositionally homogeneous domains suitable for analysis. *In situ* analyses were carried out using a laser ablation system coupled to a quadrupole ICP-MS.

U–Pb isotopic ratios were calibrated against

the Khan titanite reference material, used as the primary standard and analyzed repeatedly during the analytical session as an in-run standard to correct for instrumental drift and elemental fractionation.

The MKED titanite was analyzed as a secondary standard to monitor external reproducibility and analytical accuracy. Data reduction followed standard LA-ICP-MS routines, including background subtraction, downhole fractionation correction, and common Pb correction based on measured ^{204}Pb when applicable.

Results are presented on a Tera-Wasserburg inverse concordia diagram, with the initial common Pb composition anchored after Stacey & Kramers (1975). Ages are reported with uncertainties at the 2σ level (standard deviation), and final plots were generated using the Isoplot Excel program (Ludwig, 2008).

RESULTS

Geological framework of the Fazenda Coqueiro VHMS deposit

The Zn–Pb mineralization in the Fazenda Coqueiro deposit is hosted by the western metabasalt of the middle sequence, which predominates in the mineralized area and corresponds to a north-south-trending volcanic unit forming the hanging

wall of the massive sulfide level (Figure 3).

This lithological unit is approximately 500 m thick and extends for 5–6 km along strike within the deposit area. It consists predominantly of actinolite, plagioclase, quartz, and biotite, with calcite, titanite, and ilmenite occurring as accessory phases (Figure 4A).

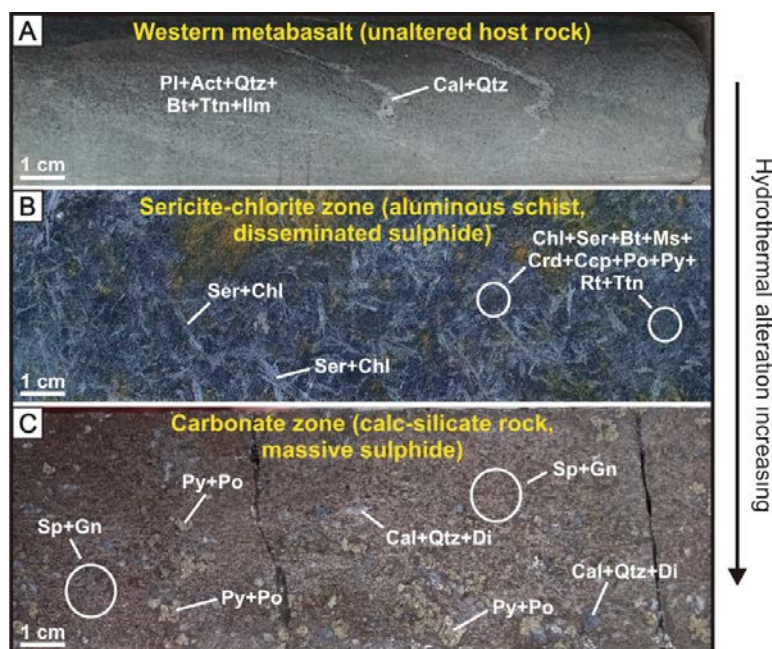


Figure 4 - Core samples of the host rock and hydrothermal alteration zones in the Fazenda Coqueiro VHMS deposit, illustrating progressive hydrothermal alteration from unaltered western metabasalt to the carbonate zone. A) Unaltered western metabasalt composed of plagioclase, actinolite, quartz, and biotite intersected by calcic-quartz veins with accessory calcite, titanite, and ilmenite. B) Sericite-chlorite zone (aluminous schist) composed of sericite, chlorite, biotite, muscovite, and cordierite, with disseminated chalcopyrite and trace amounts of pyrrhotite, pyrite, galena, sphalerite, rutile, and titanite. C) Carbonate zone (calc-silicate rock) composed of calcite, quartz, and diopside with massive sphalerite and trace amounts of galena, pyrrhotite, and pyrite. Mineral abbreviations: Act: actinolite, Bt: biotite, Cal: calcite, Ccp: chalcopyrite, Chl: chlorite, Crd: cordierite, Di: diopside, Gn: galena, Ilm: ilmenite, Ms: muscovite, Pl: plagioclase, Po: pyrrhotite, Py: pyrite, Qtz: quartz, Rt: rutile, Ser: sericite, Sp: sphalerite, and Ttn: titanite.

The stratabound massive sulfide lens and associated alteration zones are concordant with the main foliation and were affected by west-vergent thrusting that juxtaposed supracrustal rocks and basement slices within the Fazenda

Coqueiro deposit.

The antiform defined by the carbonate and sericite-chlorite zones continues westward into a sinformal structure, both characterized by subvertical axial planes and steeply dipping limbs (Figure 5).

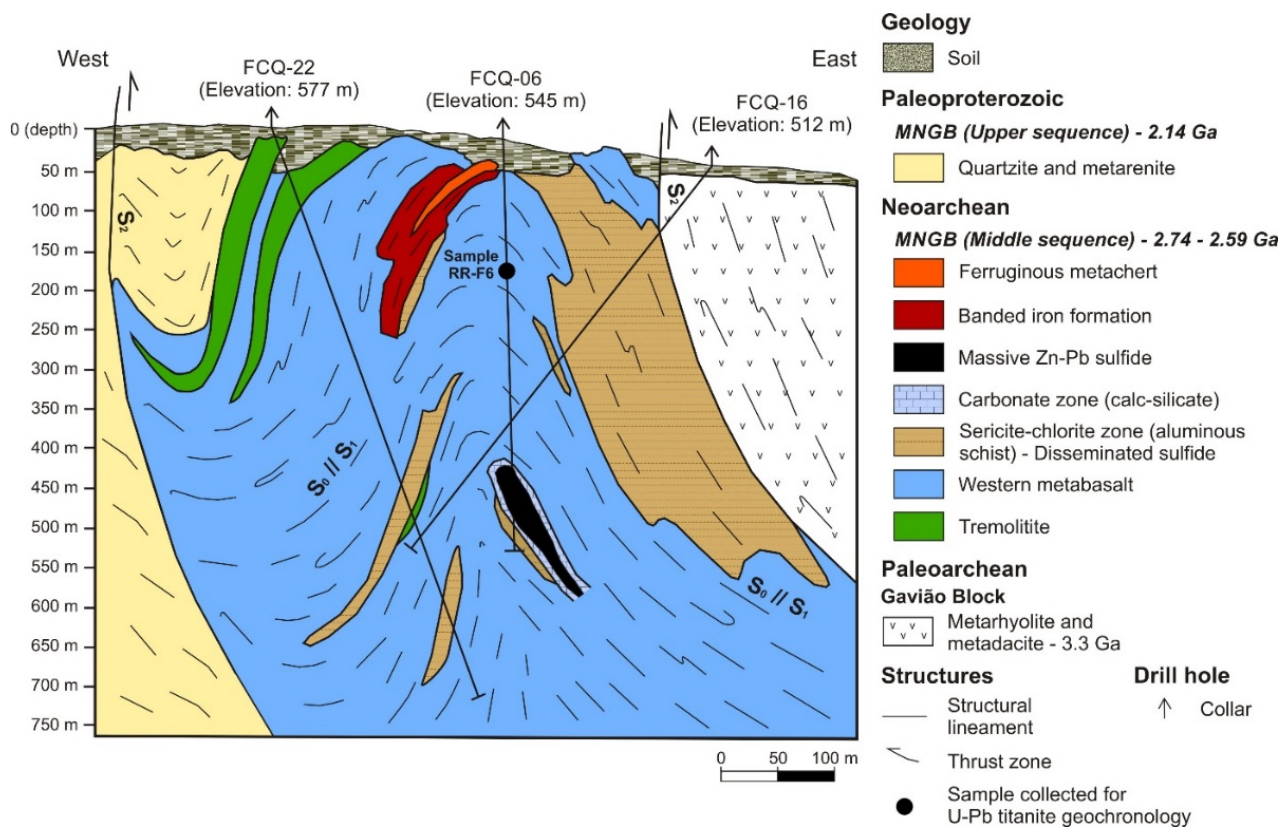


Figure 5 - Geological cross section of the Fazenda Coqueiro VHMS deposit showing the antiform, the distribution of the western metabasalt, and the carbonate and sericite-chlorite alteration zones based on outcrop observations and drill core descriptions, as well as the location of metabasalt sample RR-F6. The trace of the cross section is shown in the geological map in Figure 3.

Titanite occurrence and grain textures

Under petrographic analysis, the western metabasalt is anisotropic, inequigranular to aphanitic, green to gray in color, and exhibits a polygonal granoblastic microstructure. It is composed predominantly of actinolite, oligoclase, quartz, and biotite; hornblende was identified only in thin section (Figure 6A), whereas titanite and ilmenite occur as accessory phases. Biotite and actinolite grains are preferentially oriented, defining a well-developed foliation.

In the western metabasalt, titanite occurs in trace amounts and is uniformly distributed, aligned parallel to the foliation, and spatially associated with biotite (Figures 6B and 6C) and ilmenite (Figure 6D). Cathodoluminescence imaging of titanite grains from sample RR-F6 (location shown in Figure 5) reveals locally developed rims; however, the grains are predominantly homogeneous and lack sector zoning, oscillatory zoning, twinning, or “sugary” altera-

tion (Figure 7).

U–Pb Titanite Geochronology

Six spot analyses obtained from titanite grain cores in sample RR-F6 were considered valid and are presented in Table 2. The data were plotted on a Tera-Wasserburg inverse concordia diagram ($^{238}\text{U}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$), anchored to the initial common Pb composition. The analyses define a coherent linear array yielding a lower intercept age of 2086 ± 58 Ma (MSWD = 1.6; Figure 7) and an initial $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 1.011202.

Individual analyses display variable degrees of discordance, with percent concordance ranging from 69 to 84%. U contents range from 6.9 to 23.3 ppm and Th from 0.4 to 4.6 ppm, resulting in Th/U ratios between 0.02 and 0.26. The low Th/U ratios and the absence of internal zoning in cathodoluminescence images are consistent with chemically homogeneous titanite domains.

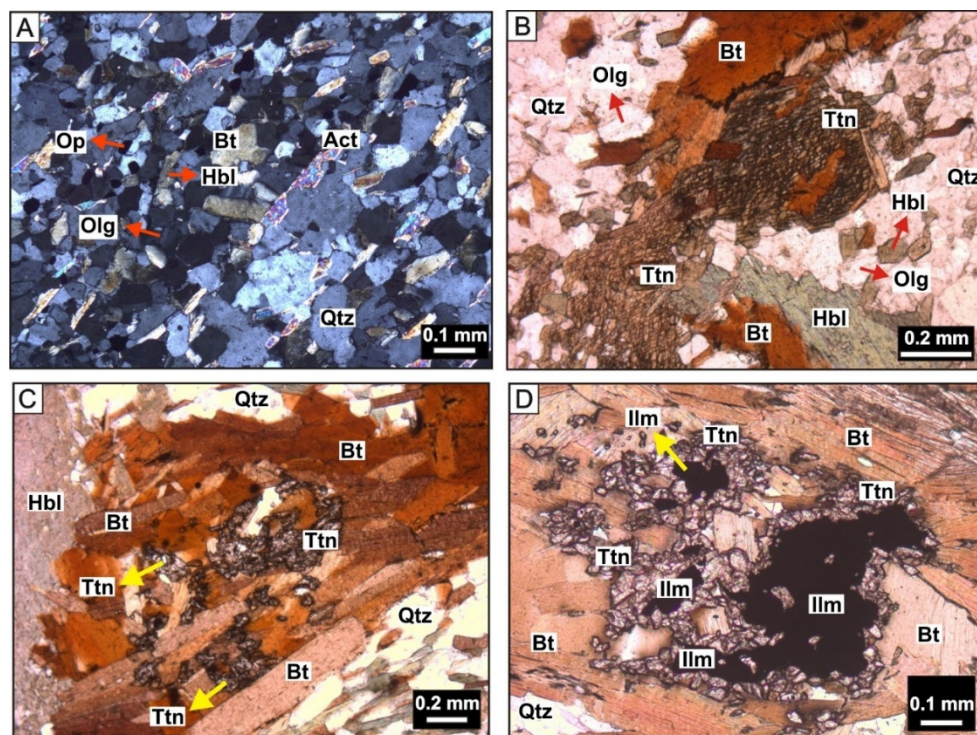


Figure 6 - Petrographic images of the western metabasalt and its titanite occurrences. A) Very fine-grained, polygonal granonematoblastic microstructure with oriented grains in the western metabasalt (cross-polarized light). B-C) Titanite grains spatially associated with biotite and aligned parallel to the foliation. D) Titanite grains bordering ilmenite within the foliation plane defined by biotite. Mineral abbreviations: Act: actinolite, Bt: biotite, Hbl: hornblende, Ilm: ilmenite, Olg: oligoclase, Op: opaquemine, Qtz: quartz, and Ttn: titanite.

Table 2 - U–Pb titanite analytical data for sample RR-F6 from the western metabasalt of the Fazenda Coqueiro VHMS deposit.

Spot number	137	141	142	144	145	149
f_{206} (%)*	0.93	0.38	0.42	0.46	0.41	0.79
U (ppm)	6.9	21.8	19.9	17.2	23.3	8.6
2se*	0.2	0.6	0.7	0.8	0.8	0.4
Th (ppm)	0.7	0.4	1.3	4.6	1.4	0.6
2se	0.1	0.1	0.1	0.3	0.1	0.1
Pb (ppm)	7.2	7.3	8.1	7.5	2.9	6.5
2se	0.3	0.3	0.3	0.3	0.2	0.2
Th/U	0.10	0.02	0.07	0.27	0.06	0.07
$^{206}\text{Pb}/^{204}\text{Pb}$	2001	4923	4492	4086	4534	2365
$^{207}\text{Pb}/^{206}\text{Pb}$ (ratio)	0.5106	0.2671	0.3033	0.2888	0.1789	0.4080
$2\sigma^*$	0.0288	0.0101	0.0111	0.0104	0.0066	0.0159
$^{207}\text{Pb}/^{235}\text{U}$ (ratio)	40.079	16.939	18.716	18.960	10.011	31.415
2σ	2.447	0.885	0.984	0.985	0.538	1.744
$^{206}\text{Pb}/^{238}\text{U}$ (ratio)	0.6036	0.4632	0.4503	0.4723	0.4050	0.5801
2σ	0.0387	0.0230	0.0218	0.0220	0.0189	0.0291
Rho*	0.47	0.45	0.52	0.42	0.39	0.59
$^{207}\text{Pb}/^{206}\text{Pb}$ age	4096	3260	3466	3352	2609	3832
2σ	73	59	57	55	61	55
$^{206}\text{Pb}/^{238}\text{U}$ age	3012	2436	2379	2473	2183	2903
2σ	154	101	95	96	85	115
$^{207}\text{Pb}/^{235}\text{U}$ age	3739	2924	3020	3030	2420	3502
2σ	60	51	52	50	48	55
% conc*	74	75	69	74	84	76

* f_{206} (%): Proportion of common Pb, expresses as a percentage. 2se: Analytical uncertainty reported as two standard errors (approximately 95% confidence). 2σ : Standard deviation. Rho: Error correlation coefficient between $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios, required for concordia calculations. % conc: Percent concordance between U–Pb ages.

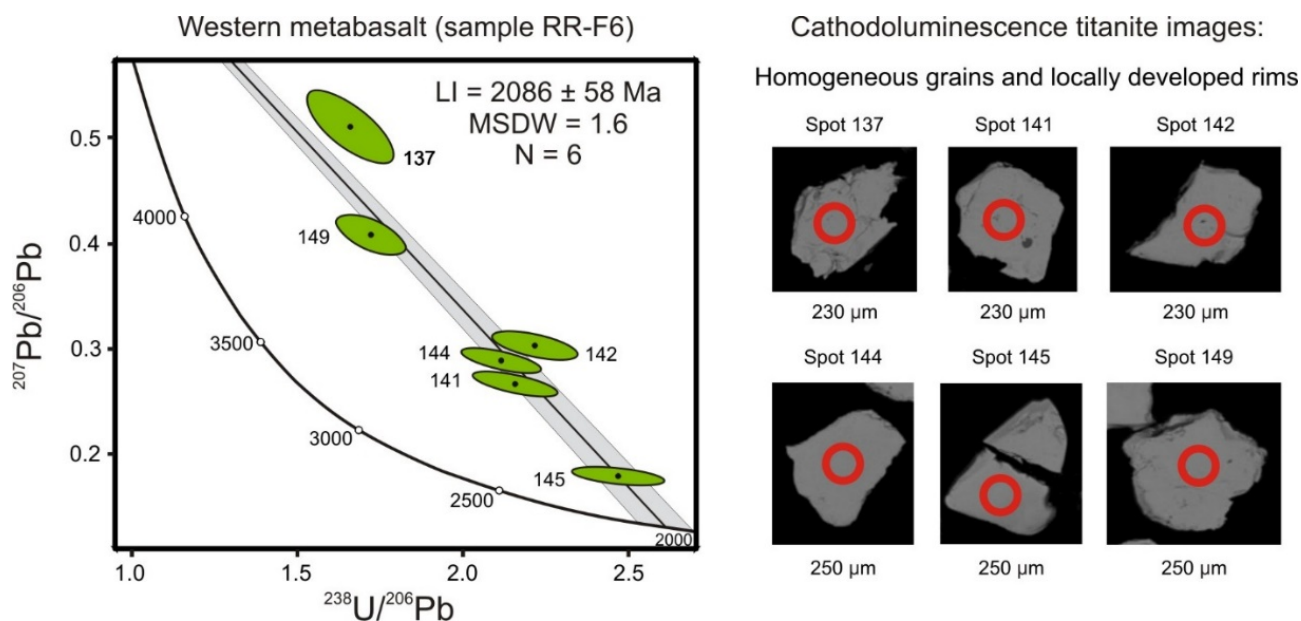


Figure 7 – Tera-Wasserburg inverse concordia diagram anchored to the initial common Pb composition of Stacey & Kramers (1975). U–Pb data from sample RR-F6 are shown alongside cathodoluminescence images of titanite grains. Circles in the images indicate the laser spot size; grain dimensions are reported separately. LI: lower intercept.

DISCUSSION

The U–Pb lower intercept age of 2086 ± 58 Ma obtained from titanite in sample RR-F6 records a Rhyacian-Orosirian tectono-metamorphic event that affected the Fazenda Coqueiro deposit and its host rocks.

The coherent linear array defined on the Tera-Wasserburg diagram, together with low Th/U ratios and cathodoluminescence features given by locally developed rims and predominantly homogeneous grains lacking sector zoning, oscillatory zoning, twinning, and “sugary” alteration, indicates that the analyzed titanite represents metamorphic recrystallization or neocrystallization. This age provides direct geochronological evidence for the regional tectono-metamorphic reworking previously inferred from structural relationships and greenschist- to amphibolite-facies mineral assemblages in the area (Spreafico et al., 2020).

Integration with the formerly established Pb–Pb sulfide age of 2747 ± 16 Ma, interpreted as the crystallization age of the Neoarchean VHMS mineralization (Spreafico et al., 2020), indicates a time gap of approximately 600 Ma between ore formation and regional metamorphism. Considering the sphalerite-galena-chalcopyrite-pyrrhotite-pyrite assemblage as cogenetic, this chronological framework establishes a temporal decoupling between the Neoarchean hydrothermal event and the subsequent Rhyacian-Orosirian tectono-metamorphic overprint. This metamorphic event

neither generated new sulfide mineralization nor reset the original Pb isotopic signature.

Textural relationships within the massive sulfide lens further support this interpretation and are consistent with the preserved architecture of a VHMS system as described by Galley et al. (2007; Figure 8A). Sulfide minerals occur as anhedral, non-elongated grains, except locally within the sericite-chlorite zone, and do not exhibit stretching. They display brittle deformation features and lack evidence of particle melting, remobilization, or high-temperature recrystallization (Spreafico et al., 2020).

The stability of the sphalerite-galena-chalcopyrite-pyrrhotite-pyrite assemblage under greenschist- to amphibolite-facies conditions is consistent with the absence of stretched or melting textures, which would require temperatures of approximately 730°C (Stevens et al., 2005; Tomkins et al., 2007). This temperature is significantly higher than the estimated metamorphic temperature of the Fazenda Coqueiro deposit (ca. 450°C; Spear, 1993). These conditions also fall within the stability field of titanite in metamafic rocks at pressures between 0.5 and 1.0 GPa (Kohn, 2017).

Although calcite in the carbonate zone exhibits polygonization and recrystallization, primary intergrowth textures between calcite and sulfides are preserved (Spreafico et al., 2020). Deformation was therefore preferentially accommodated within the surrounding sericite-chlorite alteration

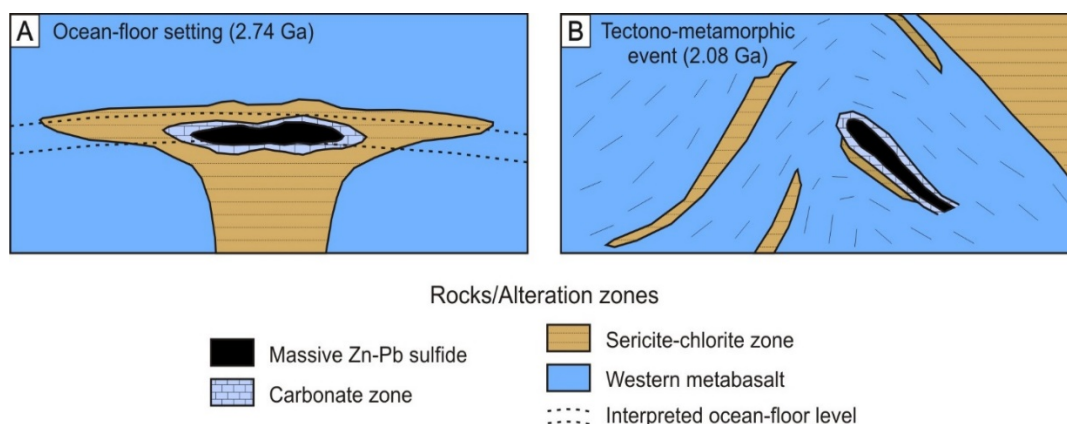


Figure 8 - Metallogenic model of the Fazenda Coqueiro VHMS deposit. A) Interpreted distribution and spatial relationships among volcanic rocks, the massive sulfide body, and hydrothermal alteration zones in an ocean-floor setting at 2747 ± 16 Ma. B) Positioning of the massive sulfide lens and associated alteration zones after the Rhyacian-Orosirian tectonic event (2086 ± 58 Ma).

zones and the metabasalt host rock, whereas the massive sulfide lens behaved as a mechanically competent body during folding and strain partitioning (Figure 8B)

The preservation of the Pb–Pb isochron age despite the Rhyacian-Orosirian metamorphic event demonstrates that the Pb isotope system in the Fazenda Coqueiro sulfides remained closed during greenschist- to amphibolite-facies metamorphism. Isotopic coherence among sphalerite, galena, chalcopyrite, pyrrhotite, and pyrite from both massive and disseminated mineralization indicates maintenance of the primary Pb signature during subsequent tectonic reworking.

The titanite age thus provides an external

chronological constraint supporting the interpretation that the Neoproterozoic isotopic system was not disturbed by later deformation and metamorphism.

These results have broader metallogenic and geodynamic implications, as the Fazenda Coqueiro deposit represents a Neoproterozoic ocean-floor VHMS system (Figure 9A) that was subsequently accreted into a collisional tectonic setting developed between the Gavião and Mairi blocks during the Rhyacian-Orosirian period (Figure 9B).

This tectonic event was coeval with the development of the Contendas-Jacobina lineament, in which the deposit is located, and preceded regional tectonic stabilization.

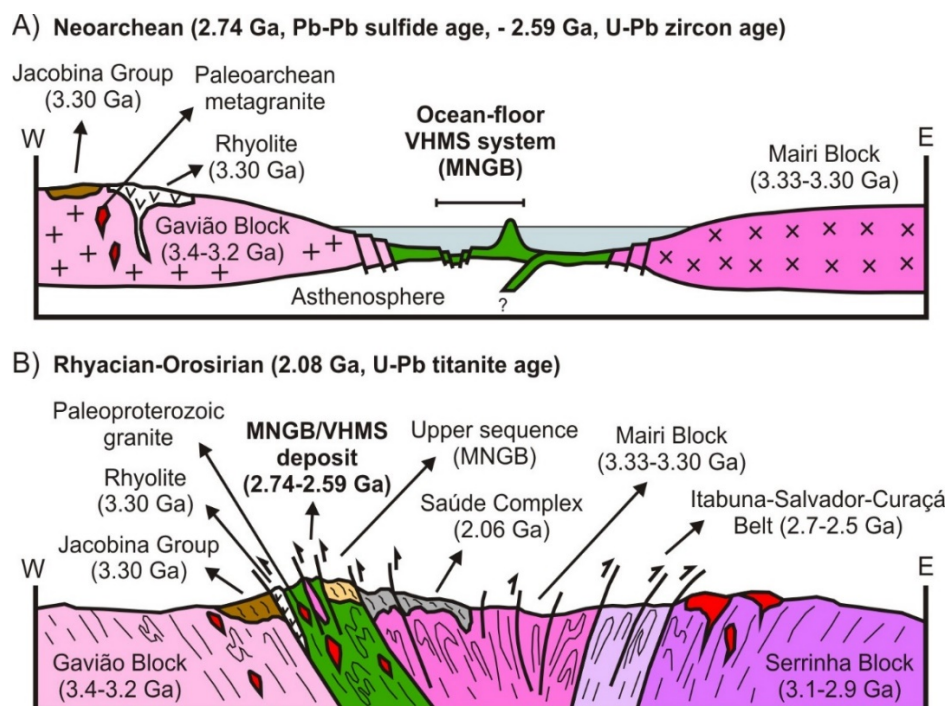


Figure 9 - Regional geological setting of the MNGB and the Fazenda Coqueiro VHMS deposit. A) Formation of the deposit in an ocean-floor VHMS system at 2747 ± 16 Ma. B) Tectonic configuration following the Rhyacian-Orosirian event, during which the MNGB and the Fazenda Coqueiro deposit were accreted at 2086 ± 58 Ma between cratonic blocks in the northern São Francisco Craton. Ages are detailed in Table 1.

The long-term preservation of primary sulfide paragenesis, textures, and isotopic signatures demonstrates that Neoarchean metallogenic systems may survive subsequent tectono-metamorphic events without complete isotopic resetting under low- to medium-grade metamorphic conditions.

Pb–Pb dating of sulfides therefore remains a reliable method for establishing primary mineralization ages in polydeformed Precambrian terranes. Although this approach has been more commonly applied to Phanerozoic terranes and VHMS deposits (Pomiès et al., 1998; Blichert-Toft et al., 2016; Tessalina et al., 2016), the Fazenda Coqueiro case demonstrates its robustness and applicability to Archean systems affected by later tectonothermal reworking.

In summary, integration of Pb–Pb sulfide and

U–Pb titanite geochronology provides a robust chronological framework for the Fazenda Coqueiro deposit.

The clear temporal decoupling between Neoarchean mineralization at 2747 Ma and Rhyacian-Orosirian metamorphism at 2086 Ma confirms the resilience of the Pb isotope system in sulfides during subsequent tectonothermal overprinting and improves the geodynamic understanding of the MNGB. Accordingly, this study highlights the potential for recognizing and reliably dating Neoarchean mineral systems in greenstone belts affected by later orogenic events, reinforcing the significance of integrated isotopic approaches in Precambrian metallogenic research and their implications for mineral exploration.

CONCLUSIONS

New LA-ICP-MS U–Pb titanite data from the metavolcanic sequence in the Fazenda Coqueiro VHMS deposit record a metamorphic event at 2086 Ma, corresponding to the Rhyacian-Orosirian tectonothermal evolution of the northern São Francisco Craton. This age constrains the timing of regional greenschist- to amphibolite-facies metamorphism that overprinted the Neoarchean volcanic succession.

When integrated with previously established TIMS Pb–Pb sulfide ages of 2747 Ma, these data demonstrate that Neoarchean mineralization predates Rhyacian-Orosirian metamorphism by approximately 600 Ma. The preservation of Archean Pb isotopic signatures in sphalerite, galena, chalcopyrite, pyrrhotite, and pyrite indi-

cates that the Pb isotopic system remained closed during metamorphism and deformation.

These results confirm that the Fazenda Coqueiro deposit represents a well-preserved Neoarchean VHMS system accreted into a reworked Paleoproterozoic terrane within the São Francisco Craton.

The combined application of Pb–Pb sulfide and U–Pb titanite geochronology provides a robust framework for resolving the temporal relationships between mineralization and metamorphism, with broader implications for metallogenic interpretation and mineral exploration in polydeformed Archean terranes, notably in Brazilian greenstone belts affected by Paleoproterozoic tectonothermal overprinting.

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