Floresta and Bodocó Mafic–Ultramafic Complexes, western Borborema Province, Brazil: Geochemical and isotope constraints for evolution of a Neoproterozoic arc environment and retro-eclogitic hosted Ti-mineralization

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ABSTRACT

The retrograde high-pressure metamorphosed Floresta and Bodocó mafic–ultramafic complexes (FMUC and BMUC, respectively) occur as clusters of small bodies, lenses and boudins with close association with granitic, gneissic rocks and metasediments in the southern limits of the Alto Pajeú and Piancó–Alto Brígida domains, Borborema Province, northeast Brazil. Ultramafic lithologies including metadunites, olivine cumulate rocks, metapyroxenites, chromitites and massive ilmenomagnetitites showing evidence of cumulus textures and mafic members include garnet amphibolites and coarse metahornblendites. BMUC rocks include Cr–Fe–Ti chromitites in the Fazenda Esperança deposit, and FMUC rocks show important Fe–Ti–V economic mineralization in the mines of the Serrote das Pedras Pretas and Lagoa dos Angicos and the Riacho da Posse deposit in development (54 Mt @13% Ti). The whole-rock and mineral geochemistry of these complexes are akin to arc cumulate rocks, particularly Alaskan-type complexes, which are widely considered to have formed above subduction zones.

A coarse metahornblendite from the Serrote das Pedras Pretas mine was dated by U–Pb zircon through laser ablation-multicollector-inductively coupled plasma-mass spectrometry (LA-MC-ICP-MS). Information obtained from the cores of igneous zircons represent an upper intercept age of crystallization at 1024 ± 18 Ma with 4.2 mean square weighted deviation (MSWD), whereas zircon exhibiting coarse rims with low Th/U at 0.008–0.038 have concordia ages of 685 ± 17 and 625 ± 6 Ma. According to their zircon textures, these ages may be representative of a high-grade eclogitic or progressive granulitic/retro-eclogitic stage during the Pan-African–Brasiliano event. Additionally, the age of the igneous protolith, 1028 ± 63 Ma, is well marked by a Sm–Nd isochron based on 12 samples.

Positive $\epsilon_{\text{Nd}}(t)$ values between 0.01 and 4.84 suggest a depleted mantle or a source close to the chondritic reservoir for the mafic–ultramafic bodies studied. The T_{DM} model ages between 1.1 and 1.6 Ga are consistent with a juvenile Mesoproterozoic source or mixing between Paleoproterozoic and Neoproterozoic sources. The dispersion of initial ratios of $^{87}\text{Sr}/^{86}\text{Sr}$ at 0.7016–0.7090 and the high fractionation of light rare earth elements (LREE) relative to heavy rare earth elements (HREE) suggest a depleted mantle source metasomatized by subduction-related melts/fluids.

The mafic–ultramafic complexes, volcanic and sedimentary rocks, and some granitic intrusions with post-collisional signature after 975 Ma constitute a proto to marginal arc-back-arc basin system that evolved between 1025 and 975 Ma. However, FMUC and BMUC which are currently arc cumulate rocks were originally picrite melts in a suprasubduction ophiolite zone.

The economic deposits of Fe–Ti associated with retro-eclogitic and ultramafic members of the FMUC and enclosed within the late Ediacaran granite can be linked in part by early accumulation under magmatic conditions, secondary enrichment of rutile up to 12% in the high-pressure (HP) stage, and hydrothermal interactions during granite emplacement.

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1. Introduction

Tectonic settings involving compressional and extensional environments and crustal evolution of mafic–ultramafic rock assemblages in orogenic belts can be reliably modeled by their petrogenetic and geochemical characterization (Coleman, 1971; Gass, 1980; Moores, 1982; Dilek, 2003; Dilek and Robinson, 2003; Eyuboglu et al., 2010, 2011; Su et al., 2013). During the subduction process, the oceanic floor is usually destroyed. However, some fragments of the ancient oceanic crust may be preserved as mafic–ultramafic ophiolite suites (Gass, 1968, 1980; Coleman, 1971; Moores, 1982; Dilek, 2003; Dilek and Robinson, 2003; Eyuboglu et al., 2010, 2011; Su et al., 2013). Furthermore, steadily increasing numbers of ultramafic–mafic complexes associated with orogenic belts have been attributed to intrusions into the continental basement or ancient arc systems (Irvine, 1974; Pearce et al., 1984; Himmelberg and Loney, 1995; Eyuboglu et al., 2010, 2011).

Among these types of intrusions, Uralian–Alaskan-type ultramafic–mafic complexes are examples of island arc magmatism or shallow crustal-level in situ intrusions into continental basement (Irvine, 1974; Johan, 2002; Pettigrew and Hattori, 2006; Thakurta et al., 2008; Ripley, 2009; Eyuboglu et al., 2010, 2011; Su et al., 2013). Such intrusions can be attributed to arc magma spreading center or arc-root complexes (Irvine, 1974; Taylor, 1967; Brüggmann et al., 1997; Debari and Coleman, 1989; Ishiwatari and Ichiyama, 2004; Farahat and Helmy, 2006; Zaccarini et al., 2008) related to the subduction environment and arc accretion (Taylor, 1967; Irvine, 1974; Pettigrew and Hattori, 2006; Su et al., 2012) and their consistent cumulate rocks can be formed as part of oceanic or continental arcs (Loucks, 1990; Eyuboglu et al., 2010).

These complexes are considered to be classic ophiolitic suites, which are mostly associated with ancient suture zones and have evolved under diverse geological environments (Yellappa et al., 2014). The most favorable of these is the Suprasubduction Zone (SSZ) environment (Irvine, 1974; Farahat and Helmy, 2006; Tian et al., 2011), which englobes the arc roots (e.g., Alaskan type) and includes the spreading centers related to the other parts of the arc environment development such as proto-arcs, fore-arcs and back-arcs formed during different stages of arc evolution (Shervais, 1982; Kusky et al., 2007; Dijkstra et al., 2006). The Uralian–Alaskan-type intrusions occur as small-scale plutons commonly characterized by concentric zoning. From core to rims, the lithologies are dunites and chromitites, wehrlites, clinopyroxenites, hornblendites, and gabbros, all showing characteristic cumulate textures (Taylor, 1967; Irvine, 1974; Himmelberg and Loney, 1995; Johan, 2002; Farahat and Helmy, 2006; Chen et al., 2009; Tian et al., 2011; Su et al., 2012). This zonal structure, however, can be discontinuous, incomplete, asymmetrical, and even reversed (Himmelberg and Loney, 1995; Eyuboglu et al., 2010, 2011). Nevertheless, many of these sequences consist of a single rock type, with hornblendite and peridotite the most abundant and clinopyroxenite or gabbro occurring in subordinate proportions (Eyuboglu et al., 2011; Himmelberg and Loney, 1995; Irvine, 1974). In most cases, the intrusions occur as kilometer-scale linear belts (Krause et al., 2007).

In addition, similar small intrusions within orogenic belts hosting Ni–Cu sulfide and Ti–Fe oxide deposits have been correlated with a post-orogenic extensional setting (Zhang et al., 2009, 2011; Song et al., 2011; Gao et al., 2012; Su et al., 2013; Xie et al., 2014).

Occasional Ti deposits have been described as eclogite-type with a ferrogabbroic parental magma, whereas the most common economic mineral in such association is rutile rather than ilmenite (Force, 1991). Because Ti is known to be fairly immobile during

chemical alteration and metamorphism, the parent rock must have had sufficient Ti to qualify as a mineral resource (Force, 1991).

Several mafic–ultramafic complexes occur as discontinuous bodies in the Alto Pajeú and Piancó/Alto Brígida domains in the western part of the Zona Transversal Subprovince, Borborema Province; these complexes are host rocks of economic Fe–Ti–V ± Cu deposits (Floresta/PE). Atypical occurrences of Cr–Ti–Fe spinels (Bodocó/PE) may mark an important tectonic association related to a subduction zone. Beurlen et al. (1992) presented evidence that these rocks underwent high-pressure metamorphic stages. However, this contention needs to be substantiated by further geochronological, geochemical, and isotopic data. In this paper, we present whole-rock geochemical and laser ablation-multicollector-inductively coupled plasma-mass spectrometry (LA-MC-ICP-MS) U–Pb, Sr–Nd isotopic data of the Floresta Mafic–Ultramafic Complex (FMUC), Serrote das Pedras Pretas Suite. In addition, we reevaluate the published data regarding FMUC–Riacho da Posse deposit and the Bodocó Mafic–Ultramafic Complex (BMUC)–Fazenda Esperança. This paper aims to utilize the geochemistry of FMUC and BMUC to infer the eclogite protolith. Our findings provide clues for understanding the tectonic architecture and conditions of Fe–Ti enrichment in some of the economically significant bodies.

2. Geologic setting and previous studies

The Borborema Province (Almeida et al., 1981) can be traced to the amalgamation of the São Francisco–Congo, São Luís, West Africa, and Amazonian cratons during the Gondwana assembly, known in this region as the Brasiliano Orogeny. It has a complex tectonic–magmatic framework marked by several episodes of magmatism (Almeida et al., 1981; Ferreira et al., 1998; Santos and Medeiros, 1999; Neves et al., 2000; Nascimento et al., 2000, 2008; Guimarães et al., 2004; Van Schmus et al., 2011). Several continental-scale high-temperature shear zones allow discrimination of this province into several tectonic domains (Fig. 1a; Caby et al., 1991; Corsini et al., 1991; Jardim de Sá, 1994; Vauchez et al., 1995). This structural mosaic has been described in terms of origin and evolution and is reflected in a variety of proposed nomenclatures (e.g., Brito Neves, 1983; Santos and Brito Neves, 1984; Jardim de Sá et al., 1992; Jardim de Sá, 1994; Van Schmus et al., 1995; Santos et al., 1999; Santos and Medeiros, 1999; Brito Neves et al., 2000, 2001a,b, 2005; Oliveira, 2008).

The study area is situated in the western portion of the Zona Transversal or Central Subprovince (Fig. 1a and b), which is limited by the large east–west (E–W) trending Patos and Pernambuco transcurent shear zones and various northeast–southwest (NE–SW)-trending crustal segments.

The FMUC, Serrote das Pedras Pretas suite (Fig. 2), occurs as clusters of small mafic to ultramafic rock sequences that are commonly mineralized by massive Fe–Ti–V oxides and minor primary disseminated Ni–Cu sulfides. Most of the bodies are subrounded and are less than 1.5 km² in diameter. Folded lenses extend beyond the subrounded “intrusions,” which are currently xenoliths. Mineralization is present in ultramafic members, as indicated by intercumulus/cumulus textures in pyroxenites and olivine cumulates (Beurlen et al., 1992). FMUC forms a part of the Alto Pajeú Domain, which consists primarily of rocks generated during the Tonian Cariris Velhos event (Brito Neves et al., 1995; Santos, 1995; Santos et al., 1999, 2010). The FMUC crops out in metavolcanic–sedimentary sequences, metagraywackes, and mica schists known as São Caetano Complex. Its minimum age has been constrained at 995 ± 8 Ma (Santos et al., 2010) on the basis of U–Pb zircon data of an intrusive metatuff situated north of Floresta. Other regional ages for volcanogenic and supracrustal rocks in the Alto Pajeú

Fig. 1. (a) Tectonic sketch highlighting Central or Zona Transversal (ZT) Subprovince in Borborema Province and their Piancó-Alto Brígida and Alto Pajeú domains, which contain the Bodocó and Floresta Mafic-Ultramafic Complexes. Modified after Medeiros (2004). (b) Simplified regional geologic map of the study area in the Central Domain of Borborema Province showing distribution of the mafic-ultramafic complexes. Modified after Gomes and Santos (2001).

Domain, at 995–965 Ma also fall within the same age bracket (Santos et al., 2010). The oldest ages found thus far are in the eastern part of the Alto Pajeú Domain and include the Sítio do Icó fine-grained gneiss, which is a subvolcanic rock with andesitic character at 1005 ± 5 Ma (Lages et al., 2014; Guimarães et al., 2015) and a gneiss at 1037 ± 30 Ma (Van Schmus et al., 1995). Detrital sedimentation determined in younger zircon by Sensitive High

Resolution Ion Microprobe (SHRIMP) at 932 ± 12 Ma (Van Schmus et al., 2011) indicates an extensional setting after the Cariris Velhos magmatism. Almost all of the metaplutonic rocks show more precise results falling in the interval of 960–925 Ma, which is generally younger than the ages of the metavolcanic rocks (Brito Neves et al., 1995; Kozuch, 2003; Santos et al., 2010; Guimarães et al., 2015). The tectonic setting of the Tonian granitoids is still

Fig. 2. Simplified geological map of Floresta Mafic-Ultramafic Complex (FMUC) and rock sampling positions. Modified after Brasilino et al. (2014).

under debate; they are related to either a continental margin magmatic arc with possible back-arc association (Brito Neves et al., 2000; Santos et al., 2010; Oliveira et al., 2010; Kozuch, 2003; de Caxito et al., 2014a; Van schmus et al., 2011) or to an extension-related setting with generation of A-type granites (Guimarães et al., 2012, 2015; Neves, 2003).

Despite this discussion, however, the major economic deposits of FMUC include the Riacho do Icó Suite as a wall rock and large

xenoliths as floats within it. The Riacho do Icó Suite is composed of a composite felsic intrusion with compositions ranging from quartz monzodiorite and granodiorite to monzogranite. U-Pb SHRIMP zircon analysis yielded a crystallization age of 608 ± 5 Ma (Santos et al., 2014).

The BMUC, Fazenda Esperança type (Fig. 3), was emplaced within the Piancó-Alto Brígida basement. The former is known as the Salgueiro-Cachoeirinha belt, which is comprised of several

Fig. 3. Simplified geological map of Bodocó Mafic-Ultramafic Complex (BMUC) highlighting the Fazenda Esperança deposits. Adapted and modified after Medeiros et al. (1993).

lensoid mafic-ultramafic bodies occurring peripheral to the NW limb of a regional anticlinal fold structure close to the tectonic contact between Neoproterozoic low to medium-grade metamorphic supracrustal rocks of the Salgueiro Complex and the Cachoeirinha Group. The core of the anticlinal structure, known as the Icaíçara fragment (Medeiros et al., 1993), is a composite granitoid (granite gneiss, migmatitic to banded gneiss) that hosts the BMUC and a psammitic-pelitic-carbonate sequence (staurolite-kyanite bearing in places) related to the Barro Complex (Medeiros et al., 1993). A single crystal zircon Pb-Pb age of 1969 ± 9 Ma was determined from an augen gneiss that crosscuts the migmatitic gneiss, which constrains the minimum age of the rocks in the core of the anticline (Medeiros et al., 1993). A detailed petrographic analysis of two garnet-rich gabbroic members of the BMUC was conducted to ascertain their eclogitic affinities (Beurlen and Villarreal, 1990; Beurlen, 1988; Beurlen et al., 1992).

A metarhyodacitic sheet interspersed within a biotite schist collected near the homonymous area has been dated at 962 Ma, which constrains the age of the Salgueiro Complex (Brito and Cruz, 2009). The Cryogenian-Ediacaran age of 650–625 Ma (U-Pb) for the Cachoeirinha Group is constrained by zircons from the rhyolite (Van Schmus et al., 1995; Kozuch, 2003; Medeiros, 2004), and recent SHRIMP U-Pb data in detrital zircons reinforced an age younger than 630 Ma (Van Schmus et al., 2011).

3. Analytical methods

The U-Pb, Sm-Nd, Sr-Sr, and microprobe analyses were performed at the University of Brasília (UnB) facilities, Brazil. Zircon, garnet, pyroxenes, and amphiboles were selectively liberated by using high-voltage pulsed power discharges provided by power fragmentation equipment (SELFRAQ, Kerzers Switzerland). The concentrations of heavy minerals were then processed by using a magnetic separator (S.G. Frantz, New Jersey, USA).

For U-Pb geochronological analysis, zircon grains were hand-picked and mounted on an adhesive tape, enclosed in epoxy resin, and polished to approximately half of their original thicknesses. U-Pb analysis was performed on a Mass Spectrometer Multi-Collector (Finnigan Neptune, Thermo Scientific, NYSE:TMO) with ICP following the methods described by Bühn et al. (2009). For data reduction and age calculations, the programs PBDAT (Ludwig, 1993) and ISOPLOT-Ex (Ludwig, 2001) were used. Isotopic errors were in the range of 1σ .

Sm-Nd analyses were performed following the method described by Gíóia and Pimentel (2000). Whole rock powders and leached minerals were mixed with an ^{149}Sm – ^{150}Nd spike solution and dissolved in Saville capsules. The Sm and Nd extraction of whole-rock samples followed conventional cation exchange techniques using Teflon columns containing LN-Spec resin (diethylhexyl phosphoric acid; HDEHP) supported on

polytetrafluoroethylene (PTFE) powder. Sm and Nd samples were loaded on a Re double-filament evaporation assembly, and the isotopic measurements were conducted by MS (Triton Plus, Thermo Scientific). Uncertainties of Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ were better than $\pm 0.4\%$ (1σ) and $\pm 0.005\%$ (1σ), respectively, based on repeated analyses of international rock standards Basalt, Hawaiian Volcanic Observatory (BHVO-1) and Basalt, Columbia River (BCR-1). $^{143}\text{Nd}/^{144}\text{Nd}$ was normalized to $^{146}\text{Nd}/^{144}\text{Nd}$ of 0.7219, and the decay constant used was 6.54×10^{-12} . T_{DM} model ages were calculated by using the procedure given in DePaolo (1981). The open-source GcdKit isotopic plug-in (Janoušek et al., 2006) was used to help generate Nd evolution curves and other graphs.

The Sr isotopic compositions were obtained by using a MS (Triton Plus, Thermo Scientific). The total analytical blank for Sr remained close to 0.2 ng. The 2σ uncertainties for the $^{87}\text{Sr}/^{86}\text{Sr}$ were less than 0.01%.

Electron microprobe analysis was performed by using a SuperProbe Electron Probe Microanalyzer (EPMA; JXA-8230, Jeol, Japan) with five wavelength dispersive spectrometers (WDS) coupled with one energy dispersive spectrometer (EDS). The available analyzer crystals (TAPJ, LIF, LIFH, PETJ, PETH, LDE1, and LDE2) allowed all chemical elements with atomic numbers greater than 4 following certain routine conditions such as (a) beam current of 10 nA; (b) beam diameter of 3 μm , and (c) accelerating voltage of 15 kV. The pyroxene group was recalculated by using the Visual Basic® program Winpyrox (Yavuz, 2013). The amphibole group was recalculated with the aid of an updated PROBE-AMPH 3.0 Excel spreadsheet (Tindle and Webb, 1994). Recalculations on coexistent pairs of magnetite and ilmenite including temperature (T ; $^{\circ}\text{C}$) and $\log_{10}f\text{O}_2$ were aided by the ILMAT Excel spreadsheet (Lepage, 2003).

Whole-rock samples were analyzed at Acme Analytical Laboratories Ltd. (Canada). A small portion of the analyses was also conducted at SGS Geosol Ltd. (Brazil) for rock samples started at AM abbrev. The opening method used was the LiBO_2 melt and multi-acid solution. The methods of multi-element analysis passed through ICP-MS, ICP-atomic emission spectroscopy (AES), and X-ray fluorescence according to elemental groups. The latest version of GCDkit 3.0 assisted in data interpretation.

Back-scattered images and EDS spots analyses were obtained by using scanning electron microscopy (SEM)/EDS (Quanta 450, FEI, Oregon, USA) coupled with ~ 10 mm WD and 20 kV of acceleration voltage.

4. Results

4.1. Mineralogy and petrography

Twenty occurrences of Fe–Ti mineralization and ultramafic rocks in the FMUC were reviewed, and eight were selected for a more detailed petrographic, microprobe, geochemical, and isotopic analyses (see Fig. 2). Rock samples from freshly exposed mining pits such as Serrote das Pedras Pretas (GL-02), Riacho da Posse (GL-08), Lagoa dos Angicos (GL-01), and Fazenda Exú (GL-15); prospecting trenches and material accessed after the installation of a high-voltage transmission line over Riacho do Tapuio (GL-04) provided material suitable for chemical, geochronological, and isotopic analyses as well as documentation of geological relationships.

Primary and high-pressure mineral assemblage, and retro-metamorphic minerals observed in thin sections from the FMUC are given in [Inline Supplementary Fig. S1](#).

4.1.1. Metadunites and olivine cumulates

Metadunite and olivine cumulates commonly occur as mineralized olivine cumulates with net ore textured intergranular ilmenite and magnetite (Fig. 4a and f). Disseminated Ni–Cu–Fe sulfides are

interstitial and occur together with Fe–Ti oxides and silicates. Serpentinized olivine in the mineralized dunite is altered to chlorite, serpentine, and crystals of an acicular amphibole (cummingtonite or anthophyllite), whereas clinopyroxenes are replaced by tremolite. A massive dark-green, strongly serpentinized metadunite (Fig. 4b) occurs in the Serrote das Pedras Pretas mine. In compacted dunites, the olivines are pseudomorphs generated by their breakdown leaving serpentinite/chlorite, iddingsite, and a corona texture of magnetite. Thick, massive ore bands of ilmenomagnetites of up to 3 m (Fig. 4c) encompass a layer concordant with these ultramafic members, and thin discordant veins crosscut them.

4.1.2. Metaclinopyroxenites

Clinopyroxenites, tremolitites, and cpx–tremolite–chlorite schists are closely associated with olivine cumulates and preserve Fe–Ti–V net textured mineralization. The gradation between wehrlites to pyroxenites, best observed in the Riacho Tapuio occurrence, consists of (olivine) clinopyroxene–tremolite–chlorite schists with pyroxenes and rare cordierite. Clinopyroxenites and wehrlites are mainly present with garnet amphibolites and metahornblendites but are also observed in fine-grained metapyroxenites. We suppose that some metaultramafic schists surrounding dunites are products of recrystallization of metaweherlites and metapyroxenites showing cumulus clinopyroxenes (augite and diopsides) mostly altered to actinolite, tremolite, or cordierite from altered serpentines (Fig. 4e).

4.1.3. Garnet amphibolite

The garnetiferous amphibolites contain up to 50 garnet modal, reaching up to 1.5 cm in an amphibole matrix (Fig. 4d). Some high modal (>50%) terms of elongated garnets with large amounts of Fe–Ti oxides can also be considered as garnetites. Porphyroblastic garnets always show intense fracturing and the presence of amphibole, rutile, plagioclase, clinozoisite, and quartz occurring as snowball texture inclusions. The most voluminous amphibole is slightly oriented, with light yellow–greenish pleochroism compatible with a hornblende composition. Other variations include tremolite/actinolite and sodic amphiboles with bluish and purple tones.

Symplectites are formed around garnets and are composed of intergrowths of amphibole, rutile, clinozoisite, and scarce small grains of plagioclase (Fig. 4d and i). Coronitic olivine (Fig. 4g) occurs in some members and indicate olivine gabbro or even troctolite protoliths.

4.1.4. Coarse metahornblendite

Metahornblendites are usually associated with garnet amphibolites (Fig. 4d). They appear as idiomorphic crystals of coarse hornblende with variable pleochroism and accessory minerals of more than 4% such as idiomorphic rutile parallel to elongated crystal faces (Fig. 4h), titanite, magnetite, and interstitial fine-grained albite plagioclase.

4.1.5. Ilmenomagnetite or massive ore shoot

Three types of massive ilmenite–magnetite bands occur, particularly in thick lenses concordant to the host rocks (Fig. 4c) and, centimeter-sized discordant veins commonly associated with cross-fiber veins of serpentinites crosscutting the third type, which consists of olivine $\pm$ pyroxene $\pm$ tremolite $\pm$ chlorite cumulates surrounded by (inter)cumulus Fe–Ti–V oxides. The amounts of disseminated mineral assemblages composed of rutile + sphene or pyrrhotite + chalcopyrite + pentlandite blebs can also be considered as an accessory mineralogy.

The interstitial xenomorphic ilmenite–magnetite ores with respect to silicates suggest a cumulative origin for the euhedral pyroxene/olivine formation of a network texture. Massive coarse-grained ores form polygonal crystals of V-magnetite and

Fig. 4. Outcrop photographs of the Floresta Mafic-Ultramafic Complex (FMUC). (a) Mineralized olivine/pyroxene cumulates showing network ore texture of ilmenite + magnetite (inter)cumulus. (b) Weathered compact, dark-green metadunite. (c) Massive ilmenomagnetite occurring as thick concordant bands and in polygonal grains of Co-V bearing magnetite and ilmenite. (d) Contact between coarse hornblende and garnet amphibolite. (e) Groundmass of tremolite-chlorite schist including idioblastic grains of pyroxene/cordierites. (f) Pseudomorph of olivine altered to carbonate + magnetite + talc surrounded by intercumulus in a network texture of ilmenite + magnetite and silicates, plane-polarized light (//). (g) Coronitic olivine in amphibolitic matrix, analyzed light or crossed n-icols (x). (h) Coarse idiomorphic hornblendes with rutile growth parallel to elongated crystal faces, polarized light. (i) Back-scattered image of symplectite texture exhibiting porphyroblast of fractured garnet (Grt) surrounded by rutile (Rt) + amphibole (Hbl) + plagioclase (Pl). (j) Back-scattered image of massive Fe-Ti oxide ore with polygonal texture with Co-V bearing magnetite (Mag) and ilmenite (Ilm). Idiomorphic Al-spinel occurs as hercynite-type bordering magnetite and ilmenite. Rare hematite and ilmenite lamellae exsolutions are also shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ilmenite intergrowths (Fig. 4c) showing complete oxidation exsolution where lamellae of ilmenite is rare in magnetite and hematite, and magnetite is virtually absent in ilmenite (Fig. 4j). The magnetite and ilmenite have approximately the same proportions in coarse massive ores. Idiomorphic grains of hercynite are in contact with ilmenites and magnetites, suggesting an exsolution origin. Titanite, rutile, siderite, sulfides, and silicate gangue are subordinate minerals.

4.2. Mineral chemistry

Three thin sections from the FMUC were selected to perform electron microprobe analysis of the following minerals: Al-spinel, magnetite, and ilmenite in a massive ilmenite–magnetite ore band from Fazenda Exú (GL-15 UTM 551130; 9063033); and amphiboles, garnet, plagioclase, epidote, titanite, and rutile in metahornblende and garnet amphibolite from Riacho do Tapuio (GL-04A and GL-04B UTM 551344; 9067350).

In addition, we recalculated all Cr-spinels, pyroxenes, and amphiboles from Fazenda Esperança (BMUC) and amphiboles from the Riacho da Posse deposit (FMUC) reported by Beurlen (1988). The results are presented here as appendices.

4.2.1. Spinel, magnetite, and ilmenite

Al-spinel, commonly hercynite, is present as an accessory phase in the massive ilmenite–magnetite ore bands from Floresta/PE and occurs at the boundary between ilmenite and vanadiferous magnetite. It is characterized by low Cr_2O_3 at 0.2–0.39 wt.% and, higher Al_2O_3 at 54.9–57.4 wt.%, FeO at 19.64–22.24 wt.%, TiO_2 at 5.5–7.4 wt.%, and V_2O_5 at 0.32–0.51 wt.%. It exhibits a low Mg# ($100 \times \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$) and a Cr# ($100 \times \text{Cr}/(\text{Cr} + \text{Al})$) ranging between 40.7–45.7 and 0.25–0.45, respectively. (Inline Supplementary Table 1)

Cr-spinel, commonly Fe-chromite, occurs in massive cumulate bands in Bodocó/PE (Inline Supplementary Appendix A) revealing that the Fe-chromites have lower contents of Al_2O_3 at 0.64–11.96 wt.%, and MgO at 0.04–8.38 wt.% in addition to wide ranges of TiO_2 at 0.92–20.71 wt.%, Cr_2O_3 at 15.25–34.68 wt.%, and FeO at 31.43–65 wt.%. Its Cr# is between 48 and 97, and its Mg# ranges from 0 to 52.8.

The magnetites are vanadiferous magnetites with low TiO_2 at 0.11–0.49 wt.%. Fe_2O_3 and V_2O_5 range from 82.87 to 85.96 and 1.82 to 2.1 wt.%, respectively, and they exhibit low contents of Al_2O_3 and Cr_2O_3 at ~ 0.4 and ~ 0.35 . The mole fraction of uvöls spinel ranges from 0.37 to 1.70%.

The ilmenites form an equigranular mosaic with magnetite in net-texture ore bodies and massive form with >40% of ilmenites. Their contents of TiO_2 range from 48.6 to 51.5 wt.%; FeO and V_2O_5 are 44.4–45.9 wt.%, and 0.34–0.98 wt.%, respectively. The mole fraction of ilmenite, >92.42%, confirms the absence of exsolution.

4.2.2. Pyroxenes

Clinopyroxene and Ca–Na pyroxene are from pyroxenites and porphyroclastic clinopyroxene tremolitites (Inline Supplementary Appendix B). The porphyroclastic clinopyroxene in the clinopyroxene tremolitites is mostly diopside and augite with high Mg# at 88.8–99.5 and high CaO 21.8–24.2%; lower contents of TiO_2 at 0.00–1.32 wt.%, Al_2O_3 at 0.00–1.68 wt.%, and Na_2O at 0.00–0.69 wt.%; and moderate to high Cr_2O_3 0.23–0.54%. The minerals in metapyroxenite show relatively low values of TiO_2 at 0.0–0.14 wt.%, Al_2O_3 at 0.83–2.09 wt.%, and Na_2O at 0.31–0.73 wt.%, and high CaO at 24.15–25.63 wt.% and Mg# at 91.8–100.

In the eclogite, Ca–Na omphacites were recognized (Appendix B; Beurlen et al., 1992), although a single crystal of augite recorded low Al_2O_3 at 4.90 wt.% and Na_2O at 1.34 wt.% and high MgO at 14.8 wt.%. The Mg# varies between 80.45 and 95.98. They are also characterized by relatively high TiO_2 at 0.51–2.03 wt.% and Cr_2O_3

at 0.22–1.92 wt.%; low Na_2O at 0.20–0.65 wt.%; and variable amounts of Al_2O_3 at 1.60–4.97 wt.%. Almost all spots present a core-to-rim variation in SiO_2 and Al_2O_3 .

4.2.3. Amphiboles and garnets

Hornblende group minerals (hbl) are the most abundant and exhibit a wide range of compositions in the FMUC (Inline Supplementary Table 2) and BMUC (Inline Supplementary Appendix C). Nomenclature names according to Leake et al. (1997, 2004). Secondary hbl has inherited precursory compositions of clinopyroxene occurring mainly as tremolite or actinolite in the case of eclogite and pyroxenite and is predominantly magnesium-hbl and tschermakitic hornblende. Some relics as inclusions or in snow-ball textures can be primary hbl that includes ferroan pargasite in addition to Fe-tschermakite (hornblende) and Mg-hbl. The most Mg-rich hornblendes have Mg# ~ 1 (c.f. between 0.43 and 1 in amphibolites). Hornblendes have higher contents of CaO at 6.26–12.65, Na_2O at 0.66–2.93, and MgO at 6.42–20.24 and they have variable contents of TiO_2 and Al_2O_3 with a positive correlation in eclogite symplectites in addition to SiO_2 . Fe-tschermakitic hornblende and (ferri)-barroisite (Na–Ca group) were identified in symplectites from eclogite (BMUC; BO-436) and grains from garnet–amphibolite (FMUC; RP-614).

Cr-poor granoblastic garnets from a garnet amphibolite (Inline Supplementary Table 2) in the FMUC have a composition of almandine_{52.09–55.24}, pyrope_{10.69–14.27}, grossular_{26.73–29.91}, and spessartite_{2.83–7.58}. Millimeter-scale xenoblastic terms in symplectite intergrowths show depletion in the mole fraction of pyrope_{7.65} with incipient replacement of Mg by Mn. These garnets have ubiquitous inclusions of quartz, rutile, and amphibole.

4.2.4. Plagioclase, epidote, titanite, and rutile

Plagioclase (Inline Supplementary Table 3) is absent in the dunite/olivine cumulates, coarse hornblendites, massive and net-textured ore bodies and is present only as part of the symplectites in the garnet amphibolite of the FMUC samples. An individual small grain and a symplectite intergrowth have a similar An content of ~ 40 , which is close to the andesine composition. A single grain found in a metahornblendite sample has an albite–oligoclase composition of An_{14.02}, which may represent a retromorphic component.

Epidote grains occur as symplectites together with quartz, rutile and minor plagioclase surrounding the garnets and are compatible with clinozoisite composition. They have high FeO at $\sim 8\%$ and Al_2O_3 at 24.63–24.77%. A general replacement of Al by Fe^{3+} depicts substitution in the monoclinic members.

All of the analyzed titanites and a unique rutile spot exhibit homogeneous compositions. Rutile is the second most abundant Ti mineral, reaching modal proportions of 4–12%.

4.3. Bulk-rock chemistry

Representative metamafic–ultramafic rock samples of the FMUC were analyzed for their major, trace, and rare earth element (REE) concentrations. In addition, 30 analyses of samples from the FMUC and BMUC reported by Beurlen (1988) were reviewed (Inline Supplementary Table 4 and Appendix D).

The control of lithology and fractional crystallization of cumulus minerals is demonstrated by the existence of some systematic trends of major oxides, as shown in Fig. 5a. The negative correlation of MgO with Al_2O_3 and its positive correlation with CaO underline a control by fractionation of olivine and clinopyroxene, whereas fractionation of Fe–Ti oxides is revealed in the expanded TiO_2 –MgO plot.

The Al_2O_3 content increases from less than 2.67 wt.% in the olivine cumulates and 2–11.6 wt.% in the metaclynopyroxenites to values between 2.5 wt.% and 21.8 wt.% in the metahornblendites/garnet amphibolites. Olivine cumulates also

Fig. 5. (a) Variation diagrams of major oxides versus MgO index plots showing major fractional indices. Mineral trends are from Shaw et al. (2003); Alaskan-type fields are from Wang et al. (2010). (b) AFM diagram for ultramafic–mafic lithologies with fields of arc-related cumulate ultramafic–mafic rocks and arc-related gabbro and diorite fields from Beard (1986), after Eyuboglu et al. (2011).

have low CaO concentrations of less than 1.4 wt.%, whereas the clinopyroxenites have the highest CaO concentration at 8.9–20.2 wt.%. The TiO_2 content is highest in the olivine cumulates at 5.3–25.3 wt.%, and decreases in the clinopyroxenite and hornblende/amphibolites at 0.41–2.27 wt.% and 1.3–14.9 wt.%, respectively.

The peridotites have moderate to high Ni at 131–2000 ppm, Cr at 49–2016 ppm, Co at 82–400 ppm and Cu at 10.9–1120 ppm, and low concentrations of Rb at 0.5–64 ppm and Sr at 3.4–58.6 ppm. The pyroxenites have concentrations of Ni of at 42–1050 ppm, Cr at 58–2809 ppm, and Co at 11–98.1 ppm as well as a high concentration of Sr at 15–499 ppm.

For the deposits of Serrote das Pedras Pretas, Riacho da Posse e Riacho da Cachoeira Grande, the TiO_2 contents of the samples of massive ore bands of the FMUC show similar values between 40.8 and 44.6 wt.%. The values of Fe_2O_3 vary between 49.84 and 54.05 wt.%, and the content of V varies from 2933 to 3633 ppm.

In the AFM diagram, the metapyroxenites plot most closely to the M axis, whereas the olivine cumulates follow a parallel trend to the MF side (Fig. 5b); this result most likely reflects the

magnetite-ilmenite mineralization. The majority of amphibolites and gabbroic rocks show a tholeiitic trend overlapping the arc-related mafic cumulate field. The metapyroxenites are in accordance with an arc-related ultramafic cumulate field.

In the primitive mantle-normalized spider and chondrite-normalized REE diagrams, the pyroxenites and amphibolites/meta hornblendites show similar distribution patterns (Fig. 6a–d) characterized by slight enrichment of large ion lithophile elements

Fig. 6. Chondrite-normalized rare earth element (REE) patterns and primitive mantle normalized trace-element patterns for the Bodocó and Floresta mafic-ultramafic rocks. Primitive mantle and chondrite normalizing values are from [McDonough and Sun \(1995\)](#). The data for the Alaskan-type field are from [Himmelberg and Loney \(1995\)](#). Average normal midocean ridge basalt (N-MORB) rocks are from [Hofmann \(1998\)](#); average island arc basalt (IAB) data are from [Kelemen et al. \(2003\)](#) and ocean island basalt (OIB) are from [Sun and McDonough \(1989\)](#). The data for subducted serpentinites are from [Deschamps et al. \(2013\)](#).

(LILE) and high field strength elements (HFSE) with respect to the primitive mantle. The chondrite-normalized patterns of the amphibolites/metahornblendites exhibit slight enrichment in LREE relative to HREE patterns (Fig. 6a and b). Furthermore, garnet amphibolites show more pronounced negative Nb, Ta, Zr and Hf anomalies when compared with metahornblendites and metapyroxenites. Strong negative Sr troughs and a positive peak of Y are also present in mafic members. The plots of garnet amphibolites and metahornblendites overlap with the island arc basalt (IAB) and ocean island basalt (OIB) trends and lie distinctly away from the average normal midocean ridge basalts (N-MORB). In the primitive mantle-normalized diagram, the metapyroxenites exhibit regular trace element patterns (Fig. 6d) and are commonly characterized by troughs for Pb, Sr, Zr, and Y.

The patterns for peridotites have smooth MREE and HREE slopes (Fig. 6e) and show a characteristic U-shaped pattern similar to that in harzburgites and wehrlites. The primitive mantle normalized peridotite spider diagram shows a well-marked positive Pb anomaly and enriched fluid mobile elements including Cs, Rb, Th, and U, suggesting the percolation of fluid during the superimposed subduction process.

4.4. Isotopic data

4.4.1. Zircon LA-MC-ICP-MS U–Pb geochronology

Zircon grains were separated from a coarse meta-hornblendite sample (GL-02_SPP) collected from the Serrote das Pedras Pretas mine within the FMUC. These zircon grains are prismatic in shape and are formed by two distinct phases: older, homogeneous or growth-zoned cores with locally occurring traces of earlier resorption and recrystallization and coarse metamorphic rims that are generally homogeneous and are separated from cores by irregular interfaces indicative of corrosion (Fig. 7a). These textures are common in zircons from high-grade metamorphic rocks such as eclogites and granulites (Corfu et al., 2003).

The cores of zircon grains have high Th/U values at 0.117–0.990, and they define an upper intercept age of 1024 ± 18 Ma (MSWD = 4.2; Table 5; Fig. 7b); this is interpreted as the crystallization age of the FMUC. A core spot (#COMP2_016-Z9) with a Th/U value lower than 0.1 yielded a discordant $^{207}\text{Pb}/^{206}\text{Pb}$ value of 1030 ± 11 Ma (σ_1) and $^{238}\text{U}/^{206}\text{Pb}$ of 967 ± 9 Ma. The age of this grain, even considering the limits of the analysis by LA, may suggest evidence of concomitant metamorphic processes during the

Fig. 7. laser ablation-multicollector-inductively coupled plasma-mass spectrometry (LA-MC-ICP-MS) U–Pb analysis of zircons from the Floresta Mafic–Ultramafic Complex (FMUC), Serrote das Pedras Pretas mine. (a) Back-scattered image of prismatic older cores homogeneous to zoned growth locally with traces of earlier resorption and recrystallization as well as coarse metamorphic growth homogeneous rims. (b) Upper intercept of concordia age at 1024 ± 18 Ma obtained from the most concordant core grains. (c) Concordia ages at 685 ± 18 Ma and 625 ± 6 Ma obtained from the rims of zircon grains.

Table 5

LA-ICP-MS U–Th–Pb results for zircons from metahornblendite within Floresta Mafic–Ultramafic Complex (FMUC; Serrote das Pedras Pretas Mine).

Samples Spots	Th/U	Ratios							ρ	Apparent Ages						Conc. (%)
		²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	$\pm 1\sigma$	²⁰⁷ Pb/ ²³⁵ U	$\pm 1\sigma$	²⁰⁶ Pb/ ²³⁸ U	$\pm 1\sigma$		²⁰⁷ Pb/ ²⁰⁶ U	(Ma)	²⁰⁷ Pb/ ²³⁵ U	(Ma)	²⁰⁶ Pb/ ²³⁸ U	(Ma)	
GL-02_SPP																
Cores																
008-Z3N	0.351	51,013	0.07323	0.36	1.5439	0.93	0.152919	0.86	0.91	1020	7	948	6	917	7.36	97
009-Z3M	0.342	2358	0.07100	0.80	1.2402	1.46	0.126686	1.22	0.85	957	16	819	8	769	8.85	94
040-Z21N	0.541	237,702	0.07470	0.26	1.6684	0.76	0.161979	0.72	0.93	1061	5	997	5	968	6.46	97
011-Zir3N	0.630	69,429	0.07367	0.0007	1.5914	1.35	0.156670	0.89	0.66	1032	19	967	8	938	7.78	91
012-Zir4	0.688	70,845	0.07269	0.0006	1.6435	1.25	0.163966	0.86	0.69	1005	17	987	8	979	7.82	97
017-Zir7	0.315	26,989	0.07252	0.0012	1.6279	2.41	0.162787	1.65	0.69	1001	34	981	15	972	14.90	97
021-Zir9N	0.618	39,088	0.07195	0.0005	1.2954	1.72	0.130571	1.53	0.89	984	14	844	10	791	11.41	20
028-Zir11	0.605	56,401	0.07375	0.0008	1.7411	1.88	0.171202	1.47	0.78	1035	22	1024	12	1019	13.86	98
034-Zir15N	0.990	94,212	0.07337	0.0006	1.9157	1.66	0.189345	1.36	0.82	1024	17	1087	11	1118	13.99	109
040-Zir18	0.802	11,823	0.07460	0.0012	1.5861	1.79	0.154196	0.57	0.32	1058	33	965	11	924	4.87	87
047-Zir21	0.625	20,151	0.07149	0.0012	1.5054	2.24	0.152699	1.4379	0.64	972	34	933	14	916	12.27	94
COMP_006-Z6N	0.418	86,207	0.07214	1.32	1.4943	1.75	0.150236	1.14	0.64	931	28	928	11	902	9.64	97
COMP_012-Z31N	0.452	37,481	0.07301	0.91	1.5507	1.41	0.154041	1.08	0.75	956	19	951	9	924	9.29	97
COMP_018-Z33N	0.225	61,409	0.07308	0.56	1.5399	0.93	0.152825	0.75	0.77	958	12	946	6	917	6.41	97
COMP2_011-Z6	0.555	104,549			1.7232	1.05	0.172355	0.81	0.74	1000	14	1017	7	1025	7.64	102
COMP2_012-Z7	0.556	54,211			1.6484	1.04	0.163601	0.72	0.66	1016	15	989	7	977	6.57	96
COMP2_024-Z15	0.155	12,482			1.5738	3.01	0.153021	2.13	0.70	1058	43	960	19	918	18.22	87
COMP2_035-Z21	0.580	233,296			1.7382	0.87	0.175112	0.74	0.82	986	10	1023	6	1040	7.09	106
COMP2_048-Z29	0.117	111,249			1.5707	2.17	0.155274	1.88	0.86	1024	22	959	13	930	16.25	91
COMP2_052-Z31	0.133	1194			1.3966	2.89	0.140187	1.70	0.64	993	47	888	17	846	13.49	85
COMP2_016-Z9	0.037	8703			1.6425	1.15	0.161898	1.02	0.87	1030	11	987	7	967	9.14	94
Rims																
007-Z2B	0.013	21,174	0.06404	0.56	0.8131	1.07	0.092081	0.92	0.84	743	12	604	5	568	4.98	94
019-Z10B	0.038	6103	0.06611	1.34	0.8583	2.40	0.094158	1.99	0.83	810	28	629	11	580	11.05	92
020-Z11B	0.018	4616	0.06310	0.92	0.8533	1.35	0.098084	0.98	0.72	711	20	626	6	603	5.62	96
023-Z12B	0.015	20,870	0.06364	0.93	0.8986	1.46	0.102409	1.12	0.76	730	20	651	7	629	6.71	97
025-Z13B	0.011	7820	0.06128	1.19	0.8601	1.82	0.101796	1.37	0.75	649	26	630	9	625	8.16	99
027-Z14B	0.008	20,281	0.06164	0.92	0.8666	1.18	0.101958	0.75	0.59	662	20	634	6	626	4.46	99
029-Z15B	0.010	5178	0.06077	0.87	0.8433	1.45	0.100645	1.16	0.79	631	19	621	7	618	6.86	100
036-Z18B	0.008	5477	0.06331	1.16	0.8254	1.64	0.094556	1.16	0.70	719	25	611	8	582	6.48	95
048-Z26B	0.024	7713	0.06645	0.92	0.8566	1.64	0.093498	1.37	0.82	821	19	628	8	576	7.53	92
049-Z27B	0.008	7843	0.06598	1.08	0.9081	1.63	0.099816	1.22	0.74	806	23	656	8	613	7.16	93
COMP2_051-Z30	0.008	19,020			0.9498	3.22	0.109569	2.23	0.69	704	50	678	16	670	14.18	95
COMP2_015-Z8	0.011	21,443			0.9686	3.32	0.115257	2.35	0.70	637	51	688	17	703	15.64	110
COMP2_046-Z27	0.010	26,738			0.9736	3.37	0.111634	2.73	0.81	717	42	690	17	682	17.67	95
035-Zir15B	0.010	21,220	0.05900	2.96	0.7559	3.88	0.092922	2.48	0.64	567	63	572	17	573	13.59	101
Inheritance																
COMP_011-Z30N	0.256	162,785	0.12426	1.90	5.6729	3.15	0.331103	2.51	0.80	1968	35	1927	27	1844	40.33	96
COMP_021-Z27N	0.431	130,943	0.11016	0.82	3.3566	1.03	0.220994	0.62	0.54	1750	15	1494	8	1287	7.18	86
COMP_022-Z34N	0.436	129,607	0.11146	0.88	3.3241	1.59	0.216292	1.33	0.83	1771	16	1487	12	1262	15.24	85

Tonian Period. Data points of zircon rims with metamorphic margins have systematically low Th/U values that range between 0.008 and 0.038. Two concordia ages of 685 ± 17 Ma (MSWD = 0.047) and 625 ± 6 Ma (MSWD = 2.8; Table 5; Fig. 7c) are identified as the progressive ages of high-grade metamorphism. Three xenocrystic zircons denote inheritance at ca. 1.9 Ga that cannot be correlated with any known event in the exposed basement rocks.

4.4.2. Sr–Nd Isotopes

One sample of each facies from Serrote das Pedras Pretas (GL-02), Riacho da Posse (GL-08) and Lagoa dos Angicos (AM-445) within the Riacho do Icó granite and the Tapuio (GL-04) and the Caraibeiras (AM-448 and AM-456), folded along with the São Caetano schist, were analyzed for Sr–Nd isotopes (Table 6).

The Sm–Nd whole-rock isochronal age obtained for 12 samples from the FMUC yields an age of 1028 ± 63 Ma (MSWD = 0.79) with an initial $\epsilon\text{Nd}(t)$ of 2.1 (Fig. 8a), which is also interpreted as a possible protolith age of the FMUC. The obtained Sm–Nd isochron age is quite similar to that obtained by the U–Pb method considering the uncertainty.

The initial isotopic ratios were calculated on the basis of 1024 Ma (Fig. 7b). The $(^{143}\text{Nd}/^{144}\text{Nd})_i$ of the FMUC mafic–ultramafic rocks range from 0.511317 to 0.511564, and the $\epsilon\text{Nd}(t)$ values are in the

range of 0.01–4.84. With the exception of two samples, their T_{DM} values range between 1.1 and 1.6 Ga suggesting that their protoliths were derived from a juvenile Mesoproterozoic asthenospheric source or a mixed Paleo and Neoproterozoic source.

The initial ratios, expressed as positive $\epsilon\text{Nd}(t)$ of 2.1 and obtained in the isochron (Fig. 8a) and Nd isotopic growth diagram (Fig. 8b), reveal that the original magma was not contaminated by the older crust. The $\epsilon\text{Nd}(t)$ values indicate a depleted mantle source with values close to the chondritic uniform reservoir (CHUR). The Sr-isotopic ratios vary markedly among the FMUC lithologies. The metahornblendite samples have $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of 0.7039 to 0.7076; garnet amphibolites vary consistently within $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of 0.7010 to 0.7090; and metaproxenite samples show lower $(^{87}\text{Sr}/^{86}\text{Sr})_i$ values of 0.7029–0.7034. The combined data suggest an isotopically enriched mantle reservoir similar to enriched mantle type II (EM-II), particularly in $^{87}\text{Sr}/^{86}\text{Sr}$.

5. Discussion

5.1. Petrogenesis and tectonic settings

Proper petrologic features that are present in Alaskan-type complexes and considered to be consistent with an arc environment

Table 6
Sm–Nd and Sr–Sr data obtained for Floresta Mafic–Ultramafic Complex (FMUC).

Sample	Rock/mineral	Location	UTM N	UTM E	Sm	Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	±2σ	εNd (0)	εNd(t) t = 1024 Ma	T _{DM}	Rb	Sr	⁸⁷ Sr/ ⁸⁶ Sr	±2σ	¹⁴³ Nd/ ¹⁴⁴ Nd _i	⁸⁷ Sr/ ⁸⁶ Sr _i
GL02(M)A	Metahornblende	Serrote das Pedras Pretas	547,817	9,062,566	9	34.671	0.1569	0.512516	0.000001	-2.38	2.84	1.40					0.511462	
GL 02(M)B	Garnet amphibolite	Serrote das Pedras Pretas			7.756	24.548	0.191	0.512636	0.000012	-0.05	0.71						0.511353	0.7058
GL 02(M)C	Fe–Ti–V cumulus	Serrote das Pedras Pretas			0.032	0.111	0.1718	0.512487	0.000012	-2.94	0.32	2.00					0.511333	
GL-02A	Metahornblende	Serrote das Pedras Pretas			8.902	31.361	0.1716	0.512537	0.000009	-1.97	1.32	1.80	14.7	124.7	0.7126	0.00001	0.511384	0.7076
GL2B	Garnet amphibolite	Serrote das Pedras Pretas			3.92	11.96	0.1981	0.512648	0.000007	0.2	0.01		15.3	196.3	0.7091	0.00001	0.511317	0.7058
GL2E	Olivine cumulate	Serrote das Pedras Pretas			0.639	1.574	0.2452	0.513064	0.000004	8.31	2.18						0.511416	
AM-446C	Metahornblende	Serrote das Pedras Pretas			7.961	33.961	0.1417	0.512433	0.000021	-4.00	3.22	1.28					0.511481	
AM-446D	Garnet amphibolite	Serrote das Pedras Pretas			1.009	1.9601	0.3111	0.513411	0.00002	15.08	0.08						0.511321	
GL 04(M)A	Coarse hornblende	Riacho Tapuio/ Arapuá	551,344	9,067,350	7.095	31.599	0.1357	0.512328	0.000007	-6.04	1.95	1.38					0.511416	
GL 04(M)C	Tremolite	Riacho Tapuio/ Arapuá			3.037	12.414	0.1479	0.512386	0.000005	-4.92	1.48	1.50					0.511392	
GL 04(M)D	Pyroxenite	Riacho Tapuio/ Arapuá			6.408	28.083	0.1379	0.512353	0.000008	-5.56	2.15	1.38					0.511426	
GL-04A	Metahornblende	Riacho Tapuio/ Arapuá			6.357	29.423	0.1306	0.512317	0.000008	-6.25	2.41	1.32	3.3	274.4	0.7044	0.00001	0.511439	0.7039
GL-04B	Garnet amphibolite	Riacho Tapuio/ Arapuá			5.618	20.576	0.1651	0.512673	0.000012	0.69	4.84	1.15	6.7	305	0.7099	0.00001	0.511564	0.7090
GL-04C	Pyroxenite	Riacho Tapuio/ Arapuá			3.149	11.748	0.162	0.512495	0.000017	-2.79	1.76	1.60	0.5	49	0.7038	0.00001	0.511406	0.7034
GL-04D	Pyroxenite schist	Riacho Tapuio/ Arapuá			6.454	28.41	0.1373	0.512347	0.000011	-5.68	2.11	1.38	9.2	499.8	0.7036	0.00001	0.511424	0.7029
GL 08(M)A	Metahornblende	Riacho da Posse	544,582	9,061,535	9.814	38.368	0.1546	0.512452	0.000013	-3.63	1.89	1.51					0.511413	
GL 08(M)C	Fe–Ti–V cumulus	Riacho da Posse			0.034	0.126	0.1625	0.512501	0.000014	-2.67	1.82	1.59					0.511409	
GL-08A	Metahornblende	Riacho da Posse			15.077	67.538	0.1349	0.512298	0.000006	-6.64	1.47	1.43	6.7	60	0.7117	0.00001	0.511392	0.7070
GL-08B	Garnet amphibolite	Riacho da Posse			5.483	19.486	0.1701	0.512656	0.000008	0.36	3.85	1.33	38.4	202.4	0.7090	0.00001	0.511513	0.7010
AM-445E	Olivine cumulate	Lagoa dos Angicos	546,436	9,061,525	1.447	3.835	0.2281	0.512976	0.000013	6.59	2.48						0.511443	
AM-448A	Garnet amphibolite	Caraibeiras road			5.538	23.432	0.1429	0.512439	0.000038	-3.89	3.18	1.29					0.511479	
AM-448D	Metahornblende	Caraibeiras road	549,944	9,066,921	3.232	14.324	0.1364	0.512401	0.000013	-4.63	3.29	1.26					0.511484	
AM-456A	Garnet amphibolite	Caraibeiras	549,195	9,067,122	3.871	16.132	0.1451	0.512424	0.000006	-4.17	2.6	1.36					0.511449

Fig. 8. (a) Whole-rock Sm–Nd isochronic age of 12 samples of Floresta Mafic–Ultramafic Complex (FMUC) yielding an apparent age at 1028 ± 63 Ma (MSWD 0.79) and $\varepsilon\text{Nd}(t)$ parameter of 2.1; (b) Nd evolution diagram of the FMUC from calculated age of 1024 Ma.

include cumulative clinopyroxene, the presence of hornblende, and commonly the absence of orthopyroxene and plagioclase (Eyuboglu et al., 2010; Helmy and El Mahallawi, 2003; Johan, 2002; Pettigrew and Hattori, 2006; Ripley, 2009; Su et al., 2014). Magnetite and ilmenite are common opaque minerals with modal abundances of ~15–20% (Taylor, 1967; Irvine, 1974; Himmelberg and Loney, 1995). Additionally, Mg-rich olivine, Ca-rich clinopyroxene, high Fe-chromite, and calcic hornblendes with a broad compositional spectrum (Irvine, 1974; Rublee, 1994; Helmy and El Mahallawi, 2003; Su et al., 2012; Farahat and Helmy, 2006) characterize the minerals of Alaskan-type complexes.

The petrologic data underline that the studied ultramafic and mafic rocks are remarkably similar to subduction-related arc cumulates and are analogous to the Island Arc and Alaskan-type complexes. Among the features noted, we highlight the petrography and mineralogy of clinopyroxene, spinel, and amphiboles and the whole-rock chemistry as follows.

5.1.1. Petrography and mineralogy

The preferred Ti mineralization with the ultramafic rocks in the FMUC resembles that in the BMUC (Beurlen et al., 1992). Despite the observed intense recrystallization, the Riacho da Posse open pit and particularly the Serrote das Pedras Pretas outcrops indicate the following possible protoliths: a cumulative rock assemblage with a mineralized metadunite core grading into a transitional phase formed by recrystallization of these dunites into tremolitites and then to chlorite–tremolite schists and clinopyroxene–tremolite–chlorite schists with variable amounts of olivine. The latter is derived from wehrlite and pyroxenite facies. Hbl-gabbros are likely a previous plagioclase-rich phase that formed garnet amphibolites and a rim of coarse pegmatitic hornblendites. We believe that coarse hornblendites can comprise a separate lithology given that the previous mineral assemblages exhibit the following characteristics: the absence of free plagioclase, the presence of non-oriented euhedral amphiboles, the absence of interstitial fine-grained amphiboles, and the presence of sharp contacts between garnet amphibolites and coarse pegmatitic metahornblendites that possibly reflects the presence of compositional cumulative layering. Orthopyroxene does not exist or has not been found, and abundant plagioclase, if present, would have been

restricted to the gabbroic member that gave rise to the relicts of eclogites. The crystallization order from the existent rocks may be assumed as apatite, olivine, Fe-chromite, clinopyroxene, magnetite, ilmenite, $\pm$ hornblende, $\pm$ plagioclase, sulfides. These rock assemblages are highly similar to typical Alaskan-type cumulate sequences (Himmelberg and Loney, 1995).

5.1.2. Clinopyroxene chemistry

Ca enrichment, high Mg# and variable Al_2O_3 and TiO_2 contents of the clinopyroxenes, as well as evidence of crystal accumulation, such as scarce graded layers, show close similarity with the clinopyroxenes from arc-related cumulates/Alaskan-type mafic-ultramafic rocks and are distinguishing features of alpine-type ophiolites and layered intrusions (Himmelberg and Loney, 1995; Farahat and Helmy, 2006; Pettigrew and Hattori, 2006; Krause et al., 2007; Wang et al., 2010; Eyuboglu et al., 2010, 2011). The data plotted in the field of the clinopyroxenes from Alaskan-type complexes and arc-related cumulates (Fig. 9a) in which the high Wo and up to 0.54 wt.% of Cr_2O_3 contents of clinopyroxenes reveal that these products are similar to those originating from near-liquidus crystallization of water-bearing basaltic magma (e.g., Sisson and Grove, 1993; Pettigrew and Hattori, 2006; Eyuboglu et al., 2011). Loucks (1990) demonstrated that the trend of the $\text{Al}^{\text{IV}}/\text{TiO}_2$ in clinopyroxene in arc cumulates is distinct from that of rift-related tholeiites. This discrimination diagram is presented in Fig. 9b, with the data from the BMUC following an arc cumulate trend and affinity with Alaskan-type complexes. A single grain (rim) plotted outside of the compositional field, where the IAB and MORB trends are similar at low Al^{IV} and TiO_2 concentrations. However, the Ural–Alaskan-type can be distinguished from MORB magma by their enriched trace element concentrations in the parent magma (Krause et al., 2007). Similar characteristics can be observed in Fig. 9c in the Al_2O_3 – SiO_2 – $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ diagram. The trend of alumina enrichment with differentiation and negative correlation with Mg# also reflects crystallization of clinopyroxene from progressively more hydrous melts characteristic of arc magmas and high-alumina basaltic magma at convergent plate settings (Murray, 1972; Conrad and Kay, 1984; Loucks, 1990; Himmelberg and Loney, 1995; Wang et al., 2010).

Fig. 9. Clinopyroxene compositions of the Bodocó Mafic–Ultramafic Complex (BMUC). (a) En–Wo–Fs diagram of pyroxenes after Morimoto (1988). The range of pyroxene compositions is shown for the Akarem gabbro intrusion (Helmy and El Mahallawi, 2003), the southeast Alaskan Complex (Himmelberg and Loney, 1995) and a typical Alaskan-type complex (Irvine, 1974). Arc cumulate complexes fields are from Spandler et al. (2003), modified after Abd El-Rahman et al. (2012). (b) Al_2O_3 versus $wt\% TiO_2$ diagram of Loucks (1990). (c) Plots of Al_2O_3 versus $Mg/(Mg + Fe^{2+})$ with the compositional range for arc cumulates from Debari and Coleman (1989); the Al–Si discrimination diagram is from Le Bas (1962) after Pettigrew and Hattori (2006). The gray area for arc cumulates is from Loucks (1990). The area enclosed by dashed–dotted lines indicate Alaskan/Ural-type ultramafic intrusions along subduction zones (Pettigrew and Hattori, 2006). The term non-alkaline is from Le Bas (1962). (d) $Ti + Cr$ versus Ca plots. The fields of non-orogenic tholeiites and orogenic basalts are based on clinopyroxene phenocrysts in basalts after Leterrier et al. (1982).

Fig. 10. Variations of trivalent diagrams of (a) Cr–Al–Fe³⁺ for spinels in the Bodocó chromites demonstrating an Fe-enrichment trend. The defined fields are from Barnes and Roeder (2001) after Wang et al. (2010). (b) Cr–Al–2Ti + Fe³⁺ plot of Cr-spinels from Bodocó chromites. Fields of ophiolites, komatiites, stratiform complexes, and southeast Alaskan-type complexes are from Jan and Windley (1990) after Salem et al. (2012).

5.1.3. Spinel chemistry

Chromites range from Fe-Chromites to Cr-magnetites and exhibit an Fe-enrichment trend (Fig. 10a). The parent magma of Alaskan-type complexes tends to show an Fe³⁺ enrichment of the primary spinel, which is attributed to the oxidized nature of the arc magma (Barnes and Roeder, 2001; Ahmed et al., 2008). According to Farahat and Helmy (2006), such an increase in Fe³⁺ is reported from spinels of the Alaskan-type complexes and is generally absent in other igneous complexes such as ophiolites or layered intrusions. This demonstrates that the continuity in compositions from chrome-spinel to magnetite in Alaskan-type complexes reflects a combination of trapped liquid reaction and oxidation. In the same diagram, the chromites plot parallel to the island arc and Alaskan-type fields and far from the OIB- and MORB-type basalt fields. As shown in Fig. 10b, the spinel compositions plotted inside the designated fields of the southeast Alaskan-type complex (Jan and Windley, 1990; Salem et al., 2012) and far from the stratiform complexes and ophiolite fields.

5.1.4. Amphiboles

The high Mg# and the TiO₂ contents of some hornblendes reinforce the inference of a primary magmatic origin, whereas a broad compositional range and negative correlation between Si and Na + K contents (Fig. 11a) show further similarity with most Alaskan-type and arc-cumulate complexes (e.g., Himmelberg and Loney, 1995; Pettigrew and Hattori, 2006; Su et al., 2012).

5.1.5. Whole-rock chemistry

Subduction-related magmas such as IAB are generally characterized by higher contents of LILE and LREE relative to HFSE and HREE (Eyuboglu et al., 2011; Kelemen et al., 2003), respectively, and negative anomalies for Nb, Ta, Zr, Hf, and Ti. Moreover, this can be associated with hydrous minerals such as hornblende and biotite (Pearce, 1982; Ringwood, 1990; Hawkesworth et al., 1991; Pearce and Robinson, 2010; Eyuboglu et al., 2011).

The ultramafic and mafic members of the FMUC and BMUC cumulates are slightly enriched in LILE and LREE and depleted in HFSE and HREE. In addition, they show high positive (cumulate phases) to slight negative (mafic phases) Eu anomalies, high Pb anomalies (cumulate phases), and moderate negative Hf and Zr

anomalies (peridotites and pyroxenites). Negative Nb and Ta anomalies are observed mainly in garnet amphibolites/garnetites.

The introduction of fluids from the subducted oceanic lithosphere including sediments may have been responsible for the enrichment in LILE and LREE (Ringwood, 1990; Hawkesworth et al., 1991).

The occurrence of ilmenite as a cumulus phase may explain the enrichment in Nb, Ta and Ti (Green and Pearson, 1987). Eyuboglu et al. (2011) also attributed the absence of negative Nb, Ta, and Ti anomalies in some Alaskan-type intrusions to presence of ilmenite and rutile. Xiong (2006) suggested that enrichment of these elements may have occurred through the melting of rutile-bearing hydrous eclogite. Furthermore, a positive Eu anomaly in peridotites is typical in cumulate rocks, whereas the absence of conspicuous positive Eu anomalies is generally noted in gabbroic rocks. A small negative Eu anomaly in gabbroic members indicates that fractional crystallization was not a major process controlling the suppression of plagioclase and Fe–Ti oxide crystallization in the evolution of the parental magma. These combined factors may explain the absence of negative Nb, Ta, Ti, and Eu anomalies (Pettigrew and Hattori, 2006; Eyuboglu et al., 2011). Further support for a subduction setting is indicated by a positive Pb anomaly with respect to the neighboring trace elements in peridotites, which is also present in some gabbroic members. The Pb anomalies are common in Alaskan-type peridotites and are better marked in subducted serpentinites and mantle wedges than in abyssal serpentinites that have experienced melt/rock interactions (Deschamps et al., 2013). The usage of relative concentrations of immobile elements is helpful in deciphering the tectonic environment for mafic and ultramafic magmatism (e.g., Pearce, 1975, 1982, 2008; Shervais, 1982; Beard, 1986; Thanh et al., 2014). In the Nb/Yb–Th/Yb diagram, most gabbroic, amphibolitic and eclogitic samples plotted within the field for arc magmatic rock, except for a single sample that showed a tendency toward the MORB array (Fig. 11b). This may be indicative of a protolith derived from a metasomatized mantle source enriched by subduction-related fluids (Pearce, 2008). These data, in combination with the LREE-enriched patterns for the FMUC and BMUC samples, suggest an arc setting.

Critical elemental ratios indicate a possible mixing between MORB magma with low Ba/La, Ce/Pb, and La/Yb and arc basalt magmas with high Ba/La, Ce/Pb, Zr/Nb, and La/Yb (Sun and McDonough, 1989; Thanh et al., 2014; Table 7).

Fig. 11. Compositional and discriminant diagrams for Bodocó Mafic-Ultramafic Complex (BMUC) and the Floresta Mafic-Ultramafic Complex (FMUC). (a) Hornblende compositions in BMUC and FMUC plotting Si versus Na + K contents (including 23 O values). The fields of the Alaskan-type complexes are for Quetico (Pettigrew and Hattori, 2006); Tulameen (Rublee, 1994) and Akarem gabbro (Helmy and El Mahallawi, 2003). The arc cumulate field is defined by Beard and Barker (1989), modified after Su et al. (2012). (b) Diagram of Nb/Yb versus Th/Yb for gabbroic, amphibolitic, and eclogitic rocks after Pearce (2008). (c) Initial $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\epsilon\text{Nd}(t)$ diagram for the FMUC showing Sr and Nd isotope compositions. The midocean ridge basalt (MORB) field is from Zimmer et al. (1995); the ocean island basalt (OIB) field is from White and Duncan (1996); and the enriched mantle types I and II (EMI, EMII) are from Hart (1988). $\epsilon\text{Nd}(t) = 0$ and $(^{87}\text{Sr}/^{86}\text{Sr})_i = 0.705$ are the values of bulk silicate earth (Zindler and Hart, 1986) modified after Cai et al. (2012). (d) Cr_2O_3 versus CaO diagram of Grütter et al. (2004) with G-number nomenclature of the classification scheme: G0: unclassified; G1: low-Cr megacrysts; G3: eclogitic; G4 and G5: pyroxenitic, websteritic, and eclogitic; G9: lherzolitic; G10: harzburgitic; G12: wehrlitic.

Table 7

Average trace element ratios in the analyzed mafic rocks. Table extracted and adapted after Thanh et al. (2014) and shown for comparison.

Ratio	Location and tectonic setting					
	FMUC	Cao Bang (a)	N-MORB (b)	Indonesian arc (c)	Mariana (d)	Aleutian (e)
Ta/Nb	0.06–0.19	0.076–0.089	0.06	0.07–0.13	0.06–0.1	0.06–0.39
Zr/Nb	4.34–18.89	12.56–20.87	31.76	14–23	37–86	21–145
Ce/Pb	4.58–179.67	1.81–6.52	25	3–7	3.5–13.4	3.16–34.39
Th/Yb	0.48–1.79	1.52–3.57	0.04	1–4	0.1–0.5	0.03–0.51
Th/Nb	0.06–0.55	0.81–1.77	0.05	0.45–1.12	0.4–0.8	0.08–0.83
Ba/La	0.44–9.57	4.00–22.19	2.52	23–36	22–60	5.2–51.45
Ba/Th	2.84–118.82	9.06–64.41	52.5	63–177	187–674	47–708
Sr/Nd	1.86–21.69	3.42–15.52	12.33	16–44	18.4–49.4	13–62
(La/Sm)N	0.61–2.28	2.2–2.8	0.59	1.92–3.57	0.8–1.7	0.4–1.6

(a) Thanh et al. (2014); (b) Sun and McDonough (1989); (c) arc-like basalts, (d) and (e) MORB- and arc-like basalts. Floresta Mafic-Ultramafic Complex (FMUC).

5.2. Parental magma and mantle source

Cr-spinel, olivine, and clinopyroxene represent early crystallization phases in FMUC and BMUC. Intercumulus minerals consist of pyroxene, magnetite, ilmenite, and hornblende. The high Mg# of clinopyroxene at >88 and abundant Mg-hornblendes in primary phases suggest an Mg-rich primary liquid. According to Su et al. (2014), the high-Mg content in silicate minerals can also be attributed to crystallization of magnetite and ilmenite, which incorporates large amounts of Fe. The modal abundance of magnetite and ilmenite in the FMUC and BMUC can reach up to 20% in peridotites. The Ti content in chromites, and Fe–Ti oxides, and Mg-bearing minerals, as earlier intercumulus/cumulus phases, calls for a high-Ti ferropicritic magma composition.

The arc tholeiitic component of the melt in the BMUC accounts for the clinopyroxene compositions, as shown in Ti + Cr versus Ca map in Fig. 9d, where the data plotted in the field of orogenic basalts. Picritic or olivine tholeiite primary melt is in accordance with Alaskan-type intrusions (Irvine, 1974) with hydrous (Loucks, 1990) and arc tholeiite affinities (Helmy and El Mahallawi, 2003).

Numerous world-class Fe–Ti oxide deposits in the Panxi district and post-orogenic intrusions occurring along the Central Asian Orogenic Belt, China (CAOB) which commonly hosts Ni–Cu sulfide mineralization (Xie et al., 2014) are assigned to a ferropicritic parental magma generated by the interaction of a plume with the lithospheric mantle. The latter is enriched in eclogitic components related to subduction (Hou et al., 2012) and occurs in the Giant Hongge deposit (Bai et al., 2012). Giant Fe–Ti–V oxide layers occur in the lower and middle parts of relatively small mafic–ultramafic intrusions, as is the case of the FMUC – Serrote das Pedras Pretas mine, Riacho da Posse deposit: 54 Mt @13% Ti and the BMUC. However, the age obtained for FMUC limits this possibility. The positive ϵNd values of 0.01 to 4.84 and the minor enrichment in light REEs are in agreement with an initially depleted lithospheric mantle source. The variations in Sr–Nd isotope characteristics (Fig. 11c) suggest an isotopically-enriched lithospheric mantle reservoir close to EM-II originating from recycled oceanic crust and small amounts of subducted sediment or recycling of melt-impregnated oceanic lithosphere (Zindler and Hart, 1986; Wilson, 1989). The wide Sr isotopic variation indicates an oceanic setting, which has been widely interpreted as a subduction signature (e.g., Rollinson, 1993; Su et al., 2014). The Nd–Sr signatures and presence of hydrous minerals such as primary hornblende strengthens a setting analogous to subduction-related arc cumulates (Irvine, 1974; Himmelberg and Loney, 1995; Helmy and El Mahallawi, 2003; Farahat and Helmy, 2006; Eyuboglu et al., 2010).

The virtual absence of relics of orthopyroxene in the peridotites rules out any noteworthy crustal contamination of parental magma. The positive Eu anomaly in peridotites in some samples is consistent with their cumulate textures and also suggests insignificant crustal contamination. In contrast, in some cases, a slightly negative Eu anomaly in gabbroic members, T_{DM} model ages >1.6 Ga in two samples, and inheritance of zircon aged at ~1.9 Ga may attest to an involvement of a crustal source in the genesis.

These factors indicate derivation of high-Ti ferropicritic parental magma from a depleted mantle source that has undergone metasomatism in a subduction setting.

5.3. Metamorphism

A similar metamorphic evolution for FMUC and BMUC can be established on the basis of almost identical paragenetic and textural attributes related to retrograde metamorphism (Beurlen et al., 1992). In both complexes, a magmatic mineral assemblage is represented by olivine $\pm$ Cr-spinel $\pm$ clinopyroxene $\pm$ magnetite $\pm$

ilmenite $\pm$ apatite $\pm$ sulfides? $\pm$ plagioclase? $\pm$ hornblende. A pre-eclogitic metamorphic stage was suggested by Beurlen et al. (1992) on the basis of the record of well-foliated, fine-grained snow-ball texture inclusions in garnet porphyroblasts. This stage has the mineral assemblage of rutile + epidote + amphibole + plagioclase. A high-pressure stage has omphacite preserved in the BMUC (Beurlen et al., 1992) $\pm$ rutile $\pm$ (clino)zoisite $\pm$ garnet, with a consistent bulk composition similar to garnets from eclogites within glaucophane schists and a small component showing a granulitic trend (Fig. 11d). According to Beurlen et al. (1992), high-pressure metamorphism is supported for the BMUC based on the jadeite content of omphacite/clinopyroxene, the Fe/Mg partitioning between omphacite/clinopyroxene and garnet, the Si activity in phengite, and the Na content of amphiboles in retrograde symplectites in gabbroic members, which suggests a progressive metamorphic evolution up to C-type eclogites (Coleman et al., 1965) at 13 kbar/525 °C. This was followed by a retrograde path of medium pressure (P)/T ratio between 10 kbar/680 °C and 7–5 kbar/450 °C, as estimated by the Si activity in the phengite, and the empirical comparison of the amphibole composition, which ranges from barroisitic to sodic Mg-hornblendes to the greenschist facies (see [Inline Supplementary Fig. S2](#)).

Sodic–calcic amphibole and almandine–pyrope garnets indicate blueschist metamorphic conditions. Tschermakitic amphibole and Fe-barroisite found in the coronas surrounding the garnets from the BMUC and as grains in the FMUC ([Supplementary Table 2](#)) can be attributed to the early stages of retrograde metamorphism derived from omphacites (Deer et al., 1966) and relics of blueschist metamorphic facies, respectively. Thus, in addition to their similarity in terms of their retrogressive high-pressure metamorphic evolution, the FMUC and BMUC are correlated by their high Ti/Fe ratios in massive ores associated with ultramafic rocks, the same gabbroic intercalations composed of only garnet and amphibole with the same mineral compositions, the absence of plagioclase, and the abundance of rutile (Beurlen et al., 1992; Beurlen and Villarreal, 1990; Beurlen, 1988; this study).

5.3.1. Subsolidus exsolution of Fe–Ti solid solutions

Ilmenite–magnetite geothermobarometry, based on the geothermometer of Andersen and Lindsley (1985) helped to calculate O fugacities and the possible Fe–Ti oxide blocking temperatures of subsolidus equilibration. These values are listed in [Supplementary Table 1](#) and are plotted in a temperature versus log $f\text{O}_2$ diagram in Fig. 12a. The calculated O fugacity values obtained for the ilmenite–magnetite coexistent couples vary from $\sim 10^{-21.04}$ to $\sim 10^{-18.26}$ and plotted as a nickel–nickel-oxide (NNO) curve, similar to arc cumulates/Alaskan-type complexes (Himmelberg and Loney, 1995). The blocking temperatures of subsolidus equilibration range from 573 to 506 °C. It should be noted that these blocking temperatures, obtained on the basis of the magnetite–ilmenite intergrowths, are significantly lower than the early crystallization temperatures of ilmenite and magnetite from Alaskan-type intrusions above 815 °C (Himmelberg and Loney, 1995). However, owing to sub-solidus cation exchange and re-equilibration during high pressure metamorphism and the influx of new fluids driven by subduction-related processes or by granitic intrusion (Riacho do Icó Suite wall rock), the calculated temperatures should be taken as minimum temperatures for these modifications rather than crystallization. For the sake of clarity, the ulvöspinel contents in the magnetite, calculated by using the method of Stormer (1983), are below 1.7 mol%, which is in accordance with the near absence of fine trellis intergrowths in magnetite crystals. The end member component (X_{Ilm}) of the analyzed ilmenite is almost pure, at >92.41% mole. These textural features show that the magnetite lost almost all of its Ti to its surroundings through solid-state diffusion, which contributed to the

Fig. 12. (a) O-fugacity and temperature determined for the massive Fe-Ti ore in the Floresta Mafic-Ultramafic Complex (FMUC) based on magnetite-ilmenite coexistent pairs. Trajectories are HM: haematite-magnetite buffer; NNO: nickel-nickel-oxide; FMQ: quartz-fayalite-magnetite; WM: wüstite-magnetite (Eugster and Wones, 1962). (b) Al_2O_3 versus Cr_2O_3 (wt.%) diagram of Franz and Wirth (2000) after Seo et al. (2013).

formation of new granular ilmenite and enhanced the quality of the ore. Moreover, the presence of interstitial Al-spinels surrounding the magnetite and ilmenite indicate complete exsolution by cooling temperature and exchange of Fe and Ti with Al, underlining a metasomatic origin (Fig. 12b). Outside of the granites, these changes do not appear to have affected the Fe-chromites of the BMUC, which remained unscathed and plotted along arc cumulate spinels distinctly far from rift-cumulate spinel fields (Fig. 12b). The occurrence of cumulus magnetite and ilmenite as the oxide phases suggests that the magma from which the ultramafic rocks crystallized was rich in Fe_2O_3 and H_2O . Considering its crystallization after clinopyroxene but before hornblende, the oxidation conditions of the magma at the time of crystallization were similar to those reported for arc-basalt ultramafic xenoliths (Conrad and Kay, 1984) with mineral assemblages that were similar to Alaskan-type ultramafic rocks (Himmelberg and Loney, 1995) and at least as high as the NNO buffer (Helz, 1973).

In summary, ilmenite growth is an unfavorable phase in the eclogitic rocks where rutile is the most common accessory phase (Force, 1991). Thus, we cannot discard late magmatic fluids as a mechanism for the enrichment of proto-ore mineralization inside

the granite, as suggested by fluid/rock interactions observed in the mines (Fig. 13a and b). Therefore, only the deposits within the Riacho do Icó Suite have economic value. We infer that some Fe-Ti ore lenses and ultramafic proto-ore probably re-equilibrated under new water/fluid content and O fugacity conditions, increasing their Ti/Fe ratios substantially by fluids from the Riacho do Icó granitic intrusion. Previously, secondary enrichment was represented by rutile growth up to 12% during high-pressure/low-temperature metamorphism.

6. Geodynamic significance and concluding remarks

The crystallization age for the FMUC, also known as the Serrote das Pedras Pretas Suite, has been constrained at ca. 1025 Ma with $\varepsilon Nd(t)$ of 2.1. This confirms a mafic-ultramafic accretionary juvenile event where such intrusions are considered to be slightly older than other rocks from the Cariris Velhos event (e.g., Kozuch, 2003; Santos et al., 2010; Van Schmus et al., 2011). Preferentially, the emplacement of Alaskan-type intrusions occurred close to the end of subduction and prior to the accretion-collision of terranes (Pettigrew and Hattori, 2006; Su et al., 2012).

Fig. 13. Late magmatic fluids from granitic-related intrusion in the Floresta Mafic-Ultramafic Complex (FMUC). (a) Metasomatic alterations caused by magmatic fluids related to pegmatoid/leucogranitoid intrusions. A channel structure filled with a chlorite/phlogopite halo is shown cutting the host rocks of the Riacho da Posse mine. (b) Sheared zone with cross-fiber asbestos texture in serpentinites that depleted mineralized host rocks, leaving massive Fe-Ti oxides as a restite in the Serrote das Pedras Pretas mine.

A closer and analogous Mesoproterozoic (~980–960 Ma) continental arc is developed on the southern margin of the Paleoproterozoic Pernambuco–Alagoas Domain (PEAL) including the intruded ~950 Ma post-tectonic Serra Negra granite (Oliveira et al., 2010). The age of the FMUC corroborates the possibility that at least this complex does not refer to the end of subduction related to this Tonian event. The recent discovery of the Sítio do Icó metavolcanic rock, originated from high-Mg magma with a chemical signature similar to an andesitic composition at 1005 ± 5 Ma (Lages et al., 2014; Guimarães et al., 2015), is consistent with these ultramafic-mafic assemblages that resemble cumulates from hydrous, high-Mg basaltic magmas having andesitic lavas as the complementary liquid fraction (Murray, 1972; Garuti, 2011).

The FMUC rocks could have originated from igneous accumulation from hydrous magma likely at shallow depth owing to the high amounts of ilmenite and magnetite as early cumulus phases, and they were emplaced along a major fault zone or in a spreading center. In contrast, the content of Ni–Cu sulfide disseminations in Neoproterozoic arcs should remit to a deeper level of the arc, where it could remain as a magma chamber crystallizing at the base of an arc system (Helmy et al., 2014).

Considering the older ages of ~995 Ma obtained for volcanic and gneissic rocks in this part (Santos et al., 2010; Brasilino et al., 2014), the FMUC likely represents magma that formed in a primitive extensional environment prior to the formation of a mature arc sequence in the southwesternmost part of the terrane. Their Sm/Nd values are typical of mafic and ultramafic rocks of primitive arc and oceanic crust fragments.

Hence, during active subduction, arc detritus likely accumulated in a back-arc/intra-arc basin, forming the São Caetano sequence. In contrast, the FMUC constitutes the basement in a proto-arc environment.

On the other hands, the BMUC occurs along the border with the Paleoproterozoic Icaicara fragment surrounded by Tonian sedimentary sequences. Presently, this is recognized as an allochthonous fragment that could have been formed through accretion of a microcontinent or as part of a disrupted continental margin.

The BMUC has the most robust criteria for classification as a deeper root of the island arc such as clinopyroxene and Fe–chromite chemistry. However, geochronological studies are needed to constrain their ages to confirm whether these rocks are slight younger than those of the FMUC.

The BMUC and FMUC may represent subduction-related magmatism, either prior to or even synchronous to the juxtaposition of the juvenile island arc with the Pernambuco–Alagoas or Alto Moxotó domains as possible terranes.

The arc affinity of metasedimentary rocks in the central and north–northeastern parts of the Alto Pajeú Domain is indicated by the geochemical signatures of metamorphosed greywackes, and lithic and arkose sandstones, which are characteristics of derivation from island arc and/or continental arc sources (Sales et al., 2011) and sources mixed with volcanogenic derivatives of mafic and intermediate igneous rocks (Santos, 1995; Kozuch, 2003; Medeiros, 2004; Santos et al., 2010).

Moreover, other samples such augen–gneisses and migmatitic facies are classified as calc-alkaline to high-K calc-alkaline, which are compatible with both continental arc and syn-to-late collisional signatures (Jardim de Sá, 1994; Santos, 1995; Santos and Medeiros, 1999; Kozuch, 2003; Medeiros, 2004; Santos et al., 2010). However, many augen–gneisses have chemical characteristics compatible with an extension-related setting with the generation of A-type granites (Guimarães et al., 2015; Neves, 2003) or A-type post-collisional granites (Cruz et al., 2014). These A-type granitoids and the absence of evidence of Tonian metamorphism can be used to argue against a continental margin-magmatic arc tectonic setting. We detected a unique zircon with low Th/U

yielding a discordant Tonian age. However, this assumption requires significantly more data; thus, the debate on the continental collision remains open. Moreover, evidence of a complete arc sequence development during the Cariris Velhos event is indicated. Therefore, based on the most reliable arc chemistry signatures, the ages can be determined by volcanic arc magmatism until 995 Ma from the appearance of extension-related plutonism, which is always younger than 975 Ma. These granitic intrusions could be post-collisional or even post-tectonic.

Some authors have suggested the development of a back-arc or fore-arc basin adjacent to a subduction zone (Santos, 1995; Kozuch, 2003; Santos et al., 2010; Sales et al., 2011). This theory is supported by the geochemical patterns of non-cumulate meta-mafic rocks from the FMUC, which are similar to tholeiitic series mixing between arc and MORB/back-arc settings.

Preserved relics of oceanic crust of Monte Orebe (Moraes, 1992) formed between the São Francisco Craton and the PEAL, far less than 200 km of the BMUC and 380 km of the FMUC, suggest the development of a young oceanic floor between the intervening Borborema Province and the São Francisco Craton at ca. 820 Ma (de Caxito et al., 2014b).

During the western Gondwana amalgamation, a large Himalayan-scale collisional orogeny (Araújo et al., 2014a,b) converged the craton blocks and consumed the large Goiás–Pharusian Ocean defined by relics of eclogitic and granulitic rocks at ca. 615–589 Ma (Amaral, 2010; Amaral et al., 2012; Santos et al., 2014a; Araújo et al., 2014a) in the Ceará Central Domain. These rocks roughly align with other HP and ultra-HP (UHP) rocks in Africa dated at c. 620–610 Ma (Bernard-Griffiths et al., 1991; Affaton et al., 2000; Jahn et al., 2001; Araújo et al., 2014a).

High-pressure metamorphism is recorded in the BMUC, whereas retrogressed phases are present in FMUC outcrops. The U–Pb zircon on the metamorphic overgrowth rims on FMUC rock samples yielded a younger Concordia age of 625 ± 6 Ma. This value is compatible with the metamorphic peak of the eclogitic or a high-grade (such as granulite) progressive stage for the Pan-African–Brasiliano event. We argue that these retrogressions of eclogitic rocks occurred in a western Gondwanan tectonic context, and that they could be associated with the closure of a branch of a Neoproterozoic ocean basin between and along the southern and southwestern borders of the Alto Pajeú and Piancó–Alto Brígida domains and Alto Moxotó and Pernambuco–Alagoas domains, probably correlating east of the Central African fold belt (Van Schmus et al., 2008).

In the beginning of a subduction event, the overlying plate and the subducting plate are not fully decoupled (Xie et al., 2013). With progressive hydration of the mantle wedge, the overlying plate is thinned by thermal flux. This process may have been responsible for the thermal erosion of the arc root–subarc mantle when considering a vigorous mantle corner flow to drag the subarc mantle peridotite into the subduction channel (Arcay et al., 2007; Hattori et al., 2010). The rapid addition of water could have produced the melt-precipitated zircons with older overgrowth rims at 685 ± 17 Ma, which may be attributed to the initial stages of subduction.

In summary, in our hypothetical scenario (Fig. 14), the generation of these mafic–ultramafic complexes was coeval with island arc volcanism and syn-orogenic sedimentation. Such a scenario can best be interpreted as a proto-to-marginal arc-back-arc system that evolved between 1025 and 995 Ma which its extension could have occurred until 975 Ma. Such a scenario can indicate a mature arc or even arc-roots. The arc cumulate complexes (FMUC) were emplaced at ca. 1025 Ma as a basement of a proto-arc upon which the Cariris Velhos arc was built. The BMUC rocks and their geodynamic interpretation as the roots of an arc coupled with still-premature evidence of metamorphism could indicate the beginning of an arc accretion/collisional stage; however, this inference

Fig. 14. Schematic illustration of the geodynamic context of Early Neoproterozoic tectonic evolution of the Cariris Velhos event based on an analogous model of Dariv Arc (Dijkstra et al., 2006). (a) Proto-arc spreading above an intra-oceanic subduction zone produced the Floresta Mafic-Ultramafic Complex (FMUC). (b) Establishment of the Cariris Velhos mature arc. (c) Arc-continent collision led to stacking of the Cariris Velhos arc and associated back-arc sediments. (d) Post-collision extension led to intrusion of Cariris Velhos granitoids. (e) Position of the main tectonic components of the western Borborema Province and adjoining regions (c. 870–650 Ma), modified after Araújo et al. (2014b). Opening of a small ocean basin connected to the Pharusian-Goias Ocean (<870 Ma) between rocks of the Cariris Velhos event and the western Paleoproterozoic Pernambuco-Alagoas Domain (PEAL) and continued rifting (c. 685 Ma) occurred with initiation of subduction. (f) Collisional stage (c. 625–610 Ma) in the west, leading to the West Gondwana Orogen marked by high-pressure (HP) and ultra-HP (UHP) metamorphism, anatexis of continental crust and arc magmatism in the south (Araújo et al., 2014b and references therein). The small ocean branch along the rocks of the Cariris Velhos event collided first, according to the HP metamorphic peak at c. 625 Ma.

requires further substantiation. Indeed, the majority of the Tonian orthogneisses in the Transversal Zone intruded after 975 Ma and have predominantly A-type chemical signatures, although also occur a transition between calc-alkaline and high-K calc-alkaline. We can infer a post-collisional or even a post-tectonic stage for these orthogneisses. The granitic intrusions and emplacement of more bimodal volcanic rocks ended at ca. 920 Ma.

Evidence of ocean crust and extension-related magmatism occurred at ca. 820 Ma.

The onset of the next subduction was initiated by westward convergence, which could have caused thermal erosion and delamination by dragging the arc root pieces into the subduction channel at 685 Ma. A short loop of these rocks in the eclogitic condition of <14 kbar reached the metamorphic peak at ca. 625 Ma, from which it was exhumed along with granitic materials and sediments.

Finally, we conclude that the high Ti/Fe ratios in the FMUC economic ore bodies are attributed to the early stages of accumulation from an enriched source in part from the Ti partitioning between silicate and oxide phases, with rutile mineral enrichment up to 12% under eclogitic conditions. After that time, the Ti enrichment occurred through hydrothermal magmatic fluids within the granitic wall rock.

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Appendix A. Supplementary data

Supplementary new data (Tables 1–4) and recalculated existent data (Appendices A–D) associated with this article can be found in the online version., at <http://dx.doi.org/10.1016/j.precamres.2016.04.017>.

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