

RESEARCH ARTICLE

2.13 Ga Lawsonite/Barroisite-Bearing E-MORB Signature Metagabbro Associated with Spinel Metaperidotite from Itaguara (São Francisco Craton, Brazil): Oldest Blueschist-Facies Fragment of Oceanic Moho?

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Abstract: In close association with Paleoproterozoic retroeclogite and accretionary prism-related mica-quartz schist, a 2.13 Ga (metamorphic titanite U-Pb age) lawsonite/barroisite-bearing E-MORB signature metagabbro associated with spinel metaperidotite is found in the Itaguara Sequence from southern São Francisco craton, Brazil. Petrography and pressure-temperature equilibrium phase diagrams suggest that the metagabbro experienced blueschist-facies metamorphism, attaining peak metamorphic conditions at ~16 kbar and ~450 °C during subduction. The retrograde metamorphic path crossed epidote amphibolite-facies, in which the mineral assemblage found in metaperidotite (olivine, clinopyroxene, spinel, serpentine, chlorite, talc, and tremolite) was stable during a ca. 2.1 Ga continental collision-related exhumation that occurred between the Archean Campo Belo/Bonfim and Divinópolis complexes. This geological framework suggests that the metagabbro and adjacent spinel metaperidotite represent a subducted and exhumed blueschist-facies fragment of a Paleoproterozoic oceanic Mohorovičić (Moho) discontinuity, thus establishing the Itaguara metagabbro as the oldest-known occurrence of retrogressed blueschist and providing evidence for the activity of the modern-style plate tectonics more than 2 Gyr ago.

Keywords: Metagabbro and metaperidotite; Blueschist; Paleoproterozoic; Moho; São Francisco craton

1. Introduction

In many orogenic belts, rocks that have undergone subduction and exhumation processes can be found in their internal sectors, such as suture zones. To under-

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stand the geotectonic timeline of these belts, it is necessary to estimate the pressure (P) and temperature (T) paths of high-pressure subduction-related rocks^[1]. Blueschists are rocks that form due to subduction, indicating high-pressure burial at relatively low temperatures (low T/P rocks)^[2,3]. The oldest blueschists known so far are Neoproterozoic, some of which are found alongside strongly serpentinized plagioclase- or spinel peridotite^[1]. Despite this, it is believed that subduction of oceanic crust to mantle depths has been occurring since 3 billion years ago^[4]. So, a major question is: Where are the pre-0.8 Ga blueschists?

An investigation into the Itaguara Sequence (IS) of the southern São Francisco Craton (SFC) has revealed that a Paleoproterozoic accretionary prism was formed above a paleo-subduction zone. The study showed that during a continental collision at around 2.05 ± 0.05 Ga, the metamorphic peak achieved ~ 18.5 kbar and ~ 626 °C^[5,6]. This episode of syn-collisional metamorphism has also been regionally described between 2.10 and 2.05 Ga from titanite and monazite geochronology^[7,8]. The study also found that a 2.20 ± 0.05 Ga retroeclogite with E-MORB signature occurs in IS included in suture zone formed by a collision between the Archean Campo Belo/Bonfim and Divinópolis Complexes, close to the cited accretionary wedge^[9]. Similar amphibole eclogite facies metamorphic peak stage of 17–20 kbar and 600–700 °C have been described for these retroeclogites during the same ca. 2.1 Ga continental collision^[9].

Several studies demonstrate that barroisite-bearing metabasites retrometamorphosed at epidote amphibolite-facies have been formed in association with tectonic processes of subduction followed by collision-related exhumation^[10,11]. By using petrography, mineral chemistry, thermobarometry, geochemistry, and titanite U-Pb geochronology, the petrology of the recently discovered lawsonite and barroisite-bearing metagabbro associated with spinel metaperidotite, which occur alongside 2.16 Ga amphibolites (zircon U-Pb age^[12]) from the Paleoproterozoic IS, is herein presented.

Lawsonite is a diagnostic mineral of paleo-subduction zone processes^[13,14]. Given that the oldest known occurrences of lawsonite-bearing blueschists are from Neoproterozoic era^[1,14], the presence of lawsonite in these Paleoproterozoic rocks from IS may represent a new constraint in the age of blueschists on Earth. The possibility of this rock association to represent the subduction and exhumation of blueschist-facies fragment of Paleoproterozoic oceanic Mohorovičić discontinuity (Moho—boundary between oceanic crust and mantle) is also herein evaluated.

2. Geological Setting

The São Francisco craton (SFC), located in Brazil, is part of a paleoplate that was consolidated at the end of the Paleoproterozoic era. It is the South American equivalent of the African Congo Craton^[15]. The southern region of SFC is surrounded by Neoproterozoic orogenic belts, such as the Araçuaí Belt^[16] in the East and the Brasília Belt^[17] in the West (Figure 1A). The Archean core of the southern SFC, which dates back to 3.2–2.6 billion years ago, comprises mainly of granite-gneisses terranes^[18] and greenstone belts (Figure 1B, 1C). The Rio das Velhas Supergroup is a part of this region and includes a mix of mafic to ultramafic rocks, intermediate to felsic volcanic with volcanoclastic rocks and clastic sediments^[19,20]. The Minas Supergroup is relatively younger and is composed of clastic and chemical metasedimentary units, which includes the Quadrilátero Ferrífero mining district (Figure 1B) that contains banded iron formations with a minimum deposition age of ~ 2.0 Ga^[21].

Machado Filho et al.^[22] characterized the Divinópolis Metamorphic Complex, which is part of the Archean granite-gneiss basement. Another study in this basement by Teixeira et al.^[18] identified three complexes—Campo Belo, Bonfim, and Belo Horizonte (Figure 1B, 1C)—each consisting of various types of rocks, including gneisses, migmatites, granitoids, and felsic, mafic and ultramafic rocks. The Archean core of the southern SFC has undergone four periods of magmatism^[23–25]. The first event, known as Santa Barbara, dates back to 3.22–3.20 Ga, and is associated with the formation of the Paleoproterozoic Tonalite-Trondhjemite-Granodiorite (TTG) crust. The second event, Rio das Velhas I, occurred between 2.92–2.85 Ga, and contributed to the growth of the crust. The third event, Rio das Velhas II, took place during the Neoproterozoic period (2.80–2.76 Ga) and was followed by a period of convergence and voluminous potassic magmatism. This period is believed to have stabilized the southern part of the SFC between 2.75–2.68 Ga^[24], and was called the Mamona event^[25]. A study on the zircon provenance of the sedimentary record preserved in the Rio das Velhas Supergroup suggests the presence of a succession of magmatic arcs and convergent basins in the region until ~ 2.7 Ga^[26].

During the Rhyacian-Orosirian cycle, which took place around 2.2–1.9 Ga, a significant period of crustal growth took place in several parts of the SFC and adjacent crustal blocks of South America. This event was previously known as “Transamazonian”^[18] and has now been renamed Minas accretionary orogeny in the southern SFC^[28]. This period is associated with the accretion of juvenile

crust that formed the Mineiro Belt^[29,30] and led to extensive reworking of terranes located at the margins of the craton^[31]. According to Alkmim and Marshak^[32], a significant part of the southern portion of the São Francisco paleoplate was in the foreland of the Transamazonian orogeny. The NW limit between these Paleoproterozoic terrains and the Archean core is defined by the NE-SW Jeceaba Bom-Sucesso lineament (JBSL in Figure 1B), as suggested by several studies^[28,30,33].

Most Paleoproterozoic rocks are located to the south-east of the JBSL, but there are a few exceptions. One of

these exceptions is the Kinawa migmatite of the Itapeçerica Metamorphic Complex, where 2.7 billion-year-old TTG metagranodiorites from the Campo Belo Metamorphic Complex were partially melted during the Paleoproterozoic in the Cláudio Shear Zone (CSZ in Figure 1B). U-Pb SHRIMP zircon age of 2.05–2.03 Ga^[34] confirm the existence of a Paleoproterozoic episode previously documented from monazite in sillimanite-cordierite-garnet-biotite gneiss (graphite-rich khondalite) near CSZ^[35]. Additionally, several generations of mafic dyke swarms (Figure 1B) are recognized in the southern SFC^[36].

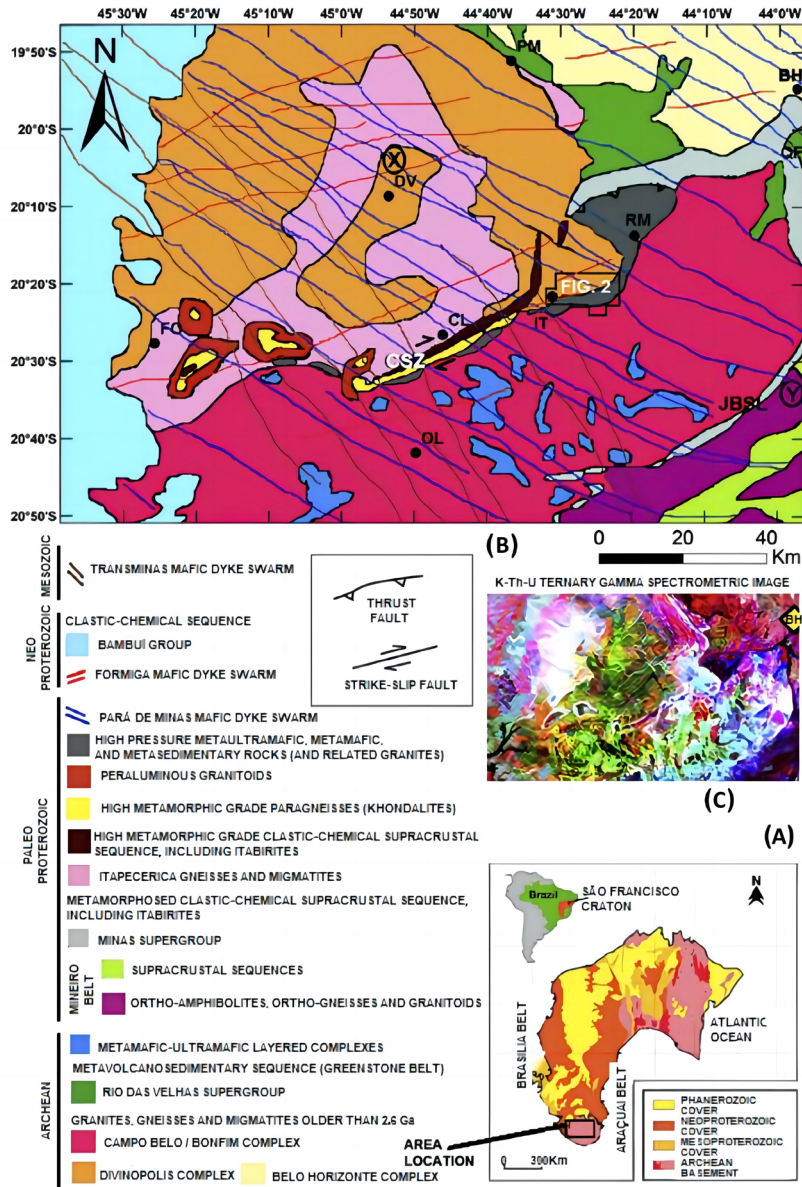


Figure 1. Regional geological setting. (A) The São Francisco Craton. (B) Geological map of the Southern São Francisco Craton^[5], permitted reproduction—copyright Elsevier. QF—Quadrilátero Ferrífero, JBSL—Jeceaba-Bom Sucesso lineament, CSZ—Cláudio shear zone. Cities: BH—Belo Horizonte, PM—Pará de Minas, 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^[27].

The region between Itaguara and Crucilândia towns hosts a narrow NE-SW belt where the Itaguara Sequence (IS) is located. This sequence comprises metamorphosed mafic-ultramafic layered rocks (Figure 2), including amphibolites (zircon U-Pb age of 2.16 Ga^[12]) and talc-actinolite metaultramafites (talc nephrites). The metaultramafic rocks are strongly folded and deformed and contain coarse olivine nodules within a fine to medium grained groundmass of talc and actinolite. Additionally, the IS also features metasedimentary rocks such as iron formations, quartzites, mica-quartz schists, and the Córrego do Peixoto granite (crystallization U-Pb age of ~2.0 Ga^[12]). The region is intersected by high angle dextral strike-slip and northward reverse faults, as well as two mafic dyke systems^[37].

Chaves and Porcher's research^[9] shows that Itaguara region, where IS is located, contains retrogressed eclogite (retroeclogite). This type of rock formed during the Paleoproterozoic era, when the Archean Divinópolis

and Campo Belo/Bonfim Complexes collided to create a suture zone. The retroeclogite in Itaguara has garnet porphyroblasts embedded in a fine-grained matrix of amphibole, biotite, and quartz, with scarce omphacite and phengite. The rock's protolith was E-MORB ($T_{DM} \sim 2.47$ Ga), which underwent eclogitization around 2.20 ± 0.05 Ga (garnet and whole rock Sm-Nd isochronic age), as evidenced by omphacite formation during high-pressure prograde stage at a depth of around 70 km. During the continental collision around 2.1 Ga, the rock experienced an amphibole eclogite-facies metamorphic peak stage of 17–20 kbar and 600–700 °C. Tectonic exhumation-related decompression during collision likely led to partial melting of the eclogitic rock. Finally, during the orogenic collapse, a late-stage decompression estimated between 5–8 kbar and 550–650 °C under amphibolite-facies overprint caused the appearance of kelyphitic reaction rims (symplectite) around garnet crystals^[9].

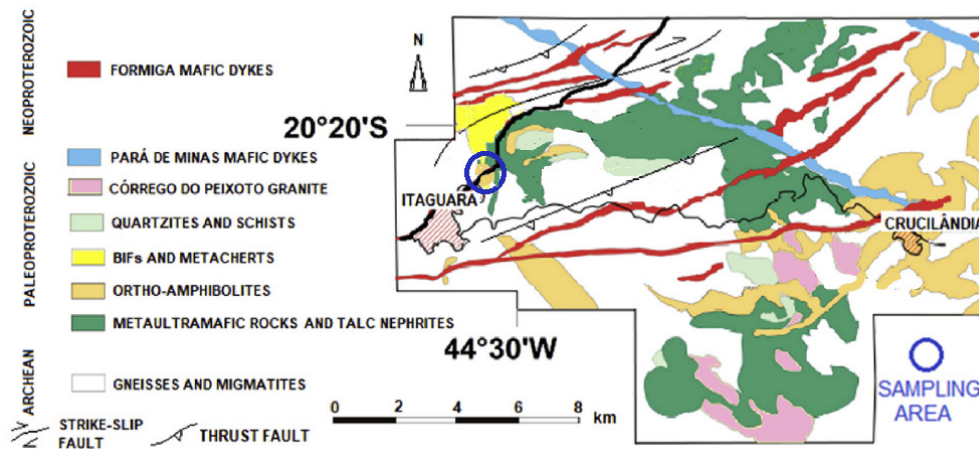


Figure 2. Geological map of the Itaguara Sequence (IS), with metagabbro sampling location close to the Itaguara town (modified from Goulart and Carneiro^[37] and Chaves et al.^[5], permitted reproduction—copyright Elsevier).

Studies conducted on the mica-quartz schist and Córrego do Peixoto granite from IS have revealed that they underwent metamorphic peak at around 2.05 ± 0.05 Ga. The metamorphism led to amphibole eclogite-facies at a depth of approximately 60 km, with a geothermal gradient of about 10 °C/km, which is typical of subduction zones in continental collision settings^[5,6]. The high-pressure (HP) mica-quartz schist underwent a decompression process triggered by continental collision-related tectonic exhumation, leading to partial melting and generation of the peraluminous (S-type) syn-collisional Córrego do Peixoto granite. The granite solidus field was in wet conditions, and the metamorphism occurred at around 18.5 kbar and 626 °C. The

monazite age of 1.93 ± 0.02 Ga found in both the mica-quartz schist and granite is probably related to the late-stage orogenic collapse-related decompression, with amphibolite-facies overprint^[5,6].

The IS extends northeast towards the Rio Manso Sequence (RMS) near the town of Rio Manso. RMS consists of a variety of meta-ultramafic rocks such as spinel-bearing ultramafic rocks, metabasalts and other types. The spinel-bearing ultramafic rocks were categorized into four petrographic types including orthopyroxene and olivine-bearing rocks, Ca amphibole-bearing rocks, talc and/or serpentine-rich rocks, and talc-bearing rocks^[38]. In the region, a type of olivine can be found exhibiting a pseudo-spinifex texture that

was formed during high-grade metamorphism alongside talc and serpentine. According to the analysis conducted by Pinheiro and Nilson ^[38], this olivine texture is similar to the spinifex texture found in metakomatiitic rocks in the RMS. Additionally, there are other rocks in the area, such as iron formations, garnet amphibolites, and metasedimentary rocks like quartzites and sericite-quartz schists. These rocks have been interpreted as Archean in age ^[38] but IS and RMS have been estimated as Paleoproterozoic in the legend of Figure 1 due to the geochronological results ^[5] and differences in K-Th-U gamma spectrometric signal between them and Rio das Velhas Supergroup rocks (Figure 1C).

According to a study by Chaves et al. ^[5], the mica-quartz schist found in the IS region is believed to be a component of a Paleoproterozoic accretionary wedge formed above a paleo-subduction zone. Ophiolites, which are typically associated with an accretionary wedge in continental collision settings, are represented in the IS and RMS by metamafic-ultramafic rocks. Additionally, the NW boundary between the Archean core and Paleoproterozoic terrains in the IS and RMS region can now be demarcated by this ophiolitic landscape and is limited southwestward by the Cláudio shear zone (CSZ).

3. Methods

After field work close to Itaguara town (Figure 2), polished thin sections of distinct bands of metagabbro and associated metaperidotite (Figure 3) from Paleoproterozoic IS suture zone (coordinates 20.367986 S and 44.470016 W) were prepared for petrographic investigation and mineral microanalyses. After examining the metagabbro minerals with a petrographic optical microscope, they were further analyzed at the Federal University of Minas Gerais (UFMG) using a JEOL electron microprobe (EMP). The analysis was performed using a wavelength dispersive X-ray spectroscopy (WDS) under operating conditions of 15 kV accelerating voltage and 20 nA sample current. Calibration was done using oxide and silicate standards including quartz (Si), rutile (Ti), corundum (Al), almandine (Fe), periclase (Mg), rhodonite (Mn), anorthite (Ca), jadeite (Na), and sanidine (K). The counting times were 20 seconds on the peak and 10 seconds on the background. Three spectrometers were used simultaneously and the ZAF correction procedure was applied. To prevent interaction between different crystals during analyses, the electron beam was focused on the minimum size of 2 micrometers. Garnet compositional maps were generated through WDS.



Figure 3. Field exposure of metagabbro and metaperidotite. (A) Bluish metagabbro top view and highlight of the sample 2 (brownish, under the hammer) taken from foliation surface. (B) Bluish layered metagabbro side view and highlighted positions of the samples 1 (light-colored) and 3 (dark-colored) in the rock. (C) Dark-colored metaperidotite with highlighted position of the sample 4. (D) Layered metaperidotite side view.

Rock samples 1 and 2, which displayed different mineralogical associations, were sent to the SGS-Geosol Laboratory in Brazil for whole rock geochemical analysis. The samples were milled in a tungsten mill and then melted with lithium metaborate and dilute nitric digestion. The laboratory conducted ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) analysis to determine the major elements and five trace elements (Ba, Nb, Sr, Y, Zr). In addition, they used ICP-MS (Inductively Coupled Plasma Mass Spectrometry) to analyze fourteen rare earth elements and other trace elements. The detection limit is approximately 0.01% for the major elements and 1 ppm for the other elements. The accuracy of the analysis ranges from 1–2% for the relative standard deviation. The laboratory also determined the loss of ignition (LOI) through mass difference after heating the samples at 1000 °C.

The 2020 version of the Theriak-Domino software^[39] with ds62 database^[40] was utilized to produce P - T equilibrium phase diagrams (P - T pseudosections) using bulk rock compositions in the system Na-Ca-K-Fe-Mg-Al-Si-H-Ti-O (NCKFMASHTO). All fluid phases were considered as H₂O. Presented throughout the text, conventional geothermobarometers have also been used in order to investigate P and T during the metamorphic evolution of the metagabbro.

Ten crystals of metamorphic titanite were selected from sample 1 to constraint the age of metamorphism of the metagabbro, since this mineral was not found in a few igneous preserved areas of the rock, but only in the metamorphosed ones, which show idiomorphic titanite. U-Pb geochronology was used on 30 to 50 micrometres polished thin section, and the data were obtained using a Thermo Scientific Element II single collector (SF) ICP-MS coupled to a CETAC UV Nd: YAG-213 nm laser ablation system of the Isotopic Geochemistry Laboratory at Federal University of Ouro Preto—UFOP—Brazil. The acquisition method produced over 810 mass scans during 25 seconds of background acquisition and 30 seconds of sample ablation. Each analysis utilized a spot size of 40 µm with a repetition rate of 10 Hz and a laser fluence of approximately 3.5 J/cm². The depth penetration was 0.6 µm/s, and the integration time was 0.9 seconds. Raw counts were adjusted offline for background signal, instrumental mass bias, and time-dependent elemental fractionation. The data were reduced by Glitter software^[41,42] and an in-house spreadsheet^[43,44]. Due to the varying initial Pb ratios of the titanite and the technical difficulties in measuring ²⁰⁴Pb via LA-ICP-MS^[45], none of the U-Pb analyses from UFOP were corrected for Pb_c. The ages have been

reported accordingly as lower intercepts on the Tera-Wasserburg Concordia diagram, obtained from Isoplot package^[46]. All uncertainties on dates/ages are reported as 2s. Four titanite reference material known as Bear Lake, BLR-1, Khan River and Mount Painter have been dated to check measurements, and produced their expected ages of 1064 Ma, 1054 Ma, 542 Ma and 444 Ma respectively^[47].

4. Results

4.1 Field Exposure, Petrography, Mineral Chemistry and Metamorphic Assemblages

In field exposure (Figure 3), there are only scattered blocks of bluish metagabbro and dark-colored metaperidotite alongside the road and it was not possible to find geological contact between them. Results of petrographic investigation and mineral microanalyses in different bands of layered metagabbro (samples 1, 2 and 3) and associated metaperidotite (sample 4), shown in Figure 3, are presented below with suggestions of the respective probable prograde, peak and retrograde metamorphic phase assemblages. This paper employs the mineral name abbreviations provided by Whitney and Evans^[48].

Sample 1

Remains of igneous texture containing labradoritic plagioclase (An₅₁₋₅₅) and augitic clinopyroxene (Wo₄₈En₃₄Fs₁₈) have been found in sample 1 of the metagabbro (Figure 4A) and representative analyses of these minerals are presented in Table 1. Figure 4B shows plagioclase (Pl), clinopyroxene (Cpx) and magnetite (Mag) scattered in a granoblastic texture. The metamorphism advanced and new minerals like garnet (Grt), clinozoisite (Czo), titanite (Ttn) and quartz (Qz) appeared (Figure 4C, 4D and Table 2), which represent the prograde metamorphic phase assemblage.

Lawsonite (Lws—preserved inside garnet that was altered to chlorite is highlighted in grey circle of Figure 4D) is probably the mineral formed during a metamorphic peak. During retrograde metamorphism, phengite (Ph) was formed, garnet (Grt) was replaced by chlorite (Chl—Figure 4D) and Cpx was replaced by magnesium-hornblende (Hbl) as shown in Figure 4E and Table 2. Subhedral to euhedral prehnite (Prh) crystals are also found in sample 1 of the metagabbro (Figure 4F and Table 2) and they seem to represent the final evolution of the rock. Thus, Ph, Chl, Hbl and, finally, Prh should be the retrograde metamorphic mineral assemblage.

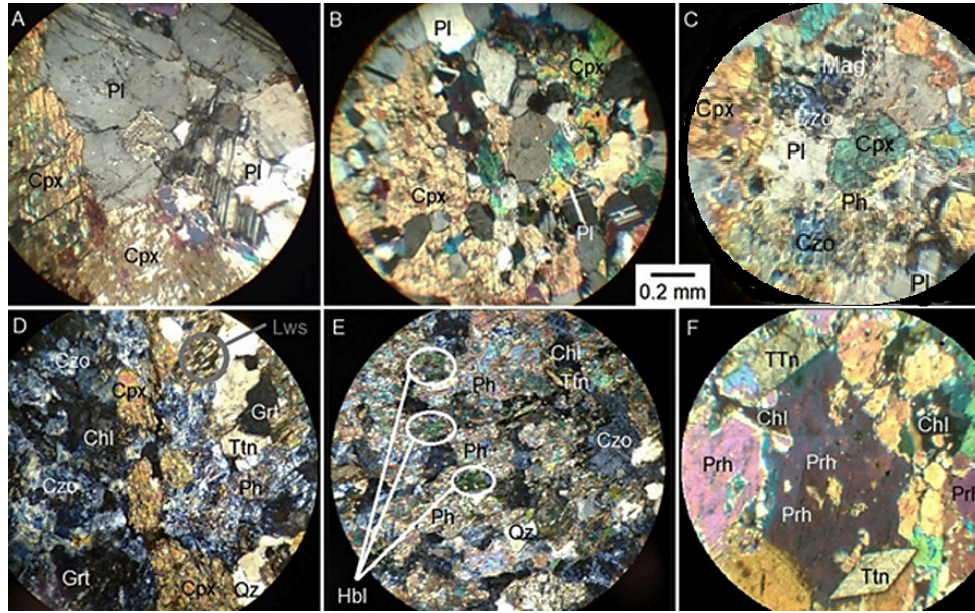


Figure 4. Photomicrographs of sample 1 under crossed polarizers. (A) Preserved igneous gabbroic texture. (B) Metagabbro with recrystallized plagioclase (Pl) and clinopyroxene (Cpx). (C) Magnetite (Mag), phengite (Ph) and clinozoisite (Czo). (D) Clinopyroxene (Cpx), garnet-Grt (in substitution to chlorite-Chl), quartz (Qz), clinozoisite (Czo), titanite (Ttn) and lawsonite (Lws—preserved inside garnet). (E) Hornblende (Hbl), clinozoisite (Czo), and more phengite (Ph). (F) Prehnite (Prh) and titanite (Ttn).

Table 1. Representative analyses of plagioclase (Pl) and clinopyroxene (Cpx) from a preserved igneous portion of the metagabbro (sample 1).

	Pl-1	Pl-2	Pl-3	Pl-4		Cpx-1	Cpx-2
SiO ₂	55.24	54.92	55.32	54.75	SiO ₂	54.03	53.17
TiO ₂	0.03	0.05	0.00	0.07	TiO ₂	0.04	0.00
Al ₂ O ₃	27.53	27.87	27.72	27.75	Al ₂ O ₃	0.76	0.72
FeO	0.09	0.17	0.13	0.14	FeO	10.77	10.90
MnO	0.01	0.00	0.02	0.00	MnO	0.54	0.50
MgO	0.08	0.10	0.04	0.06	MgO	11.40	11.76
CaO	11.00	11.52	11.10	11.25	CaO	22.78	23.05
Na ₂ O	5.47	5.32	5.74	5.80	Na ₂ O	0.31	0.31
K ₂ O	0.11	0.07	0.14	0.06	K ₂ O	0.12	0.10
Total	99.56	100.01	100.19	99.89	Total	100.75	100.50
32 ox					6 ox		
Si	10.02	9.94	9.99	9.93	Si	2.02	2.00
Ti	0.00	0.01	0.00	0.01	Al	0.05	0.03
Al	5.88	5.94	5.90	5.93	Fe	0.34	0.34
Fe	0.01	0.03	0.02	0.02	Mn	0.02	0.02
Ca	2.14	2.23	2.15	2.18	Mg	0.63	0.66
Na	1.92	1.86	2.01	2.04	Ca	0.91	0.93
K	0.02	0.02	0.03	0.01	Na	0.02	0.02
Total	20.01	20.03	20.09	20.13	K	0.01	0.00
					Total	3.98	4.00
An	52.32	54.27	51.27	51.55	Wo	47.93	47.72
Ab	47.08	45.33	47.98	48.13	En	33.39	33.87
Or	0.61	0.40	0.75	0.32	Fs	18.68	18.42

Table 2. Representative analyses of clinozoisite (Czo), phengite (Ph), lawsonite (Lws), chlorite (Chl), titanite (Ttn), hornblende (Hbl) and prehnite (Prh) from metamorphosed portion of the metagabbro (sample 1).

	Czo-1	Czo-2		Ph-1	Ph-2	Ph-3	Ph-4	Ph-5	Ph-6	Ph-7
SiO ₂	39.68	39.62	SiO ₂	49.68	49.26	49.48	49.89	49.43	49.52	49.59
TiO ₂	0.05	0.00	TiO ₂	0.02	0.06	0.00	0.00	0.13	0.01	0.00
Al ₂ O ₃	29.27	29.10	Al ₂ O ₃	32.81	32.37	33.47	32.40	32.64	32.82	32.75
Fe ₂ O ₃	4.29	4.61	FeO	1.96	1.60	1.81	1.84	1.58	1.68	1.54
MnO	0.16	0.00	MnO	0.00	0.04	0.00	0.04	0.02	0.00	0.03
MgO	0.13	0.24	MgO	2.86	2.56	2.26	2.47	2.53	2.66	2.45
CaO	23.88	23.91	CaO	0.17	0.24	0.15	0.17	0.17	0.20	0.17
Na ₂ O	0.17	0.16	Na ₂ O	0.18	0.30	0.13	0.22	0.16	0.21	0.14
K ₂ O	0.08	0.04	K ₂ O	10.03	10.31	10.16	10.90	10.82	10.66	10.03
Total	97.72	97.67	Total	97.71	96.73	97.46	97.93	97.47	97.75	96.71
25 ox			11 ox							
Si	6.24	6.25	Si	3.21	3.22	3.21	3.24	3.22	3.21	3.23
Ti	0.01	0.00	Al(IV)	0.79	0.78	0.79	0.76	0.78	0.79	0.77
Al	5.43	5.41	Al(VI)	1.71	1.72	1.76	1.71	1.72	1.72	1.75
Fe(iii)	0.25	0.27	Fe(ii)	0.11	0.09	0.10	0.10	0.09	0.09	0.08
Mn	0.02	0.00	Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.03	0.06	Mg	0.28	0.25	0.22	0.24	0.25	0.26	0.24
Ca	4.02	4.04	Ca	0.01	0.02	0.01	0.01	0.01	0.01	0.01
Na	0.05	0.05	Na	0.02	0.04	0.02	0.03	0.02	0.03	0.02
K	0.02	0.01	K	0.83	0.86	0.84	0.90	0.90	0.88	0.83
Total	16.07	16.08	Total	6.96	6.98	6.94	6.99	6.99	6.99	6.94

Table 2 (continued)

	Lws-1	Lws-2		Chl-1	Chl-2		Ttn-1		Hbl-1	Hbl-2		Prh-1	Prh-2
SiO ₂	38.99	38.68	SiO ₂	28.16	28.60	SiO ₂	31.62	SiO ₂	46.16	46.52	SiO ₂	44.80	44.23
TiO ₂	0.00	0.03	TiO ₂	0.30	0.39	TiO ₂	37.82	TiO ₂	0.56	0.71	TiO ₂	0.04	0.00
Al ₂ O ₃	32.52	32.71	Al ₂ O ₃	18.56	18.48	Al ₂ O ₃	1.36	Al ₂ O ₃	8.35	9.07	Al ₂ O ₃	24.06	24.44
FeO	0.86	0.28	FeO	27.66	27.22	FeO	0.51	FeO	13.16	13.28	FeO	0.21	0.16
MnO	0.02	0.03	MnO	0.24	0.28	MnO	0.16	MnO	0.41	0.30	MnO	0.12	0.18
MgO	0.21	0.10	MgO	12.64	12.76	MgO	0.04	MgO	13.58	13.30	MgO	0.11	0.10
CaO	17.28	17.94	CaO	0.12	0.19	CaO	28.48	CaO	11.71	11.47	CaO	26.56	26.76
Na ₂ O	0.77	0.90	Na ₂ O	0.02	0.02	Na ₂ O	0.06	Na ₂ O	1.05	1.10	Na ₂ O	0.10	0.15
K ₂ O	0.16	0.08	K ₂ O	0.65	0.71	K ₂ O	0.03	K ₂ O	0.20	0.25	K ₂ O	0.03	0.02
Total	90.79	90.75	Total	88.35	88.65	Total	100.08	Total	95.18	96.00	Total	96.02	96.05
								23 ox					
								Si	6.88	6.89			
			28 ox					Al(IV)	1.12	1.11			
8 ox			Si	5.96	6.01	5 ox		Al(VI)	0.35	0.48	11 ox		
Si	2.00	1.99	Al(IV)	2.04	1.99	Si	1.03	Fe(iii)	0.30	0.11	Si	3.06	3.02
Ti	0.00	0.00	Al(VI)	2.59	2.59	Ti	0.93	Ti	0.06	0.08	Ti	0.00	0.00
Al	1.97	1.98	Ti	0.05	0.06	Al	0.05	Fe(ii)	1.34	1.54	Al	1.94	1.97
Fe	0.04	0.01	Fe(ii)	4.89	4.79	Fe	0.01	Mn	0.05	0.04	Fe	0.01	0.01
Mn	0.00	0.00	Mn	0.04	0.05	Mn	0.00	Mg	3.02	2.94	Mn	0.01	0.01
Mg	0.02	0.01	Mg	3.99	4.00	Mg	0.00	Ca	1.87	1.82	Mg	0.01	0.01
Ca	0.95	0.99	Ca	0.03	0.04	Ca	0.99	Na	0.30	0.32	Ca	1.94	1.96
Na	0.08	0.09	Na	0.01	0.01	Na	0.00	K	0.04	0.05	Na	0.01	0.02
K	0.01	0.00	K	0.18	0.19	K	0.00	Total	15.34	15.36	K	0.00	0.00
Total	5.06	5.07	Total	19.77	19.73	Total	3.02	Name	Mg-Hbl	Mg-Hbl	Total	6.98	7.00

Source: Amphibole name according to Leake et al. ^[49].

Sample 2

Visible in hand sample and with pleochroism in shades of blue, elongated barroisite (Brs) crystals occur partially replaced by brownish tschermakite (Ts) amphibole (Figure 5A and Table 3). Biotite (Bt) and phengite (Ph) also occur associated with these minerals (Figure 5A). With irregular edges, few almandine garnet porphyroblasts appear, being replaced by chlorite

(Figure 5B and 5C), which is the most abundant mineral of sample 2, responsible by lepidoblastic texture. Table 4 shows the chemical composition of 12 spots from one edge to the other in garnet. Core-rim chemical zoning can be seen in Figure 6, where EMP Fe (richer in rim) and Mg (richer in core) concentration maps (Figure 6A and 6B) are presented with a quantitative graphical profile from spot X to spot X' (Figure 6C).

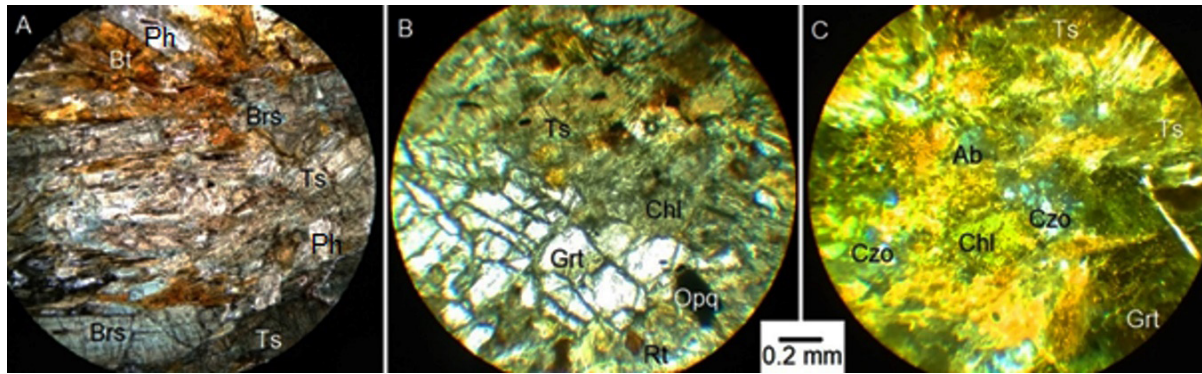


Figure 5. Photomicrographs of sample 2 under uncrossed polarizers. (A) Bluish barroisite (Brs) is being replaced by tschermakite (Ts) and biotite (Bt). Some phengite (Ph) also appears. (B) Garnet (Grt) replacement by chlorite (Chl). Opq—opaque mineral, Rt—Rutile. (C) Photomicrography of sample 2 under crossed polarizers, showing tschermakite (Ts), clinozoisite (Czo), albite (Ab), garnet (Grt) and chlorite (Chl).

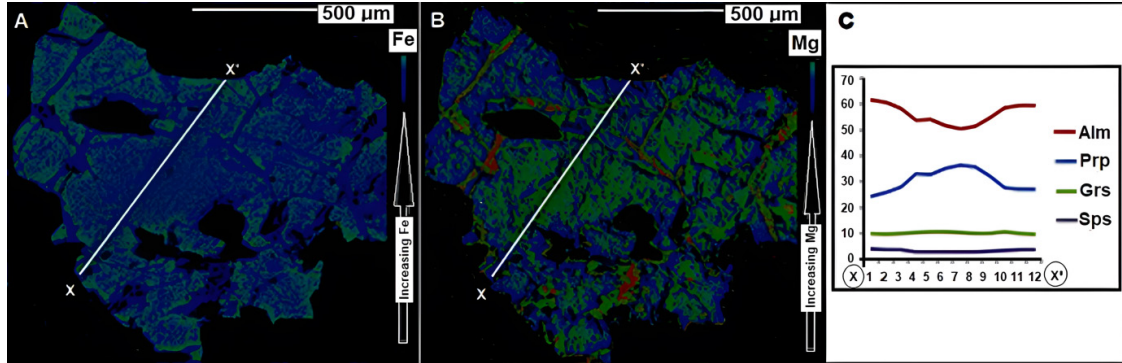


Figure 6. EMP-WDS garnet compositional maps. (A) Fe, (B) Mg, (C) Quantitative graphical profile from spot X to spot X' (data from Table 4). Prp = pyrope. Alm = almandine, Grs = grossular. Sps = spessartine.

Table 3. Representative analyses of tschermakite (Ts), barroisite (Brs), plagioclase (Pl), clinozoisite (Czo) and chlorite (Chl) from sample 2.

	Ts-1	Ts-2	Ts-3	Ts-4		Brs-1	Brs-2		Pl-5		Czo-3		Chl-3
SiO ₂	43.31	43.04	43.57	43.08	SiO ₂	49.69	49.72	SiO ₂	71.03	SiO ₂	39.86	SiO ₂	29.01
TiO ₂	0.71	0.39	0.83	0.53	TiO ₂	0.72	0.74	TiO ₂	0.00	TiO ₂	0.04	TiO ₂	0.02
Al ₂ O ₃	16.04	16.06	16.20	15.78	Al ₂ O ₃	13.10	13.08	Al ₂ O ₃	18.80	Al ₂ O ₃	29.82	Al ₂ O ₃	22.05
FeO	11.75	12.14	11.25	11.36	FeO	11.36	11.37	FeO	0.44	Fe ₂ O ₃	4.06	FeO	17.18
MnO	0.22	0.30	0.27	0.39	MnO	0.27	0.26	MnO	0.03	MnO	0.10	MnO	0.34
MgO	12.96	12.71	12.57	12.89	MgO	10.68	10.84	MgO	0.12	MgO	0.05	MgO	19.92
CaO	10.83	11.10	10.56	11.31	CaO	9.59	9.63	CaO	0.70	CaO	23.35	CaO	0.13
Na ₂ O	2.43	2.50	2.38	2.42	Na ₂ O	1.96	1.90	Na ₂ O	8.77	Na ₂ O	0.09	Na ₂ O	0.04

Table 3 continued

	Ts-1	Ts-2	Ts-3	Ts-4		Brs-1	Brs-2		Pl-5		Czo-3		Chl-3
K ₂ O	0.22	0.19	0.31	0.19	K ₂ O	0.29	0.32	K ₂ O	0.19	K ₂ O	0.05	K ₂ O	0.05
Total	98.46	98.44	97.95	97.94	Total	97.65	97.86	Total	100.08	Total	97.40	Total	88.75
23 ox					23 ox								
Si	6.25	6.23	6.29	6.25	Si	7.07	7.06	32 ox					
Al(IV)	1.75	1.77	1.71	1.75	Al(IV)	0.93	0.94	Si	12.28			28 ox	
Al(VI)	0.97	0.97	1.05	0.95	Al(VI)	1.27	1.25	Ti	0.00	25 ox		Si	5.74
Fe(iii)	0.00	0.00	0.00	0.00	Fe(iii)	0.00	0.03	Al	3.83	Si	6.26	Al(IV)	2.26
Ti	0.08	0.04	0.09	0.06	Ti	0.08	0.08	Fe(ii)	0.06	Ti	0.00	Al(VI)	2.88
Fe(ii)	1.42	1.47	1.36	1.38	Fe(ii)	1.35	1.32	Ca	0.13	Al	5.52	Ti	0.00
Mn	0.03	0.04	0.03	0.05	Mn	0.03	0.03	Na	2.94	Fe(iii)	0.24	Fe(ii)	2.84
Mg	2.79	2.74	2.71	2.79	Mg	2.27	2.29	K	0.04	Mn	0.01	Mn	0.06
Ca	1.67	1.72	1.63	1.76	Ca	1.46	1.47	Total	19.29	Mg	0.01	Mg	5.87
Na	0.68	0.70	0.67	0.68	Na	0.54	0.52			Ca	3.93	Ca	0.03
K	0.04	0.04	0.06	0.04	K	0.05	0.06	An	4.18	Na	0.03	Na	0.02
Total	15.67	15.72	15.60	15.70	Total	15.05	15.04	Ab	94.51	K	0.01	K	0.01
Name	Ts	Ts	Ts	Ts	Name	Brs	Brs	Or	1.32	Total	16.00	Total	19.71

Source: Amphibole names according to Leake et al. ^[49].**Table 4.** Chemical analyses of 12 spots from one edge to the other in garnet crystal from sample 2, as shown in Figure 6.

	Grt1	Grt2	Grt3	Grt4	Grt5	Grt6	Grt7	Grt8	Grt9	Grt10	Grt11	Grt12
	rim	rim	rim	core	core	core	core	core	core	rim	rim	rim
SiO ₂	38.37	38.50	38.41	38.80	39.42	39.02	39.43	40.63	38.80	38.93	38.80	38.52
TiO ₂	0.03	0.09	0.04	0.15	0.12	0.03	0.04	0.05	0.07	0.01	0.01	0.01
Al ₂ O ₃	21.51	22.26	21.45	22.72	22.43	22.49	22.23	21.31	22.25	22.29	22.40	22.56
FeO	27.72	27.68	26.68	24.27	23.99	23.64	23.50	23.78	24.98	26.72	26.79	26.30
MnO	1.75	1.64	1.71	1.23	1.22	1.25	1.29	1.28	1.32	1.52	1.57	1.61
MgO	6.17	6.58	7.17	8.39	8.13	9.03	9.54	9.27	8.27	7.10	6.85	6.72
CaO	3.46	3.47	3.60	3.62	3.67	3.78	3.79	3.63	3.60	3.71	3.55	3.34
Na ₂ O	0.13	0.06	0.11	0.06	0.14	0.10	0.06	0.00	0.13	0.09	0.09	0.10
K ₂ O	0.03	0.04	0.03	0.03	0.02	0.08	0.02	0.03	0.06	0.02	0.07	0.08
Total	99.18	100.32	99.19	99.26	99.14	99.41	99.89	99.99	99.48	100.40	100.12	99.24
24 ox												
Si	6.04	5.98	6.02	5.98	6.07	6.00	6.02	6.18	6.00	6.01	6.01	6.01
Ti	0.00	0.01	0.00	0.02	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Al	3.99	4.07	3.96	4.13	4.07	4.07	4.00	3.82	4.05	4.05	4.09	4.15
Fe	3.65	3.59	3.50	3.13	3.09	3.04	3.00	3.03	3.23	3.45	3.47	3.43
Mn	0.23	0.22	0.23	0.16	0.16	0.16	0.17	0.17	0.17	0.20	0.21	0.21
Mg	1.45	1.52	1.67	1.93	1.87	2.07	2.17	2.10	1.91	1.63	1.58	1.56
Ca	0.58	0.58	0.61	0.60	0.61	0.62	0.62	0.59	0.60	0.61	0.59	0.56
Total	15.96	15.97	15.99	15.94	15.88	15.96	15.98	15.90	15.97	15.96	15.95	15.92
Prp	24.48	25.77	27.89	33.14	32.62	35.11	36.45	35.72	32.27	27.71	27.06	27.11
Alm	61.72	60.81	58.24	53.81	54.01	51.57	50.36	51.43	54.69	58.51	59.35	59.54
Grs	9.86	9.77	10.08	10.27	10.58	10.57	10.39	10.05	10.10	10.41	10.08	9.67
Sps	3.94	3.66	3.79	2.77	2.79	2.75	2.79	2.81	2.94	3.37	3.52	3.68

In sample 2 from metagabbro are still found accessory rutile (Rt—analyzed with $\text{TiO}_2 = 99.13$ and $\text{FeO} = 0.43$ by WDS-EMP), opaque minerals (Opg), albite (Ab_{95}) and clinozoisite (Figure 5B, 5C and Table 3). Brs, Almandine Grt, Rt and Czo are prograde metamorphic minerals and Ph would be probably of the metamorphic peak. Ts, Bt, Chl, and Ab seem to be retrograde minerals. Qz is almost nonexistent.

Sample 3

With granonematoblastic texture, sample 3 has mineralogy composed of magnesium hornblende (Hbl), clinozoisite (Czo) and andesine plagioclase (Ab_{54-63}), with respective analyses presented in Table 5. Some portions of the rock are constituted by Hbl and Czo, and metagabbro was renamed to epidote hornblende (Figure 7A). Other ones are constituted by Hbl and plagioclase (Pl), with sporadic Czo (Figure 7B). This assemblage suggests that sample 3 passed through epidote amphibolite metamorphic facies.

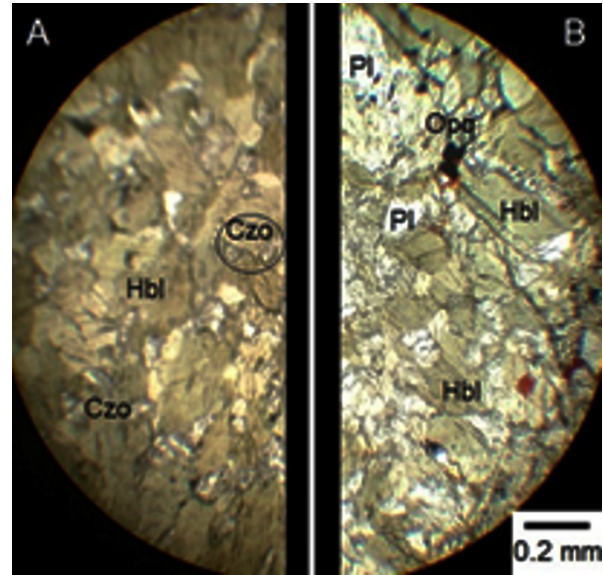


Figure 7. Photomicrographs of sample 3 under uncrossed polarizers. (A) Clinozoisite (Czo) and hornblende (Hbl). (B) Plagioclase (Pl) and hornblende (Hbl).

Table 5. Representative analyses of plagioclase (Pl), clinozoisite and hornblende from sample 3.

	Pl-6	Pl-7	Pl-8		Czo-4		Hbl-3	Hbl-4
SiO_2	57.65	58.26	58.71	SiO_2	38.39	SiO_2	46.97	47.09
TiO_2	0.36	0.00	0.05	TiO_2	0.06	TiO_2	0.86	0.80
Al_2O_3	26.05	26.72	25.59	Al_2O_3	29.74	Al_2O_3	13.51	13.37
FeO	0.20	0.14	1.83	Fe_2O_3	2.89	FeO	12.10	12.27
MnO	0.07	0.00	0.01	MnO	0.26	MnO	0.31	0.28
MgO	0.06	0.13	0.51	MgO	0.10	MgO	11.00	11.01
CaO	8.75	7.57	6.02	CaO	25.26	CaO	11.04	11.08
Na_2O	6.20	5.64	6.57	Na_2O	0.27	Na_2O	2.21	2.18
K_2O	0.18	0.83	0.73	K_2O	0.26	K_2O	0.24	0.18
Total	99.51	99.28	100.02	Total	97.21	Total	98.24	98.24
32 ox						23 ox		
Si	10.39	10.48	10.58			Si	6.75	6.77
Ti	0.05	0.00	0.01			Al(IV)	1.25	1.23
Al	5.53	5.66	5.44	25 ox		Al(VI)	1.04	1.03
Fe(ii)	0.03	0.02	0.28	Si	6.06	Fe(iii)	0.00	0.00
Ca	1.69	1.46	1.16	Ti	0.01	Ti	0.09	0.09
Na	2.17	1.97	2.30	Al	5.53	Fe(ii)	1.45	1.47
K	0.04	0.19	0.17	Fe(iii)	0.17	Mn	0.04	0.03
Total	19.90	19.77	19.92	Mn	0.03	Mg	2.36	2.36
				Mg	0.02	Ca	1.70	1.71
				Ca	4.27	Na	0.61	0.61
An	43.35	40.37	32.06	Na	0.08	K	0.04	0.03
Ab	55.62	54.38	63.34	K	0.05	Total	15.34	15.33
Or	1.03	5.26	4.61	Total	16.23	Name	Mg-Hbl	Mg-Hbl

Source: Amphibole name according to Leake et al. ^[49].

Sample 4

Metaperidotite has spinel wehrlite as protolith and shows its original mineralogy of olivine (Ol), clinopyroxene (Cpx) and spinel (Spl) is replaced by serpentine (Srp),

chlorite (Chl), talc (Tlc) and tremolite (Tr), as shown in Figure 8A, 8B, 8C and 8D. According to Winter^[50], in metaperidotites the mineral association Ol-Cpx-Srp-Tlc-Tr is stable around 500 °C and between 6 and 12 kbar.

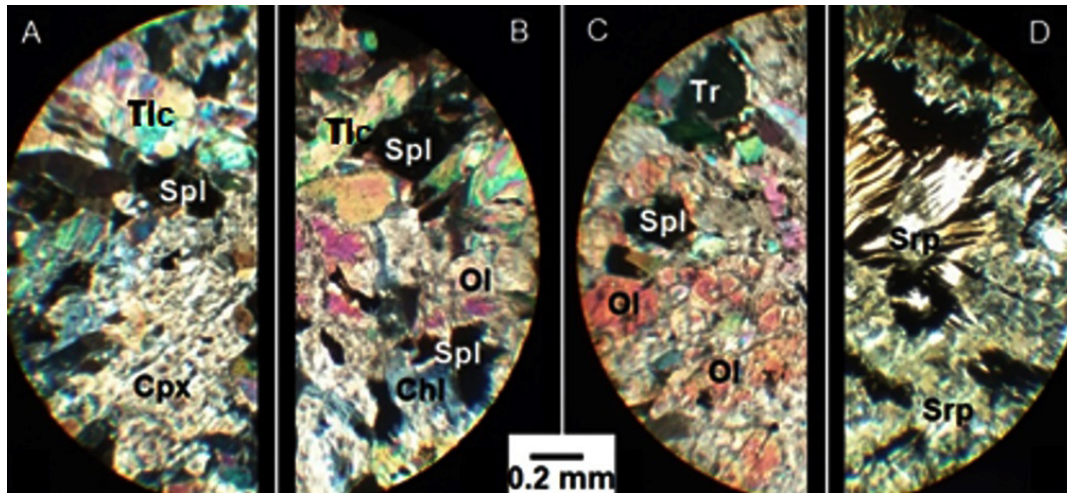


Figure 8. Photomicrographs of sample 4 under crossed polarizers. Olivine (Ol), clinopyroxene (Cpx), spinel (Spl), serpentine (Srp), chlorite (Chl), talc (Tlc) and tremolite (Tr) represent the rock mineralogy. (A), (B), (C) and (D) are different parts of the same thin section.

4.2 Thermobarometry

P-T pseudosections have been obtained for samples 1 (High Si and Ca) and 2 (Low Si and Ca) of the metagabbro and are respectively shown in Figures 9 and 10. Usually described in low *T/P* subduction-related rocks, sodic-calcic amphiboles (like Brs—found in sample 2, Figure 5A) appeared in both pseudosections. Typical of blueschist-facies metamorphism, lawsonite (Lws) found in sample 1 (Figure 4D) appeared only in pseudosection of sample 1 (Figure 9) above 14 kbar (low Ca does not favor the appearance of Lws in sample 2). Rutile (Rt) found in sample 2 (Figure 5B) appeared in pseudosection of sample 2 (Figure 10) above 8 kbar. Based on these observations from petrography and pseudosections, it is reasonable to suggest that metagabbro attained high-pressure conditions (> 10 kbar).

The prograde *P-T* path herein proposed in both pseudosections followed toward metamorphic peak conditions determined by the occurrence of Lws in Figure 9 and by the presence of Ph in Figure 10, inside blueschist metamorphic facies. Therefore, it is herein suggested that the prograde path had a trajectory around 25 °C/kbar (~250 °C/GPa) in both pseudosections, which in turn pointed together to metamorphic peak around 16 kbar and 450 °C, corresponding to ~50 km depth subduction (Figures 9 and 10).

Chlorite (Chl) is the most abundant mineral in sample 2 (Figure 5B and 5C) and appeared in all stability fields of equilibrium assemblages in pseudosection of Figure 10. However, in sample 1 pseudosection (Figure 9), the first appearance of Chl, described in petrography as replacing garnet (Figure 4D), was around 16 kbar and 500 °C, condition that drives the retrograde section of the *P-T* path to this region of *P* and *T*, from blueschist-facies to epidote amphibolite-facies. Albite (Ab) has been described in petrography as a retrograde mineral in sample 2 (Figure 5C) and its first appearance in Figure 10 took place around 4 kbar during final retrograde section of the proposed *P-T* path.

Taken together, tschermakite replacing barroisite crystals (sample 2—Figure 5A) and garnet rim (sample 2—Figure 6) seem to indicate metagabbro exhumation (drop in *P* and *T*) occurred after metamorphic peak. Regarding conventional thermometry, the pressure-independent Grt-Hbl Fe-Mg geothermometer^[51] has been tentatively used to estimate *T* during metagabbro exhumation (retrograde metamorphism). Average tschermakite compositions (Table 3) and average compositions of the garnet rim (Table 4) yielded 521 ± 26 °C. This temperature is consistent with epidote amphibolite-facies and agrees with an intermediate section of the retrograde path in pseudosection of Figure 10.

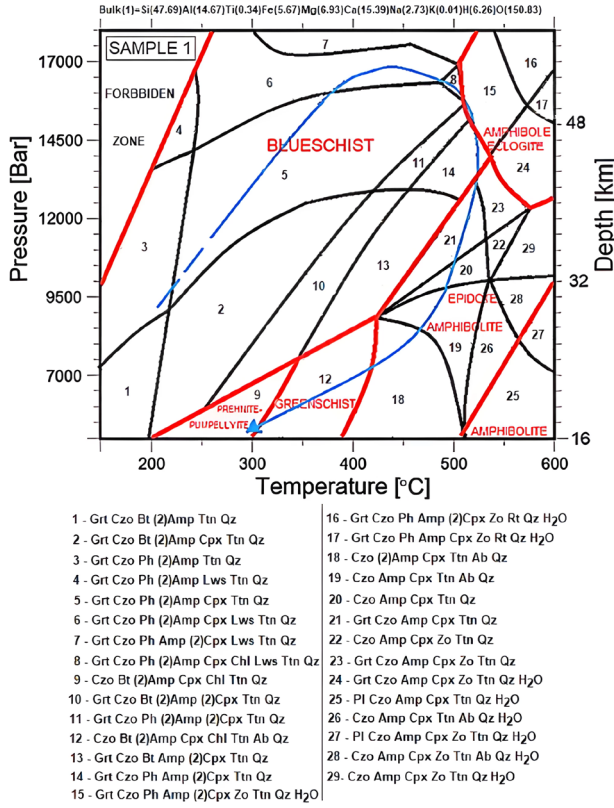


Figure 9. P - T pseudosection of sample 1 showing stability fields of several equilibrium mineral assemblages and the probable metamorphic evolution (path in blue) of the metagabbro from Itaguara Sequence. Mineral abbreviations are as in text and metamorphic facies are separated by red lines. Forbidden metamorphic zone and approximate depths are after Palin et al. [52].

Phengite from sample 1 is low-Si (Table 2) and therefore understood herein as a retrograde metamorphic mineral. For phengite with Si < 3.25 apfu, Kamzolkin et al. [53] have proposed the following equation to calculate P :

$$P(\text{GPa}) = [0.0237T(^{\circ}\text{C}) + 5.99\text{Si} + 1.76\text{Al} + 12.89(\text{Mg} + \text{Fe}) - 31.91]/10$$

By using average apfu data from phengite analyses (Si < 3.25 apfu; Table 2) and by considering $T = 521^{\circ}\text{C}$ previously obtained, the pressure found for metagabbro using this equation is 0.81 ± 0.34 GPa (8.1 ± 3.4 kbar). This pressure occurs in epidote amphibolite-facies and also seems to represent metagabbro exhumation, in agreement with intermediate section of the retrograde path in pseudosection of Figure 9. In this figure, the retrograde path ends around 300°C in which prehnite (Prh) found in rock (Figure 4F) is

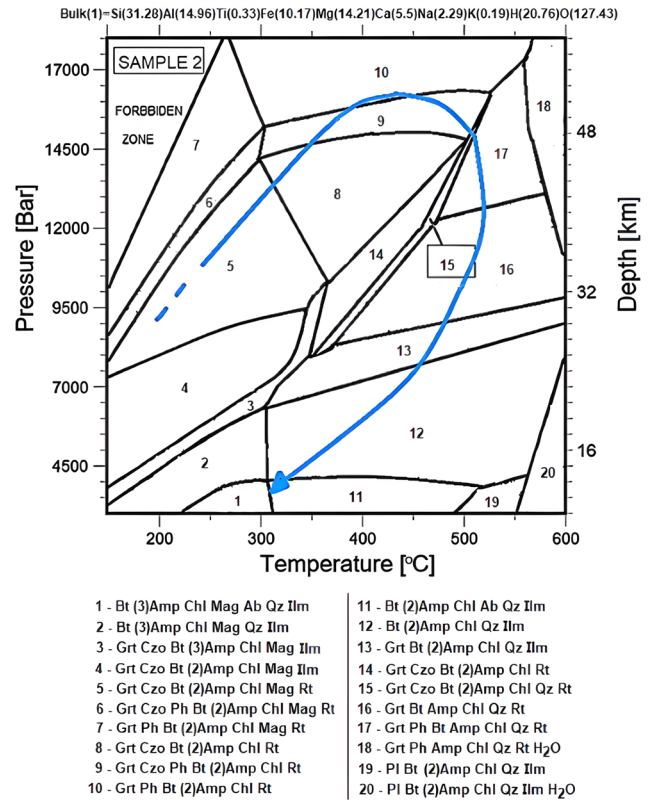


Figure 10. P - T pseudosection of sample 2 showing stability fields of several equilibrium mineral assemblages and the probable metamorphic evolution (path in blue) of the metagabbro from Itaguara Sequence. Mineral abbreviations are as in text. Forbidden metamorphic zone and approximate depths are after Palin et al. [52].

stable. The mineral assemblage constituted by magnesium hornblende (Hbl), clinozoisite (Czo) and andesine plagioclase (Ab_{54-63}) from sample 3 is additional evidence for metagabbro path through epidote amphibolite-facies. The mineral assemblage Ol-Cpx-Srp-Tr found in metaperidotite (sample 4—Figure 8) is stable around 500°C and between 6 and 12 kbar [48], which are the respective T and P of the retrograde path.

4.3 Geochemistry

Geochemical data of samples 1 (high silica and Ca and low Mg and Fe) and 2 (low silica and Ca and high Mg and Fe) are presented in Table 6. When plotted in SiO_2 versus Nb/Y diagram (Figure 11A) of Xia and Li [54], both metagabbro samples are classified as sub-alkaline basalt.

Table 6. Chemical composition of samples 1 and 2. Major elements oxides in % and trace elements in ppm. LOI—Lost On Ignition.

	Sample 1	Sample 2
SiO ₂	52.82	41.01
TiO ₂	0.50	0.58
Al ₂ O ₃	13.79	16.64
Cr ₂ O ₃	0.10	0.14
FeOt	7.51	15.94
MnO	0.30	0.35
MgO	5.15	12.50
CaO	15.91	6.73
Na ₂ O	1.56	1.55
K ₂ O	0.01	0.20
P ₂ O ₅	0.10	0.08
LOI	1.04	4.08
Total	98.79	99.80
Co	41.60	91.80
Ni	212.00	352.00
Cs	0.71	1.70
Rb	2.90	12.20
Ba	47.00	105.00
Sr	144.00	47.00
Nb	3.53	3.90
Ta	1.46	1.00
Y	12.93	30.49
Zr	43.00	68.00
Hf	1.21	1.52
V	124.00	268.00
Cu	40.00	42.00
Ga	10.00	19.00
Th	2.80	1.60
U	0.72	0.44
La	6.20	8.60
Ce	11.70	13.10
Pr	1.26	2.05
Nd	6.80	9.50
Sm	1.80	2.50
Eu	0.53	0.60
Gd	2.07	3.10
Tb	0.31	0.45
Dy	2.34	3.41
Ho	0.43	0.71
Tm	0.23	0.28
Er	1.70	2.36
Yb	1.70	2.00
Lu	0.24	0.29

In AFM ternary diagram (Figure 11B) after Irvine and Baragar^[55] and in Zr-Ti/100-Y×3 ternary diagram (Figure 11C) of Pearce and Cann^[56], the metagabbro protolith is classified as MORB-like tholeiitic basalt. Both chondrite-normalized rare earth element variation plot (Figure 11D) and primitive mantle-normalized trace element variation plot (Figure 11E) (normalization and reference curves after Sun and McDonough^[57]) reveal that metagabbro has an E-MORB pattern. Negative anomalies of Nb and Ti can be related to fluid release from protolith during dehydration under subduction process^[58,59]. E-MORB signature of the met-

agabbro protolith is reinforced in TiO₂/Yb versus Nb/Yb diagram^[60] and Y/Nb versus Zr/Nb diagram^[54], respectively shown in Figures 11F and 11G.

4.4 U-Pb Geochronology

Figure 12A shows the laser spots on the metamorphic titanite crystals of the metagabbro from sample 1. The acquired U-Pb data of 56 spots are presented in Table 7. The lower intercept on the Tera-Wasserburg Concordia diagram (Figure 12B) yielded an age of 2135 ± 15 Ma for the metamorphic titanite crystals.

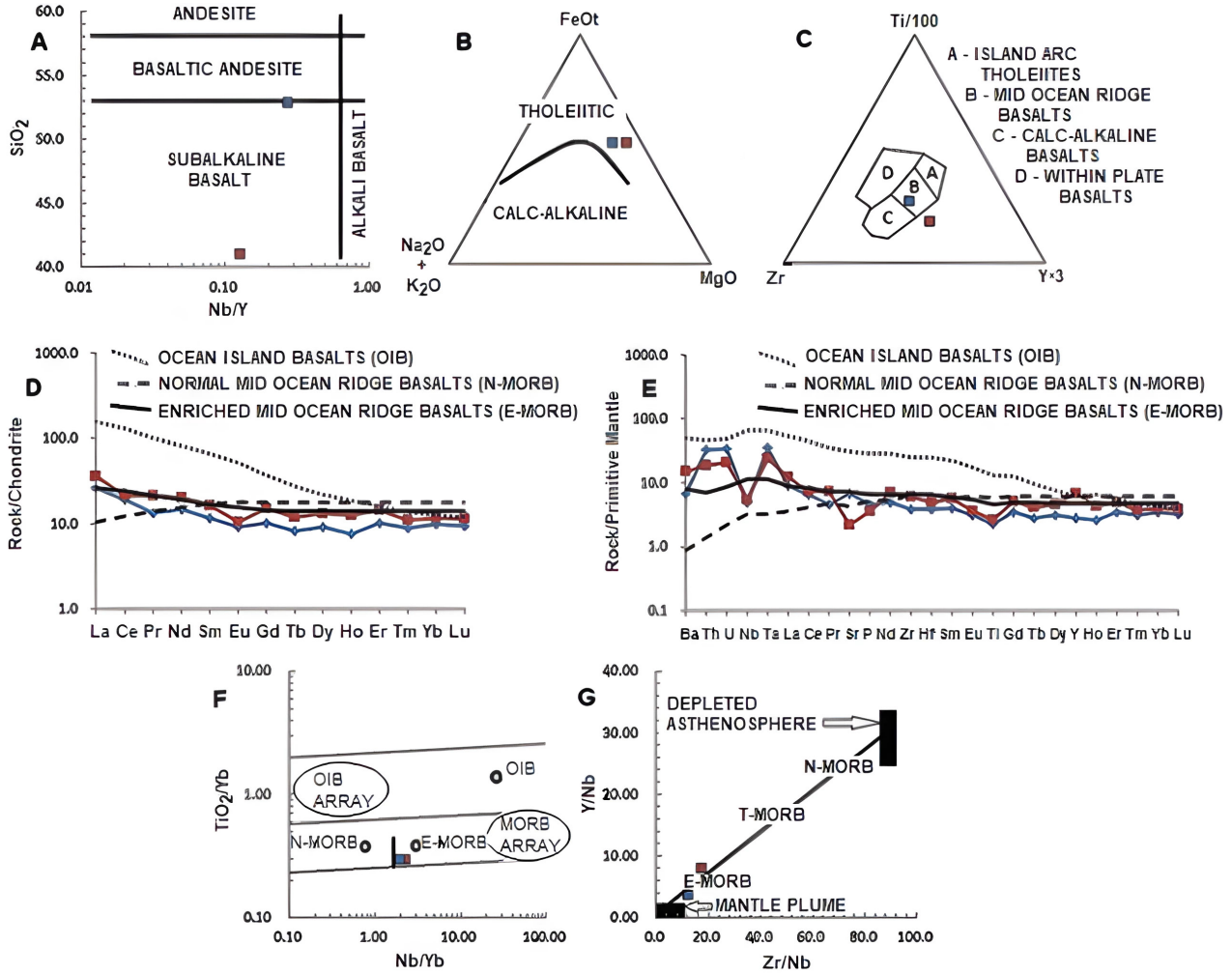


Figure 11. Geochemical diagrams. (A) SiO₂ versus Nb/Y classification diagram^[54]. (B) AFM ternary diagram after Irvine and Baragar^[55]. (C) Zr-Ti/100-Y×3 ternary diagram^[56]. (D) Chondrite-normalized rare earth element variation plot (normalization and reference curves after Sun and McDonough^[57]). (E) Trace element variation plot normalized to primitive mantle (normalization and reference curves after Sun and McDonough^[57]). (F) TiO₂/Yb versus Nb/Yb diagram^[60]. (G) Y/Nb versus Zr/Nb diagram^[54], where T-MORB is transitional MORB. Blue square—sample 1, red square—sample 2.

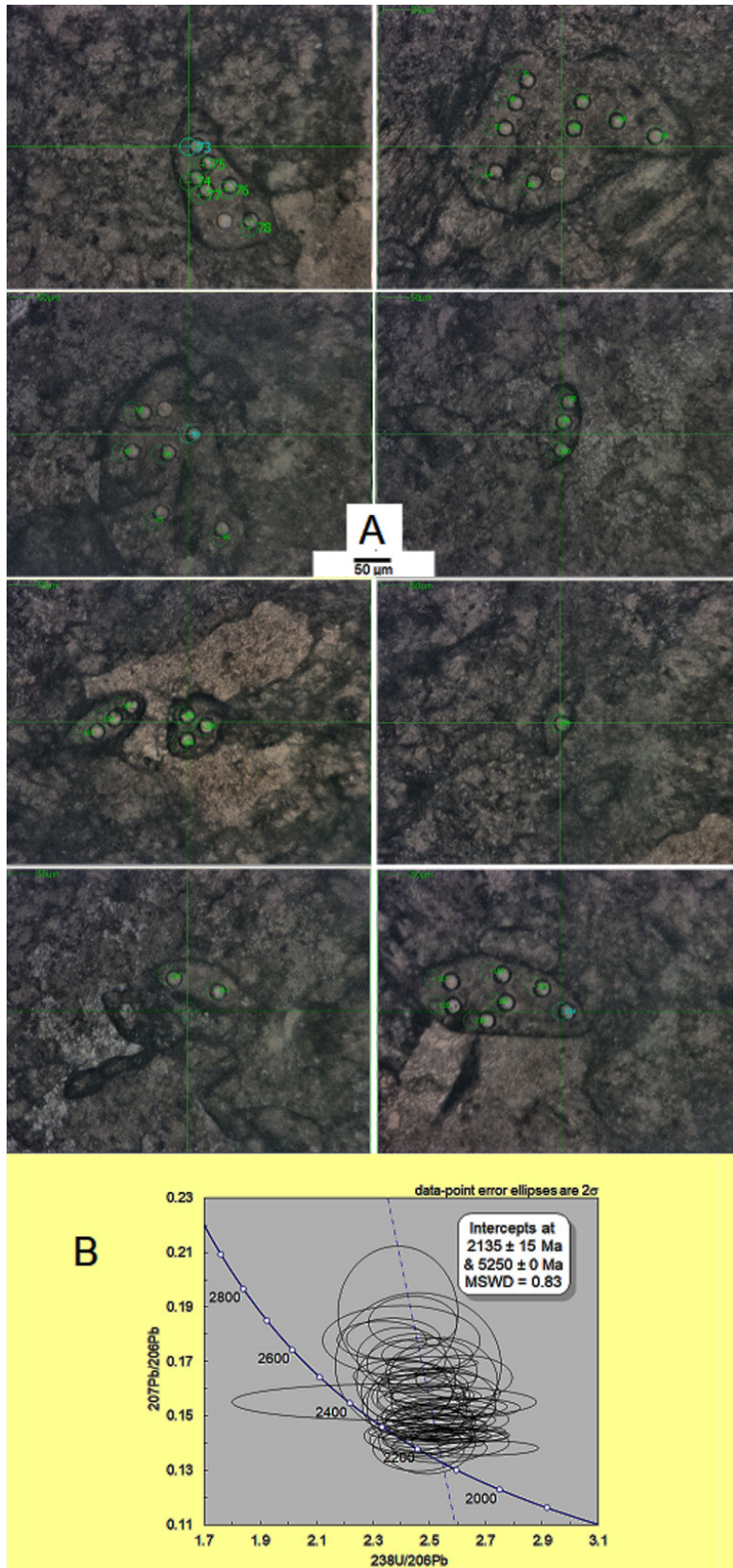


Figure 12. Titanite U-Pb geochronology. (A) Photomicrographs under reflected light of the laser spots on titanite crystals. (B) $^{207}\text{Pb}/^{206}\text{Pb}$ versus $^{238}\text{U}/^{206}\text{Pb}$ Tera-Wasserburg Concordia diagram of the titanite crystals from metagabbro of sample 1.

Table 7. U-Pb data of titanite crystals from metagabbro of the sample 1.

SPOT	238U (ppm)	232Th (ppm)	238U/232Th	207Pb (cps)	206Pb (cps)	208Pb (cps)	202Hg (cps)	204Pb (cps)	207Pb/206Pb	2sigma (%)	207Pb/235U	2sigma (%)	206Pb/238U	2sigma (%)	Rho
073 GRN	20.42597	49.887464	2.4423542	1443048	94483.62	6.16603E	10149.22	315.1973	0.16462	2.991611	947583	6.366376	0.41747	5.619698	0.88271
	357	09	86	379	148	-06	752	904	1357	22	8779	271	4748	312	539
074 GRN	22.02747	50.910894	2.3112453	1335975	100095.5	8.75198E	9878707	238.9732	0.14406	1.553306	8.14340	5.479352	0.40997	5.254573	0.95897
	255	26	85	755	615	-06	737	871	0064	228	0217	839	8328	94	7108
075 GRN	23.84391	59.761717	2.5063715	1407749	107617.5	4.34539E	9717.630	247.0460	0.14119	3.393505	7.94470	6.395832	0.40808	5.421327	0.84763
	785	57	6	718	058	-06	355	357	6461	667	6253	161	6999	173	4371
076 GRN	21.63064	42.190555	1.9504988	1319992	95160.65	4.13025E	9449.427	261.5403	0.14973	1.573270	8.21032	5.700760	0.39768	5.479369	0.96116
	873	38	46	745	919	-07	647	464	2542	342	3871	746	8303	81	4668
077 GRN	19.95918	42.833110	2.1460346	1180647	89330.71	1.51305E	9279.520	234.3989	0.14266	3.710265	7.99775	7.348539	0.40659	6.343103	0.86317
	908	38	01	598	293	-06	714	827	2619	175	6945	34	004	559	8826
078 GRN	21.54277	51.479238	2.3896290	1673966	101588.4	1.8133E	9106.669	375.5749	0.17788	3.194491	10.5212	6.385263	0.42896	5.528726	0.86585
	436	69	16	727	52	-06	471	395	7042	206	6005	518	5304	447	7209
079 GRN	33.74793	80.035284	2.3715607	2449487	154288.8	5.93324E	8986.140	515.6280	0.17139	5.307225	9.84173	7.552999	0.41645	5.374118	0.71152
	728	84	92	862	361	-06	645	731	6344	448	326	039	5652	767	1177
080 GRN	32.78370	80.351959	2.4509725	1896611	144057.5	1.82625E	8842.803	235.8367	0.14205	1.393628	7.83948	5.423331	0.40025	5.241213	0.96641
	507	75	06	251	126	-05	93	9	2575	443	8904	371	5552	879	9627
083 GRN	32.34701	79.220966	2.4490967	1841178	143639.5	2.74176E	8520.398	264.4506	0.13838	5.115925	7.74924	7.451349	0.40612	5.417555	0.72705
	419	07	11	633	553	-05	861	446	9519	851	8617	081	0695	336	6977
084 GRN	16.45603	36.765566	2.2341698	1251071	75753.59	1.06471E	8327.622	337.3164	0.17833	3.473300	10.3657	6.712201	0.42157	5.743677	0.85570
	044	62	23	128	543	-05	719	327	0147	868	018	17	2884	013	6923
085 GRN	24.31691	48.785879	2.0062529	1614171	106378.7	2.21271E	8302.722	288.3736	0.16385	1.561659	9.04625	5.717352	0.40041	5.499940	0.96197
	391	35	13	003	609	-06	706	649	3529	879	6696	98	6378	32	3196
086 GRN	26.68487	59.891758	2.2444083	1681772	117140.2	1.4421E	8188.840	251.4843	0.15503	2.568988	8.62554	6.004815	0.40350	5.427532	0.90386
	553	7	97	02	023	-05		034	7544	177	1948	541	4364	536	3324
087 GRN	27.12061	67.684255	2.4956752	1744693	120009.1	7.89305E	8094.761	318.6304	0.15699	4.233375	8.79750	6.901828	0.40640	5.451033	0.78979
	783	47	79	523	059	-06	08	143	817	432	7646	221	944	41	5578
088 GRN	30.47530	73.109057	2.3989608	1843053	133750.8	1.53849E	8089.213	279.5207	0.14881	2.611352	8.29715	5.865665	0.40437	5.252320	0.89543
	222	87	81	335	565	-05	004	928	4161	696	7719	389	4545	206	4679
089 GRN	30.85969	83.647459	2.7105732	1758327	134539.9	6.73158E	8102.706	240.9285	0.14109	2.669311	7.80280	5.888256	0.40108	5.248460	0.89134
	382	82	26	718	137	-06	274	569	6548	539	1963	068	1768	292	3758
090 GRN	39.27197	111.76637	2.8459579	2236630	170581.7	9.24697E	8075.564	355.2544	0.14160	7.419853	7.83179	9.320661	0.40111	5.640966	0.60521
	138	77	12	992	47	-07	84	213	8527	348	4853	23	659	411	0969
093 GRN	38.13008	107.93210	2.8306285	2639593	168466.9	1.62367E	8219.148	533.1675	0.16923	5.266283	9.55101	7.615440	0.40932	5.501016	0.72235
	374	34	45	241	254	-05	464	593	1933	654	576	236	2833	857	0473
094 GRN	41.10446	116.22869	2.8276413	2496581	173769.2	1.06963E	8356.830	396.1904	0.15515	6.683281	8.38546	8.944927	0.39197	5.945206	0.66464
	725	3	92	508	478	-05	255	702	4028	788	0343	73	8801	19	5525
095 GRN	29.52214	70.829164	2.3991875	2021374	129390.2	8.90451E	8534.823	441.3089	0.16874	12.82390	9.45662	16.12380	0.40645	9.773671	0.60616
	622	51	11	37	597	-06	928	935	2138	443	1602	768	3802	232	3967

Table 7 (continued)

SPOT	238U (ppm)	232Th (ppm)	238U/ 232Th	207Pb (cps)	206Pb (cps)	208Pb (cps)	202Hg (cps)	204Pb (cps)	207Pb/ 206Pb	2sigma (%)	207Pb/ 235U	2sigma (%)	206Pb/ 238U	2sigma (%)	Rho
096	31.24811	66.251663	2.1201808	1867947	135016.2	6.00308E	8683953	361.7018	0.14943	4.436075	8.26282	6.919592	0.40101	5.310554	0.76746
GRN	812	14	98	057	756	-06	111	471	9389	303	5564	14	6486	707	6434
097	32.41054	63.386682	1.9557423	1737004	133566.4	1.211155E	8909600	251.0024	0.14033	3.139365	7.40845	6.238531	0.38286	5.391072	0.86415
GRN	839	5	63	892	473	-05	228	895	9056	852	9603	715	7138	25	7224
098	30.52436	87.022787	2.8509286	1935895	132776.9	5.29092E	9173551	260.5522	0.15749	4.222857	8.76176	6.872553	0.40348	5.422127	0.78895
GRN	461	01	97	248	682	-06	203	123	269	502	9495	167	7557	032	3814
099	25.59008	57.997037	2.2663874	1396849	105521.3	1.10531E	9267892	225.7773	0.14299	1.445565	7.55941	5.731875	0.38341	5.546596	0.96767
GRN	016	21	78	587	848	-05	559	385	368	502	6228	244	592	631	5742
100	24.94615	79.411356	3.1833106	1549246	109030.4	9.75757E	9514036	275.3492	0.15349	8.743278	8.61874	10.55116	0.40724	5.906107	0.55975
GRN	337	75	92	817	249	-06	785	553	2212	697	8448	267	5773	965	8972
103	27.47258	70.764989	2.5758402	1542269	115854.7	3.08223E	9853669	244.0629	0.14346	1.410316	7.79394	5.517737	0.39400	5.334457	0.96678
GRN	461	24	52	372	632	-06	936	75	7769	691	0568	984	4761	732	3444
104	24.59990	74.143974	3.0139938	1808353	109566.0	3.56831E	9877010	388.8998	0.17772	5.895736	10.2069	11.18747	0.41652	9.507887	0.84986
GRN	885	22	59	735	644	-08	058	955	7888	942	1536	667	1726	26	879
105	22.62568	57.942769	2.5609288	1505273	99482.13	2.92293E	9977973	274.8256	0.16263	7.674436	9.27862	9.709666	0.41378	5.948163	0.61260
GRN	507	86	59	57	47	-06	567	672	3236	352	7858	481	351	57	2254
106	29.61442	103.53201	3.495999	1847925	129611.8	1.21988E	1003465	326.7687	0.15371	6.130314	8.70503	8.436849	0.41073	5.796522	0.68704
GRN	817	81	23	515	161	-05	13	912	1174	414	0221	368	6756	445	8232
107	30.66514	100.85839	3.2890241	1970859	132171.7	8.63712E	9967927	340.2836	0.16100	3.286110	8.95226	6.187112	0.40327	5.242312	0.84729
GRN	235	43	69	81	09	-06	149	351	1058	388	6132	716	6561	684	5487
108	37.17848	134.18170	3.6091223	2169980	158188.8	8.77233E	9940068	256.4643	0.14818	3.193279	8.15726	6.127185	0.39923	5.229280	0.85345
GRN	676	58	05	176	617	-07	119	372	9269	039	1317	447	2919	111	5499
109	43.30302	78.927347	1.8226752	2805816	190390.9	1.09965E	9887572	424.1339	0.15898	5.856060	9.06152	8.001359	0.41338	5.452367	0.68143
GRN	162	21	84	439	766	-07	629	195	2214	649	3338	785	1843	567	0121
110	28.48719	92.791993	3.2573233	1532442	119332.9	4.10885E	9830759	277.2527	0.13833	3.240841	7.52312	6.325911	0.39443	5.432688	0.85879
GRN	148	25	24	93	661	-06	841	62	3374	906	9248	923	0309	598	9279
113	30.39145	83.559177	2.7494301	1726007	128740.1	5.23807E	9440427	294.8785	0.14401	5.444437	7.96071	7.621771	0.40090	5.333808	0.69981
GRN	337	16	16	63	462	-06	025	076	7033	065	9212	772	103	207	2113
114	68.65429	155.99660	2.2722046	3871583	286867.5	9.36235E	9317825	378.3611	0.14578	2.574366	7.90088	5.795358	0.39306	5.192188	0.89592
GRN	191	37	84	343	597	-06	323	461	4707	879	2832	583	3195	005	1785
115	46.09509	70.744642	1.5347543	2636389	192942.4	7.87243E	9251833	293.1806	0.14747	0.973413	8.01471	5.423976	0.39414	5.335914	0.98376
GRN	046	08	82	963	01	-06	593	29	9241	606	8034	398	5054	722	437
116	49.19295	96.721396	1.9661637	3039070	208279.2	1.71323E	9200372	439.8430	0.15728	2.473910	8.67210	5.750388	0.39987	5.191024	0.90272
GRN	046	51	61	838	345	-05	053	365	9499	792	9846	47	4553	268	5841
117	63.12275	118.19245	1.8724221	3458736	261430.8	8.94964E	9041906	324.5115	0.14267	1.396762	7.68967	5.374993	0.390904	5.190338	0.96564
GRN	806	05	53	126	995	-06	337	566	1033	384	4223	583	672	222	5473
118	82.43484	245.80589	2.9818203	4471356	344778.7	3.39377E	9131865	343.5724	0.13994	1.102950	7.61430	5.293537	0.394626	5.177358	0.97805
GRN	618	98	25	933	904	-08	612	207	038	417	5786	206	267	065	2645

Table 7 (continued)

SPOT	238U (ppm)	232Th (ppm)	238U/ 232Th	207Pb (cps)	206Pb (cps)	208Pb (cps)	202Hg (cps)	204Pb (cps)	207Pb/ 206Pb	2sigma (%)	207Pb/ 235U	2sigma (%)	206Pb/ 238U	2sigma (%)	Rho
119 GRN	47.98642 664	117.83270 88	2.4555424 73	29370.53 616	201438.8 188	2.92243E -06	9087.702 802	399.6686 854	0.15732 0426	1.739903 22	8.59795 0042	5.504298 72	0.396377 075	5.222072 499	0.94872 6216
120 GRN	61.11055 427	111.63183 12	1.8267193 38	35491.60 965	251500.4 977	1.96752E -05	9056.979 316	401.0685 36	0.15243 4606	2.061977 013	8.16254 108	5.548418 8	0.388365 401	5.151038 922	0.92837 9617
143 GRN	33.15223 168	88.386302 7	2.6660739 93	21615.36 553	140445.5 487	4.68341E -06	8564.219 033	448.7637 712	0.16611 9943	4.918362 282	9.13146 3968	7.211002 554	0.398673 493	5.273354 748	0.73129 2869
144 GRN	34.97304 672	125.53441 8	3.5894618 8	18757.13 427	142033.1 53	1.46756E -06	8351.006 188	198.2414 763	0.14253 5183	1.359543 425	7.53124 0541	5.544367 281	0.383215 588	5.375095 368	0.96946 9571
145 GRN	31.41262 701	84.125499 05	2.6780790 74	20877.59 432	132860.5 793	5.39098E -07	8118.132 614	348.2995 981	0.16954 7439	1.033028 881	9.31535 6377	5.428977 405	0.398480 4	5.329788 644	0.98172 9753
146 GRN	12.70807 671	35.080977 84	2.7605261 31	8321.056 14	57883.39 398	1.58953E -06	7979.221 087	193.7332 672	0.15514 0148	3.446236 851	9.14104 1923	19.17852 309	0.427336 732	18.86635 099	0.98372 2829
147 GRN	25.74096 8	64.044767 73	2.4880481 47	17532.67 647	109561.6 287	1.12307E -05	7781.224 047	328.6821 129	0.17233 3201	3.001863 783	9.53230 3445	6.066393 981	0.401169 243	5.271617 376	0.86898 6979
148 GRN	27.48189 13	85.396918 59	3.1073887 04	20400.54 604	119212.9 095	1.1314E -05	7620.668 19	443.7346 822	0.18435 2752	4.282479 822	10.4116 2037	6.781491 88	0.409607 051	5.258231 518	0.77537 9756
149 GRN	20.18575 805	57.748270 8	2.8608423 16	11801.67 026	83008.01 603	3.17339E -05	7497.146 767	186.8148 27	0.15340 8744	1.831142 353	8.15531 5406	6.046171 221	0.385557 692	5.762213 473	0.95303 5113
150 GRN	24.29375 486	56.826765 62	2.3391511 91	13869.25 243	100763.2 326	6.80112E -07	7374.845 775	188.6788 808	0.14850 8745	2.160423 685	7.99080 9334	5.894193 222	0.390245 107	5.483984 248	0.93040 456
153 GRN	21.77676 861	61.495703 62	2.8239131 67	16905.46 616	97117.34 446	7.9012E -06	7061.172 797	457.0504 259	0.18778 0653	10.70539 223	10.8406 4313	12.95093 651	0.418699 968	7.288438 355	0.56277 3074
154 GRN	31.07933 215	125.80126 21	4.0477466 34	17477.71 821	126722.0 524	4.06471E -06	6906.885 937	214.1057 066	0.14877 3274	2.718415 661	7.84993 1292	5.930564 894	0.382683 432	5.270845 877	0.88875 9498
155 GRN	33.66996 901	142.19232 96	4.2231202 98	18544.72 086	138553.0 106	5.32289E -06	6810.173 136	206.7992 896	0.14429 2455	1.450556 617	7.65793 5151	5.647562 491	0.38491 673	5.458099 265	0.96645 2213
156 GRN	28.91376 433	74.344355 5	2.5712444 3	14611.68 622	114015.4 417	1.48133E -06	6728.975 505	174.5013 959	0.13822 0022	1.562627 25	7.03856 486	5.638861 651	0.369327 703	5.418021 483	0.96083 6037
157 GRN	20.67709 332	45.272041 36	2.1894780 2	12646.97 803	86100.55 691	6.29311E -06	6611.397 493	222.0937 46	0.15841 0919	3.866557 373	8.54051 3142	7.264789 016	0.391018 744	6.150357 187	0.84659 8184
158 GRN	29.54467 587	75.149571 68	2.5435910 01	18656.53 453	123650.2 969	1.11462E -05	6568.141 432	361.5330 621	0.16270 8228	8.115276 039	8.80006 4836	10.20942 381	0.392260 955	6.194725 935	0.60676 5479
159 GRN	25.71636 976	63.926992 77	2.4858482 5	14806.71 793	104372.5 251	3.21258E -05	6466.391 606	233.5183 346	0.15297 3105	1.881229 546	7.97618 4808	5.815922 044	0.378162 839	5.503264 905	0.94624 1174
160 GRN	22.92704 645	54.299516 06	2.3683607 12	14204.64 697	93350.19 609	8.20983E -06	6477.874 587	210.7483 517	0.16406 8733	4.079049 922	8.62529 67	6.730342 742	0.381282 563	5.353397 534	0.79541 232

5. Discussion and Conclusions

Preserved igneous texture in sample 1 has confirmed gabbro as the protolith of the investigated layered metabasic rock. Throughout the stability fields of the sodic-calcic amphibole (barroisite) crystals present in the metagabbro (Figures 9 and 10), the prograde path followed a ~ 25 °C/kbar subduction trajectory within the blueschist-facies field.

The reason why lawsonite is relatively scarce in the rock record worldwide can be explained by two factors. Firstly, it may be due to dehydration during subduction, which occurs before reaching the lawsonite stability field. As a result, the rock became H₂O undersaturated, which prevented the formation of lawsonite^[61]. Alternatively, it could also be due to extensive retrogression during exhumation^[62]. During this process, lawsonite often transforms into minerals like epidote.^[13,14,61] Remarkably, sample 1 preserves lawsonite because its formation occurred inside garnet, which has acted as a shieldin0g mineral that was slowly replaced by chlorite. Lawsonite is a remnant of metamorphic peak that probably occurred around 16 kbar and 450 °C in blueschist-facies as suggested by P - T path in Figure 9, and also sample 2 preserves rutile (stable Ti phase at higher P - T conditions; Figure 10) and phengite.

The estimated P - T - t paths for blueschists and eclogites containing lawsonite propose that temperature rise might occur before uplift, leading to the transformation of blueschist-facies assemblages into amphibolite-facies assemblages through recrystallization^[62]. Hornblende, clinozoisite and andesine found in sample 3 register post-peak metamorphic conditions in epidote amphibolite-facies, during collision-related tectonic exhumation. This exhumation in turn also promoted the retrograde metamorphism of the metagabbro to prehnite/pumpellyite-facies conditions as indicated by prehnite found in sample 1 (Figure 9).

According to Maruyama et al.^[1], orogenic peridotites are believed to be the uppermost mantle that constitutes the foundation of fragments of oceanic lithosphere added to the continental crust along subduction zones. These fragments are disintegrated parts of ophiolites—sections of oceanic crust and mantle that either separate from the descending slab and become part of the subduction zone's accretionary wedge, or get trapped between two terranes during an accretion event. In orogens, pieces of ultramafic bodies are situated along major fault zones that separate diverse terranes. These pieces are remnants of that once separated collisional terranes, and therefore mark the

suture zone, which is the representation of the ancient subduction zone that happened before the collision^[1]. The co-occurrence of blueschist-facies rocks with ultramafics, mafics, and sediments supports the hypothesis of a subduction-related origin^[63]. Ophiolites can represent either a marginal sea behind an offshore island arc (like present-day Japan) in cases where the arc gets pushed back toward the continent behind it or typical oceanic crust between colliding continents. Spinel peridotites are smaller fragments of the presumed ophiolitic ultramafics^[1].

Sample 4 was revealed to be spinel metawehrlite and the metamorphic assemblage with olivine, clinopyroxene, serpentine, chlorite, talc and tremolite is stable around 500 °C and between 6 and 12 kbar^[50], the respective T and P of the exhumation-related retrograde metamorphism established for its associated metagabbro (Figures 9 and 10). Itaguara metagabbro E-MORB signature points out to oceanic setting and the association of the metagabbro to spinel metawehrlite between Campo Belo/Bonfim and Divinópolis Archean complexes suggests they represent subducted and exhumed meta-ophiolitic rocks. The accretionary prism (characterized by mica-quartz schist^[5]) and retroeclogite^[9] from Paleoproterozoic Itaguara Sequence (IS) supports the scenery of subduction and collision-related exhumation for the investigated region. The age of 2135 Ma found for titanite from metagabbro investigated herein (Figure 12), also belonging to this meta-ophiolitic sequence, seems to indicate the timing of the prograde blueschist-facies metamorphism of this rock, just before the ~ 2.1 Ga regional continental collision.

Evidence in support of the collision that occurred at about 2.1 Ga is found in monazite inclusions in corundum from IS^[64]. Metamorphic corundum crystals are associated with continental collision zones and serve as tectonic indicators of continental collision. These crystals form due to metasomatism accompanying reactions between aluminosilicate-rich rocks (granitoids, gneisses, migmatite) and silica-poor ultramafic rocks^[65]. The monazite found in metamorphic corundum between gneiss and metaultramafic rock from Itaguara revealed an age of 2126 ± 97 Ma, which is interpreted as the age of corundum growth. This supports the hypothesis of continental collision between Campo Belo/Bonfim and Divinópolis Archean complexes at that time^[64], which was preceded by subduction of IS.

Brown and Johnson^[66] and Palin et al.^[52] suggest that the Paleoproterozoic Era may have experienced subduction-related processes similar to those seen on the Earth today. Just before tectonic exhumation relat-

ed to the ca. 2.1 Ga collision between the Archean Campo Belo/Bonfim and Divinópolis complexes, the 2.13 Ga subduction setting envisaged for the IS is presented along X-Y section of the Figure 13 (this geodynamic illustration is the reconstruction previous to geological setting found along X-Y section of Figure 1B). Figure 13 shows the geological scenario of the accretionary prism (represented by mica-quartz schist^[5]) and the 2.20 ± 0.05 Ga retroeclogite with an E-MORB signature^[9] from the Paleoproterozoic IS close to the ~ 600 °C isotherm (~ 60 km depth).

The 2.13 Ga metagabbro and associated metaperidotite from Paleoproterozoic IS presented in Figure 3 occur alongside 2.16 Ga amphibolites (zircon U-Pb age^[12]), as shown in Figure 2. Regarding the location of the investigated metagabbro and metaperidotite in Figure 13, they appear above ~ 500 °C isotherm (i.e., around 450 °C), corresponding to ~ 50 km depth attained during metamorphic peak. This is the location of the oceanic Moho discontinuity in the proposed subducting slab. Therefore, according to petrographic, chemical and thermobarometric data alongside geological setting presented in this manuscript, it is reasonable to

suggest that lawsonite and barroisite-bearing metagabbro (although lawsonite and barroisite are not from the same sample, they are from the same rock) with E-MORB signature associated with spinel metaperidotite represent a subducted and exhumed Paleoproterozoic blueschist-facies meta-ophiolitic fragment of oceanic Moho, now exposed in IS of the southern São Francisco craton.

There are several Paleoproterozoic subducted and exhumed rocks represented by 2.10–1.80 Ga eclogite remnants^[9,67–73] in collisional and accretionary orogens distributed in the new configuration of Columbia (Nuna) supercontinent, which has been elaborated by Chaves^[74] and presented in Figure 14. The location of the subducted and exhumed Paleoproterozoic blueschist-facies metagabbro herein investigated is highlighted by white arrow in Figure 14. Based on all geological aspects presented in this manuscript, the IS metagabbro could be considered the oldest retrogressed blueschist known so far, constraining the age of such rocks to Paleoproterozoic, pushing back considerably the previous notion of Neoproterozoic as the oldest age of blueschists.

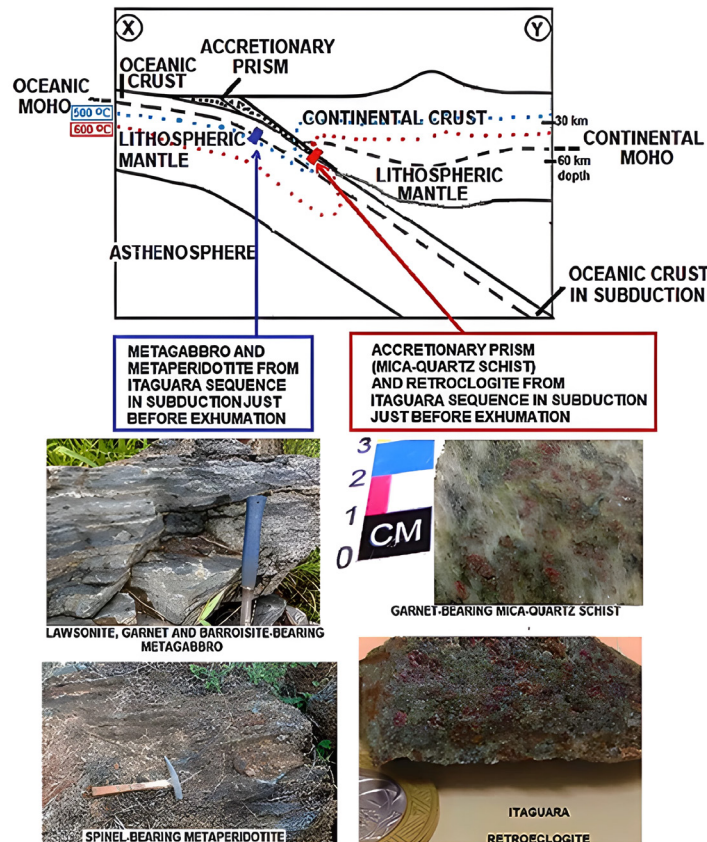


Figure 13. The ca. 2.13 Ga subduction setting envisaged for the Itaguara Sequence just before tectonic exhumation related to the ca. 2.1 Ga collision between Archean Divinópolis (X—not shown in the figure) and Campo Belo/Bonfim (Y) complexes.

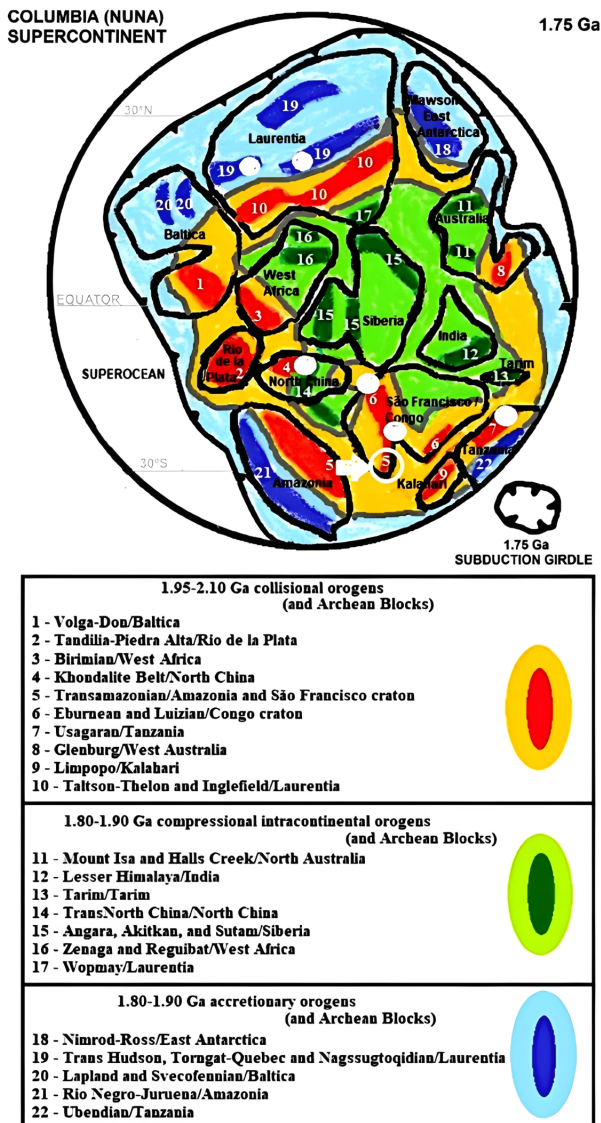


Figure 14. Distribution of concentric collisional (1.95–2.10 Ga), accretionary and compressional intracontinental (1.80–1.90 Ga) orogens and undiscriminating Archean blocks on 1.75 Ga Columbia (Nuna) supercontinent. White circles represent locations of 2.10–1.90 Ga retroeclogites preserved inside contemporary accretionary and collisional orogens. White arrow indicates the location of the IS (open white circle), with ~2.1 Ga retroeclogite and probable blueschist investigated herein (modified from Chaves^[74], permitted reproduction—copyright Elsevier).

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Data Availability Statement

The corresponding author guarantees that the data used to carry out this study are integrally published in the paper.

Conflict of Interest

The author disclosed no conflicts of interest.

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