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ABSTRACT

The metamorphosed mafic-ultramafic sequences of the Eastern Andean Metamorphic Complex outcropping in the Patagonian Andes are critical to disclose the late Paleozoic tectonic evolution of the southwestern margin of Gondwana. In the study area, mafic-ultramafic bodies are thrusted onto polydeformed metasedimentary rocks and intruded by the mid-Carboniferous composite Leones Pluton. The metabasalts (mostly tremolite-chlorite schists and amphibolites) show N-MORB and BABB chemical affinities pointing that formed part of an oceanic crustal section with components of the marginal basin, emplaced after the main pulse of Devonian arc magmatism, possibly in a retreating convergent margin. Interleaved serpentinites consist of serpentine polymorphs (antigorite, lizardite, and late chrysotile) and magnetite, with variably distributed minor amounts of chlorite, tremolite, and traces of ilmenite. Serpentinites have high Cr, Ni, Ti, and Yb contents, and show slightly enriched LREE and flat HREE patterns with a noticeable Eu positive anomaly. Mineralogical and geochemical features indicate that olivine-rich clinopyroxene-spinel-bearing peridotites were metamorphosed in a newly formed east-dipping subduction zone. The closure of the marginal basin continued with the tectonic underthrusting and tectonic juxtaposition of mafic-ultramafic rocks within an accretionary wedge. The tectonic cycle of the oceanic basin finished with the intrusion of mid-Carboniferous subduction-related plutons and pluton-driven thermal metamorphism.

1. INTRODUCTION

The overall Paleozoic tectonic evolution of the southwestern margin of Gondwana involved the collision and/or accretion of micro-continental plates with Gondwana affinities and oceanic terranes (Fig.1A; Ramos et al., 1986; Ramos 1989, 2008; Hervé et al., 2007; Hyppolito et al., 2016; González et al., 2018; Calderón et al., 2020). The continental collision of the Chilenia terrane along the 27-39ºS Pacific margin (Ramos, 1984; Massonne and Calderón, 2008; Willner et al., 2011; Boedo et al., 2015), was partially contemporaneous with the development of a NNW-SSE-trending Devonian continental magmatic arc in the North Patagonian Massif and the Chaitenia island-arc in the Northern Patagonian Andes (41-43°S; Fig.1B) (Pankhurst et al., 2006; Duhart, 2008; Quezada et al., 2015; Hervé et al., 2016, 2018). The proposed southern limit of Chilenia and pre-Devonian accreted terranes of the southwestern Gondwana margin in northern Argentina (e.g. Cuyania), is represented by the nearly east-west-trending Huincul lineament (cf. Ramos et al., 1984, Ramos2008).

The older core of South American continental lithosphere located to the south of the Huincul lineament is constituted by several crustal blocks cropping out near the Atlantic Ocean (Söllner et al., 2000; Pankhurst et al., 2003; Guido et al., 2004, 2005) or deeply buried beneath the sedimentary successions of the Magallanes-Austral basin in Tierra del Fuego (Söllner et al., 2000; Hervé et al., 2010). These crustal blocks were initially considered as constituents of the allochthonous Patagonia Terrane (Ramos, 1984, 2008) envisaged as an independent continental block bounded to the north by a fault zone along the Colorado river that collided with western Gondwana in Carboniferous times. However, this scenario is still widely discussed (e.g., Rapalini et al., 2010; González et al., 2018), whether the overall evolution of the Patagonia Terrane is coherent with the Paleozoic tectonic evolution of the southwestern margin of Gondwana that has been primarily considered as an accretionary evolution (cf. Forsythe et al., 1982). The geochronological and geochemical data on plutonic belts allow interpreting that the North Patagonian and Deseado massifs collided with each other during the Carboniferous, during the closure of a NW-SE-trending oceanic-type basin, culminating with widespread Permian silicic magmatism related to the slab-break off beneath the northern continental block (cf. Pankhurst et al., 2006). A NW-SE-trending calk-alkaline Carboniferous plutonic belt

(Pankhurst et al., 2003, 2006) constrain the age of amalgamation between the North Patagonian and Deseado massifs.

Meanwhile, on the Andean ranges and coastal Archipelago in Chile, the older basement rocks correspond to pillowed and massive metabasalts with oceanic affinities and metapelites (Crignola et al., 1997) intruded by subduction-related plutonic suites of Devonian age (Hervé et al., 2016, 2018). The oceanic-type lithosphere separated the ancestral South American continent from an island-arc, the proposed Chaitenia terrane, constituted by an approximately 150 km long and north-south trending plutonic belt defined by isolated outcrops of Devonian diorite-tonalite suites (cf. Hervé et al., 2018). Late Paleozoic to Triassic accretionary complexes with tectonic slices of metamorphic rocks formed in a subduction setting (Godoy and Kato, 1990; Hervé et al., 2003; Ramirez-Sánchez et al., 2005; Willner et al., 2000; Reyes et al., 2018), located to the west of the present-day Devonian plutonic belt. The southern end of the Chaitenia terrane and the time of accretion is not well established yet (Fig. 1A).

The study area (46-47ºS) comprises heterochronous metamorphic units without well-defined contacts, grouped in the Eastern Andean Metamorphic Complex (EAMC; Hervé et al., 1998). They consist mainly of Upper Devonian to Triassic polydeformed turbidite successions (Hervé et al., 2003; Augustsson et al., 2006; Suárez et al., 2019), with exceptional intercalations of limestones (marbles), metabasites, and serpentinites (Ramirez-Sánchez et al., 2005; Lacassie, 2003; Quiroz and Belmar, 2010; Hervé et al., 2008; Quitral et al., 2015; Díaz, 2018; Mura, 2018). Our study focus on the petrology of mafic-ultramafic lenses thrusted onto metasedimentary sequences within the EAMC near the western area of Lago General Carrera (Fig. 1C). The early sedimentary successions of the EAMC were deposited in a passive continental margin fed by felsic and continental old detritus from the core of Gondwana (Augustsson and Balhburg, 2003; Hervé et al., 2008), and subsequently metamorphosed at shallow depths (3-5 kbar) within an accretionary wedge developed before the late Permian (Thomson and Hervé, 2002; Ramirez-Sánchez et al., 2005). The complex structural configuration of the EAMC probably resulted either from microplate interactions and the development of an orogenic belt (Bell and Suárez, 2000) or by the development of a fold-and-thrust belt during the closure of a marginal basin (Suárez et al., 2021).

We report the first finding of mafic-ultramafic rocks located up-hill in the Valle Leones (Fig. 2), intruded by a mid-Carboniferous granite pluton. New field data integrated with detailed petrography, mineral, and bulk rock chemical composition, and U-Pb zircon geochronological data, clarify the origin and tectonic evolution of this area. We propose that mafic and ultramafic rocks formed part of an oceanic-type lithosphere formed in a supra-subduction setting, probably during the late Devonian - early Carboniferous times. The basin closure and metamorphism occurred when oceanic sections were incorporated into the accretionary wedge. The tectonic emplacement of ophiolitic rocks culminated with the intrusion of Carboniferous calk-alkaline diorite-granite suites.

2. GEOLOGICAL BACKGROUND

In the Andean ranges, near Lago General Carrera (Fig. 1C), metamorphic complexes crop out to the east of the Meso-Cenozoic North Patagonian Batholith (Hervé 1988; Pankhurst et al., 1999). Metamorphic rocks are grouped into the EAMC, which is constituted mainly by polydeformed and schistose metaturbiditic sequences with scattered bodies of pillow metabasalt and marbles (Lagally, 1975; Hervé 1995; Hervé et al., 1999; Bell and Suárez, 2000; Augustsson et al., 2006). The metasedimentary sequences were initially referred to as Cochrane and Lago General Carrera formations (Lagally, 1975), which can be correlated with the late Devonian-early Carboniferous successions of the Bahia de la Lancha and Río Lácteo formations in Argentina (Riccardi, 1971; Bell and Suárez, 2000; Giacosa and Marquez, 2002). Metamorphic basement rocks are also located in the extra-Andean Deseado Massif (Fig. 1), known as the Cerro Negro schists, with Devonian maximum depositional ages (Permuy-Vidal et al., 2014). The EAMC was exhumed and deformed in the latest Paleozoic times, and subsequently covered in angular unconformity by Upper Jurassic volcanic and volcaniclastic successions of the Ibañez Formation and El Quemado Complex (Pankhurst et al., 1998; Thomson and Hervé, 2002; Giacosa et al., 2012; Suárez et al., 2021).

The combination of detrital zircon U-Pb and fission-track ages indicate that portions of the EAMC were metamorphosed before the late Permian (Thomson and Hervé 2002), under conditions of 3-5 Kbar and 320-380°C (Hervé et al., 1998, 1999; Ramirez-Sánchez et al., 2005) similar to those values reported in frontal accretionary complexes in subduction zones (cf. Willner et al., 2009) as well in the accretionary complexes developed during the closure of back-arc basins (Muller et al., 2021). High-grade metamorphic rocks (andalusite-sillimanite series) are restricted to the margins of Meso-Cenozoic plutons (cf. Calderón et al., 2016).

Two metamorphic belts within the EAMC without well-constrained limits have been differentiated based on U-Pb detrital zircon age patterns (cf. Calderón et al., 2016 and references therein). The **northeastern belt** includes sedimentary components deposited between the late Devonian and the early Carboniferous, whereas the **southwestern belt**, was deposited between the Permian and Triassic (Augustsson et al., 2006; Augustsson and Bahlburg, 2008). The northeastern belt yields a distribution of U-Pb detrital zircon ages with Ordovician, Devonian, and early Carboniferous peaks whereas the southwestern belt show younger peaks of Permian and Triassic ages (Hervé et al., 2003; Augustsson et al., 2006).

At Valle Leones, a tectonic slice of mafic-ultramafic rocks is thrusted onto metasedimentary rocks and intruded by a tabular pluton consisting of two-mica and garnet-bearing granites and amphibole-bearing diorites (Fig. 2). A K-Ar muscovite age of 307±10 Ma is reported in the Leones Pluton (De la Cruz and Suárez, 2006), which is considered to reflect the minimum age of crystallization and pluton emplacement. Other mafic-ultramafic rocks occur within the metasedimentary sequences of the EAMC cropping out near Lago General Carrera at Valle Traiguanca (Quiroz and Belmar, 2010) where serpentinites are interleaved with amphibolites (Quitral et al., 2015; Díaz, 2018). New mineral and chemical data of rocks from both localities are presented.

3. METHODS

Field descriptions and sample collection were carried out in several outcrops (Figs. 2 and 3). Petrographic thin sections from selected metamorphic and igneous rocks allowed the determination of mineral assemblages, textures, and microstructures. Structural data of foliations and lineations at Valle Leones were plotted in stereographic diagrams (Fig. 2). The geological map of De la Cruz and Suárez (2006) was complemented with new field data showing geological contacts among main lithological units. The chemical composition of minerals of representative samples of metamorphic and igneous rocks (serpentinites, tremolite-chlorite schists, and a garnet-bearing granite) was obtained with an electron microprobe. The crystalline structure of serpentine polymorphs was constrained by micro-Raman spectroscopy.

3.1. Induced Coupled Plasma Mass-Spectrometry (ICP-MS)

Major and trace elements were analyzed at Activation Analytical Laboratories in Vancouver, Canada. Analyses were performed using lithium metaborate/tetraborate fusion with measurements by inductively-coupled plasma optical emission spectrometry (ICP-OES) for major elements and inductively-coupled plasma mass-spectrometry (ICP-MS) for trace elements. The results are presented in Table 1.

3.2. Electron Probe Micro-Analyzer (EPMA)

The major element compositions of serpentine polymorphs, chlorite, amphibole, white mica, plagioclase, K-feldspar, garnet, opaque minerals from mafic, ultramafic, and granitoid rocks were obtained on selected rock samples using a CAMECA SX100 with 5 wavelength-dispersive spectrometers at Universität Stuttgart, Germany. Operating conditions were set at 15 kV acceleration voltage and a beam current of 15 nA, beam size of 1–10 μm or a focussed beam (for very small crystals), all crystals were analyzed in situ in polished thin sections. The standards used were natural wollastonite (Si, Ca), natural orthoclase (K), natural albite (Na), natural rhodonite (Mn), synthetic Cr2O3 (Cr), synthetic TiO2 (Ti), natural hematite (Fe), natural baryte (Ba), synthetic MgO (Mg), synthetic Al2O3 (Al) and synthetic NiO (Ni). The PaP correction procedure provided by CAMECA was applied. Analytical errors of this method are given by Massonne (2012). The calculation of cationic proportions of the oxides was done with the software CALCMIN (Brandelik, 2009) and ILMAT (Lepage, 2003). Representative mineral compositions are presented in Tables 2,3,4 and 5.

3.3. Micro-Raman spectroscopy

We used micro-Raman spectroscopy to observe the serpentine minerals as reported in Rinaudo and Gastaldi (2003), occurring in different microstructural positions. The serpentine minerals from Valle Leones were analyzed by Micro-Raman and spectra were acquired at the Institut für Mineralogie und Kristallchemie, Universität Stuttgart, Germany. The wavelength analyzed were between 100 and 1200 (cm^{-1}).

The serpentinites from Valle Trainguanca (Fig. 1C) were analyzed by E. Clavijo through a Micro-Raman and spectra acquired at the Vibrational Spectroscopy Laboratory of the Faculty of Sciences, Universidad of Chile. The materials were irradiated by a 785 nm laser with a coupled Leica microscope. The analysis of the mineral phases was performed using a 50x objective lens and wavelength between 200-1200 (cm^{-1}).

4. RESULTS

4.1. Field data

At Cerro Bayo (Valle Leones; Fig. 2) a 130-m-thick layer of amphibole-bearing mafic schists and minor bodies of dark green serpentinites (Figs. 3 A, B, C) are tectonically juxtaposed onto metasedimentary rocks through an inferred top-to-the-east fault zone (Fig. 2). Locally, granoblastic plagioclase-bearing amphibolites are intruded by granite dikes of the Leones Pluton (Figs. 3D and 3E).

The metasedimentary sequence consists mainly of metapelites and metasandstones defining a N-S-trending compositional banding subparallel to the main foliation (S_1) (Fig. 4A). The mafic rocks show a N-S- to NE-SW-trending main axial plane cleavage (S_1), defined by aligned elongated amphibole grains, associated to tight and moderately-gently plunging folds (F_1) (Fig. 4B) overprinted by a subparallel crenulation cleavage (S_2), associated to kink folds (F_2) (Figs. 4 A-D). Near the summit, dark green serpentinites exhibit the S_1-S_2 foliations locally folded and overprinted by shear bands (Fig. 4E).

Near Bahía Murta (Valle Traiguanca; Fig. 1C) a body of massive serpentinites is overlaid by foliated serpentinites (Sp N15W/20W) with a contact zone of brecciated rocks with an anisotropic matrix concordant to the main foliation. Serpentinites show dark bluish colors with different tones of pale to dark green and yellow. The contact zone is cross-cut by mm- to cm-thick carbonate veins with fibrous and columnar textures. The massive serpentinites are delimited to the east by foliated medium-grained amphibolites, whose contact relationship is not exposed (Fig. 3F).

4.2. Petrography

4.2.1. Metamafic rocks

At Cerro Bayo (Valle Leones) mafic rocks consist of tremolite-chlorite schists and amphibolites. Mafic schists show nematoblastic and decussate textures (Figs. 5 C-E) which are constituted essentially of tremolite (traces of relic hornblende), chlorite, subordinate amounts of titanite and ilmenite. Chlorite mostly occurs as isolated aggregates with skinny tabular shapes, which are locally folded (F_2). In brecciated rocks, fragments of folded tremolite schists show subrounded and elongated shapes, placed subparallel to the S_1 main foliation (Figs. 5C-E).

Amphibolites from Leones and Traiguanca valleys show granoblastic texture and are composed of variable proportions of amphibole (hornblende) and plagioclase, traces of titanite, and opaques.

4.2.2. Metaultramafic rocks

At Cerro Bayo (Valle Leones) these rocks exhibit mesh textures formed of almost completely subidiomorphic serpentine laths showing an hourglass arrangement (Fig. 5A). Besides, they present interlocking textures, related to irregular and almost equant grains. The ultramafic rocks include multiple domains and dismembered bands of needle-like tremolite and minor chlorite, displaying a decussate texture. Also, minor needle-like chlorite bundles occur locally (Fig. 5A). The serpentinites host fibrous and crack seal type serpentine veinlets (Figs. 5A, B). The opaque minerals are magnetite and ilmenite. Large grains of magnetite, with irregular shapes, preserve texturally distinctive cores with dimmed reflectivity (Fig. 7D). The second generation of magnetite occurs as scattered small grains clustering in strings in the matrix and as vein filling (Fig. 5A and 5B). Some of them are displayed in serpentine mesh rims.

At Valle Traiguanca, the ultramafic rocks are fully serpentinized wherein primary silicate minerals of the protolith were not identified. The mineral assemblage consists mainly of serpentine polymorphs, magnetite, and variable amounts of chlorite, talc, carbonate, and gypsum. The serpentinites possess a wide variety of textures and the principal corresponds to the interpenetrating texture (Fig. 5F), defined by a serpentine mesh with scattered subhedral grains of magnetite. Interlocking texture, microcrystalline aggregates, and bastites are present as well. The fibrous veins are mostly filled with carbonate and talc.

4.2.3. The Leones pluton

Metamorphic rocks at Cerro Bayo are intruded by plutonic rocks (Fig. 3E), consisting mainly of granitic and minor dioritic components, locally with enclaves of biotite-bearing metasedimentary rocks. Granites (*s.l.*) vary from tonalite to granodiorite, most of them with leucocratic color index (Fig. 6A), including minor amounts of white mica, biotite, and garnet and traces of Fe-Ti oxides (Fig. 6B). Biotite transformed into white mica and chlorite display a preferred orientation in poorly-defined cleavage domains. Quartz show microstructures associated with processes of subgrain rotation and feldspars are locally fractured, signaling brittle to semi-ductile deformation after crystallization. The main foliation is N-S-trending. Irregular meter-thick zones of igneous breccias composed of a granite matrix and subangular enclaves of mesocratic diorite reveal processes of magma mingling in marginal zones of the pluton (Fig. 6C). Quartzdiorites and tonalites are mainly constituted by plagioclase, amphibole, biotite, traces of K-feldspar and quartz, and display a melanocratic color index. The amphibole is partially altered to chlorite, while the feldspars, in general, show local replacement by sericite and clay minerals (Fig. 6D).

4.3. Mineral chemistry and serpentine species

The chemical composition of serpentine, amphibole, chlorite, titanite, magnetite, and ilmenite from mafic-ultramafic rocks, together with the mineral composition of garnet, feldspars, and white mica from a leucocratic granodiorite of the Leones pluton, are listed in Table 2 to Table 5.

In serpentinites, serpentine is colorless with the first-order birefringence but rarely do some grains reach abnormal second-order color. The chemical composition of serpentine from both bodies is similar, with average contents of SiO_2 of 42-43 wt%, MgO of 39-42 wt%, and FeO of 3-6 wt%, with loss of ignition ranging between 11-13 wt%. Subtle differences of Al_2O_3 contents are detected, with lower (0.2-0.5 wt%) and higher (1.0-2.6 wt%) contents in serpentinites from the Leones and Traiguanca bodies, respectively.

According to Rinaudo and Gastaldi (2003), these values in the Traiguanca body would be closer to lizardite and antigorite. Micro-Raman spectra were obtained from selected serpentine grains of the matrix and veinlets in serpentinites, allowing to identify (Fig. 8): (1) bands at 375 and 680-683 cm^{-1} for the serpentine phase in the matrix and veins of the Leones body (FO1932), indicating antigorite, and band at 1092-1096 cm^{-1}, suggesting the presence of lizardite; (2) in the Traiguanca body, a band around 375-380 cm^{-1}, possibly corresponding to antigorite, and a band ~690 cm^{-1} indicative of lizardite and chrysotile.

In serpentinites of the Leones body, there are late veinlets with a typical chrysotile texture, which is confirmed seeing the spectrum of 3600-3710 cm^{-1} (cf. Rooney et al., 2017), indicating that chrysotile veinlets overprint early serpentinization stages.

Magnetite in serpentinites of both localities shows similar texture and composition. The large and anhedral magnetite grains preserve Cr-rich cores (Cr_2O_3 content varying from 7 to 21 wt%), classified as Cr-rich magnetite (Fig. 9A). The Cr-content decreases abruptly towards the edges of the large grains (Fig.7D, G; Tables 2-5), showing the same composition of the small magnetite grains with negligible Cr contents. Elongated grains of ilmenite were only identified in the serpentinites from the Leones body, which is characterized by high MnO content, varying between 7.0 and 8.5 wt%.

Chlorite in serpentinites and tremolite-schists from the Leones body is classified as clinochlore (Fig. 9B). Chlorite from serpentinites show higher Mg and lower Al and Fe contents than those from schists. Most of the amphibole in serpentinites and mafic schists is tremolite and minor Mg-hornblende are also present in schists (Fig. 9C). Ilmenite in tremolite-chlorite schists shows moderate contents of MnO of ~2.4 wt%.

The garnet-bearing granodiorite is composed of pure K-feldspar and albite (Ab_{92-98}). White mica is phengite in composition with variable Si contents ranging between 3.07 and 3.34 (a.p.f.u.) showing high FeO contents varying between 4 and 6 wt% and low MgO content of ~0.50 to 0.65 wt%. Garnet, which is almost almandine-spessartine in composition, shows a concentric compositional zonation with increasing FeO and CaO and decreasing MnO content towards the rim (Table 5).

4.4. Bulk-rock geochemistry

The bulk-rock major and trace element concentration in mafic and ultramafic rocks and granitoids are reported in Table 1. The results are integrated with previously published data of metabasites from the EAMC (Quiroz and Belmar, 2010). Because the original composition of mafic and ultramafic protoliths was modified by metamorphic and metasomatic processes, the data presented will be centered in elements widely considered to be low mobility elements during metamorphic and metasomatic processes (Ti, V, Y, Zr, Nb, Th, HREE; cf. Furnes et al., 2020 and references therein). The chemical patterns and elemental anomalies are discussed when appropriate.

4.4.1. Metamafic rocks

Metabasites from the Leones and Traiguanca bodies show bulk composition with SiO_2 content varying between ~48-51 wt% and CaO varying between ~9-12 wt%. In general, they show variable contents of FeO and MgO, with #Mg ranging between 0.40 and 0.75 (MgO/(MgO+FeO); total Fe is considered Fe^{+2}). Metabasites plot in the tholeiitic field in the AFM diagram and display low Nb/Y ratios, characteristic of sub-alkaline basalts (Figs. 10A, B). Chondrite-normalized Rare Earth Elements (REE) display a flat pattern, slightly depleted in LREE, with $[La/Sm]_N$ of 0.56-0.87, $[La/Yb]_N$ of 0.65-0.99, and without Eu anomaly (Fig. 11A). The spider-diagram of trace elements normalized to Normal Mid-Ocean-Ridge-Basalts (N-MORB of Sun and McDonough, 1989) (Fig. 11B), shows a rather variable composition in Large Ion Lithophile Elements (LILE) and Ta-Nb depletion in most samples. The High-Field Strength Elements (HFSE) show a nearly flat pattern with slight depletion in Sr and P, only one sample shows a negative Ti anomaly.

Metabasites show low Th/Yb and Nb/Yb values and low V/Ti typical of N-MORB. Two samples from the Leones and Traiguanca bodies show a chemical affinity with back-arc basin basalts (BABB) and island arc tholeiites (IAT) (Figs. 11C, D). Tectonic discrimination diagrams (Fig. 11E, F) indicate the same tectonic environments mentioned above (N-MORB, IAT, and BABB).

A plagioclase-bearing granoblastic amphibolite (FO1921) intruded by granite dikes show low SiO_2 content (~39 wt%), high FeO (~22 wt%; #Mg = 0.19) and TiO2 (~5.3 wt%). This rock has negligible contents of Cr and Ni (below the detection limit) and high contents of V (433 ppm) and Zr (583 ppm) compared to metabasites (Table 1).

The enriched chondrite-normalized REE patterns of amphibolites from both localities are flat and show a slight depletion of LREE. This pattern is similar to those of metabasites.

4.4.2. Metaultramafic rocks

The metaultrabasite of the Leones body is a serpentinite (FO1932), with SiO_2 contents of ~39 wt%, MgO content of ~36 wt% (#Mg = 0.79), and similar in major element composition to serpentinites from the Traiguanca body, with SiO_2 and MgO contents varying between 32-43 wt% and 39-33 wt% (#Mg ~ 0.80), respectively (data from Quiroz and Belmar; 2010 and this work). Our serpentinite samples (FO16201-FO16202) show high contents of Cr (ca. 2400 ppm) and Ni (ca. 1800 ppm) and low content of V (ca. 45 ppm).

Two serpentinites from both mafic-ultramafic bodies show similar composition to chondrite, with a subtle enrichment in LREE (both with $[La/Sm]_N$=2.3), a nearly flat pattern of HREE (with $[Tb/Yb]_N$=0.9 and 0.4; the Leones and Traiguanca bodies, respectively) with an exceptional positive Eu anomaly (both of ca. Eu*=2.6).

4.4.3. Leones Pluton

The compositional variation of the Leones Pluton, constituted by a suite of quartzdiorites, tonalites, and granodiorites, with SiO_2 ranging from 58 to 76 wt% and #Mg ranging from 0.1 to 0.3, resembles those of the low-K and subalkaline series. All samples display a distinctive calc-alkaline trend in the AFM diagram (Fig. 10B). The amphibole-bearing tonalite and inclusions of quartzdiotrite show higher concentrations of FeO, MgO, CaO, and TiO_2 compared to biotite- and garnet-bearing tonalites and granodiorites. In general, most samples show high Na_2O/K_2O ratios ranging from 1.8 to 3.7, with exceptionally high values of 9.1 and 11.2 in the biotite-bearing tonalite and granodiorite. All samples have Al/(Na+K) values ranging from 1.0 to 2.1 and the alumina saturation index (ASI=Al/[Ca+Na+K]) varying between 0.9 and 1.2. Amphibole-bearing rocks are metaluminous and the others plot in the field of peraluminous rocks, where garnet-bearing granodiorites show the higher ASI values (> 1.1; Fig. 12A). The igneous suites of the Leones Pluton show chemical affinities with volcanic arc granitoids in tectonic discrimination diagrams, with exception of one sample (amphibole tonalite) akin to within-plate granites (Fig. 12B). On basis of Zr content and 10^4*Ga/Al values (diagram of Whalen et al., 1987; not shown) two samples can be classified as A-type.

The chondrite-normalized REE patterns show a little enrichment of LREE and a flat shape in HREE (Fig. 12C). Small marked negative Eu anomalies are present in the two amphibole-bearing granitoids and one garnet-bearing granodiorite, reflecting processes of plagioclase fractionation during the evolution of magma batches. The Primitive Mantle-normalized diagram of LILE and HFSE (Sun and McDonough, 1989) show positive anomalies on K and Pb, with Nb, Ta, and Ti depletion in most samples (Fig. 12D), which is a distinctive chemical feature of magmas generated in a subduction environment. The low to moderate Sr/Y and La/Yb values (up to 27 and 12, respectively), together with chemical features mentioned above, suggest the lack of amphibole and garnet in the source and/or residue at the site of intermediate magma formation (cf. Kay and Kay, 1993).

5. Discussion

The metabasites of the EAMC near the Lago General Carrera have oceanic geochemical affinities (N-MORB, IAT, BABB) which are consistent with the V and Ti contents and low Th/Nb ratios (mostly <0.1), indicating negligible or null assimilated continental components during magma genesis (cf. Pearce, 2008). Thus, it is relevant to discuss the origin of ultramafic rocks and evaluate whether or not the protolith of serpentinites formed part of oceanic spreading centers lately subducted. Besides, the petrotectonic assemblage at Cerro Bayo, constituted by mafic-ultramafic rocks tectonically interleaved within a thicker sequence of quartz-rich micaceous schists, are intruded by the mid-Carboniferous Leones Pluton (De La Cruz and Suárez, 2006), will be discussed in a new tectonic model proposed in this study.

5.1. Origin of serpentinites

Serpentinites usually originate from the hydration of ultramafic protoliths, commonly associated with mid-oceanic ridges and transform faults environments where great masses of mantle rocks interact with seawater-derived fluids (Morishita et al., 2009), or are influenced by hydration of the subducting lithosphere near to trench, as a result of the faulting associated with plate bending (Ranero et al., 2003; Contreras-Reyes et al., 2007). However, the serpentinization process may also occur in the fore-arc mantle wedge in a subduction setting, through the infiltration of slab-derived fluids (Mottl et al., 2004) that will be strongly controlled by the temperature of the subducting slab (Guillot et al., 2015). The record of serpentinites in the southern Patagonian Andes is scarce and indeed their nature and processes for their formation are still uncertain.

The original mineralogy of serpentinites from the Leones and Traiguanca bodies was entirely replaced by serpentine polymorphs (a mixture of antigorite and lizardite in the matrix), Cr-rich relic cores in large grains of magnetite, and variable proportions of chlorite, tremolite, talc, pure magnetite, and Mn-rich ilmenite. Bastites of serpentine reveal the presence of pyroxene in the precursor peridotite of the Traiguanca body. The crystallization of tremolite and Mn-rich ilmenite in serpentinites can be related to thermal-driven metamorphism (cf. Cassidy et al., 1988; Nozaka and Shibata, 1995) during the intrusion of the Leones Pluton.

Based on the variable Al_2O_3 content (up to 3 wt%) and high concentration of Cr and Ni in serpentinites, their protolith must have been an olivine-rich clinopyroxene-bearing peridotite (harzburgite, lherzolite, and/or wehrlite). The high Cr and Ni contents could be related to olivine accumulation after processes of partial melting of fertile lherzolites. A distinctive feature in serpentinites from both localities is the presence of Cr-rich magnetite in the core of large anhedral magnetite (Fig. 7D and 7G). Sleep et al. (2004) proposed that high Cr content in magnetite could be the result of the olivine degradation during progressive serpentinization. This would indicate an early stage of serpentinization, recorded by the Cr-rich magnetite formation, succeeding to a later phase in which Cr was no longer available in the fluid phases. From the textural and compositional transformations experimented by spinel during serpentinization, another alternative arises (e.g. Boedo et al., 2015). It is suggested that large and anhedral magnetite grains with Cr-rich core composition would have been formed by alteration of Cr-spinel, from rim to core, by dissolution processes during progressive serpentinization, and followed by late crystallization of pure magnetite coeval with serpentine phases. In consideration that Cr and Ni contents in peridotites can be modified during serpentinization (Saumur and Hattori, 2013; Deschamps et al., 2013) to elucidate the likely presence of Cr-spinel in the precursor peridotite more studies are required.

The REE geochemical composition of serpentinites can be influenced by the environment of fluid/rock interactions as well as the REE contents of primary phases and their stability during serpentinization (Niu, 2004; Dechamps, et al., 2013). In mid-ocean ridges, several processes, summarized as melt/rock interactions during the ascent of basaltic magmas, can modify the composition of the ambient mantle before the serpentinization (Niu, 2004; Paulick et al., 2006). On the other hand, the bulk chemical composition of mantle wedge serpentinites can be influenced by metasomatic processes linked to dehydration of the subducted oceanic slab (hydrated basalts and pelagic sediments) and continental derived material (c.f. Dechamps et al., 2013 and references therein). Ultimately, the composition of serpentinites is a function of the temperature and nature of fluids (Deschamps et al., 2013). The serpentinite from the Leones body displays a noticeable positive Eu anomaly (Fig.11A) similar to those reported in the Atlantic oceanic lithosphere (Paulick et al., 2006) and Paleozoic ophiolites in the Precordillera of north-western Argentina (Boedo et al., 2015). This compositional feature suggests processes related to ocean floor serpentinization (cf. Deschamps et al., 2013). However, the slightly enriched LREE compositions in the serpentinite and high contents of Ti (594 ppm) and Yb (0.2 ppm), are typical for subducted serpentinites (Deschamps et al., 2013), indicating late processes of serpentinization of the oceanic-type lithosphere in a subduction setting. Although the serpentinites from the Traiguanca body have lower Ti (ca. 100 ppm) and Yb (ca. 0.1 ppm) contents they still can be interpreted as subducted serpentinites. The temperature conditions during serpentinization can be inferred from the presence of lizardite and antigorite in the matrix, which can be stable at a temperature of ca. 300ºC (cf. Guillot et al., 2015). The chlorite composition in serpentinites and mafic schists suggests that the temperature did not exceed 300ºC (Al^{IV} ranging between 1.25 and 2.12; using the geothermometer of Cathelineau, 1998 and Jowett, 1999). Late veinlets filled with chrysotile can be associated with the exhumation of the serpentinite bodies to shallow depths (< 20 km; cf. Guillot et al., 2015). It is proposed that ultramafic rocks were buried and metamorphosed in a shallow subduction setting.

5.2. Tectonic evolution model

The pre-Pennsylvanian metasedimentary sequences and mafic-ultramafic bodies of the northeastern belt of the EAMC (47ºS) were sourced from felsic and recycled old continental rocks from the interior of Gondwana (Augustsson and Bahlburg, 2003; Hervé et al., 2003). The Devonian detrital zircons in the EAMC were probably sourced from igneous belts from the Deseado and North Patagonian massifs (Loske et al., 1999; Varela et al., 2005; Pankhurst et al., 2003, 2006; Guido et al., 2005; Hervé et al., 2016) and/or recycled from metasedimentary sequences formerly deposited in forearc basins (cf. Cerro Negro schists; Permuy-Vidal et al., 2014). Sequences of psammopelitic schist are tectonically interleaved with metabasites with N-MORB, BABB, and IAT geochemical affinities that formed part of a marine basin with active mid-ocean ridges and spreading-centers located in the upper plate of a subduction zone (Fig. 13A).

It is considered that the formation of a late Devonian and early Carboniferous marginal back-arc basin was ultimately controlled by trench-roll back tectonics, as has been proposed in northern latitudes for the tectonic evolution of the Chaitenia island arc terrane (43ºS; Hervé et al., 2016, 2018). We hypothesize that at the latitude of the study area the northern portion of the Antarctic Peninsula continental block was drifted from the southwestern Gondwana margin as proposed by previous works (cf. Calderón et al., 2016; Suárez et al., 2019; Navarrete et al., 2019). In this scenario, the Devonian and Early Carboniferous orthogneisses in Antarctic Peninsula (cf. Millar et al., 2002; Riley et al., 2012) may represent the magmatic products generated within an ensialic island arc (Fig. 13A).

Mineralogical and chemical data show that ultramafic rocks were probably serpentinized in a mid-ocean-ridge environment and lately chemically modified in a shallow subduction setting. Thus, mafic-ultramafic sequences were metamorphosed and off-scrapped from the oceanic slab at shallow depths of the subduction interface and tectonically incorporated into the base of an accretionary wedge. The ocean basin closure and tectonic juxtaposition of metamorphic rocks were followed by the intrusion of the Leones Pluton and the late hypothetical docking of the Antarctic Peninsula block (Fig. 13B).

The mid-Carboniferous Leones Pluton (cf. De la Cruz and Suárez, 2006) is composed of metaluminous and peraluminous suites showing compositional features of calc-alkaline and Na-rich magmas generated in a subduction setting. The lithological and geochemical diversity suggest that amphibole-bearing intermediate rocks and garnet-bearing granodiorites resulted from open-system fractional crystallization of precursor mafic magmas and assimilation processes at different crustal depths (cf. De Paolo 1981). It is proposed that mantle-derived magmas intruded at the base of a relatively thin continental (accretionary wedge) crust evolving to intermediate compositions through fractional crystallization processes and assimilation of lower crustal rocks. Intermediate magmas then ascended to shallow crustal depths of a previous accretionary wedge (Fig. 13B) leaving behind plagioclase- and pyroxene-bearing cumulates (or residues). The generation of peraluminous garnet- and mica-bearing granodiorites may have involved the anatexis of country rocks (e.g. metasediments, metabasites) at the site of pluton emplacement. These processes have been reported in continental magmatic arcs (Hervé et al., 1993) and in plutonic belts formed by near-trench magmatism during the subduction of active ocean-ridges (e.g. Cabo Rapper pluton in Taitao Peninsula; Anma et al., 2009). In a broad sense, the locus of arc magmatism in the present-day South American Plate migrated from the Deseado Massif in the Middle Devonian and earliest Carboniferous, to Valle Leones in mid-Carboniferous times (Fig. 13B).

6. Concluding remarks

The integrated field data, petrography, mineral, and bulk rock chemical composition indicate that metabasites from the Leones and Traiguanca lenses, with N-MORB, IAT, and BABB geochemical affinities, formed part of the upper section of the oceanic-type lithosphere of a marginal basin developed in a suprasubduction zone. The marginal basin was sourced from rocks located near the Deseado Massif and generated the space for the deposition of older sedimentary successions of the northeastern belt of the EAMC, with Devonian and early Carboniferous detrital zircon components. Global tectonic plate reorganization resulted in the closure of the marginal basin, being consumed in an east-dipping subduction zone where partially subducted serpentinites were metamorphosed. The mafic-ultramafic ophiolitic rocks and metasedimentary sequences were tectonically juxtaposed at the base of an accretionary wedge at shallow conditions. The off-scrapping of ophiolitic slices and accretion to the upper plate involved the development of the main S_1 foliation. The oblique crenulation cleavage S_2 was probably formed during the growth and exhumation of the accretionary wedge. These processes culminated with the intrusion of Na-rich calk-alkaline diorite-granite suites of the Leones Pluton during mid-Carboniferous times.

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Figure Captions

Figure 1. A) Generalized terrane map of southern South America, modified from Hervé et al. (2018). B) Sketch geological map of Patagonia with showing U-Pb zircon crystallization ages (numbers in red) from Paleozoic intrusive rocks from the Patagonian Andes (Chaitenia island arc, sensu Hervé et al., 2018), North Patagonian Massif (Pankhurst et al., 2006) and Deseado Massif (Loske et al., 1999; Pankhurst et al., 2003, 2006; Guido et al., 2004, 2005;

Permuy-Vidal et al., 2014). Detrital zircons ages (numbers in black) from metamorphic complexes (Hervé et al., 2008), and K-Ar from metamorphic and plutonic rocks from Valle Leones (De la Cruz and Suárez, 2006). The study area is indicated. C) Geological data adjacent to Lago General Carrera showing the location of mafic-ultramafic lenses: (1) Leones area and (2) Traiguanca area, geological information modified from De la Cruz and Suárez (2006) and Quiroz and Belmar (2010). BMMC: Bahia Mansa Metamorphic Complex; CMC: Chonos Metamorphic Complex; DAMC: Diego de Almagro Metamorphic Complex; EAMC: Eastern Andean Metamorphic Complex; MDAC: Madre de Dios Accretionary Complex.

Figure 2. Geological-structural sketch map of the Cerro Bayo and surrounding areas. NNW-SSE trending inferred brittle thrust fault juxtaposes the western block (metaigneous domain) over the eastern metasedimentary domain. Structural stations (Stn) are located, and to the right equal area stereograms of identified foliations.

Figure 3. Field photographs showing: A) Field relations between metabasites and serpentinites intruded by the Leones Pluton at Stn2 locality at Cerro Bayo, Valle Leones. B) Foliated metabasites with marked S_1 foliation. C) Serpentinites adjacent to metabasites. D) Contact relation between amphibolites and a granodiorite dykes. E) Granitoids on top of the CerroBayo. F) Outcrop of the Traiguanca mafic-ultramafic lens, adjacent to the road.

Figure 4. Field photographs showing details from the primary and secondary (tectonic) fabric of the ortho- and para-derived metamorphic rocks at Cerro Bayo. A) Interleaved metapsammopelites and phyllites, showing the petrative S1 foliation subparallel to comopositional banding (S_0). B) Tight, moderately-gently plunging folds (F_1) in serpentinites. C) Kink bands and associated crenulations cleavage (S_2) overprinting the

older, sub-parallel S_0-S_1 structure. D) Crenulation cleavage developed in metabasites (S_2). E) Development of S-C structures in serpentinites, folding and shearing S_1 and S_2.

Figure 5. Photomicrographs showing: A) Serpentinite from the Leones lens (sample FO1932) with chlorite and magnetite. B) Crack seal type serpentine vein in the same serpentinites. C) Metabasite of the Leones lens (sample FO1922) that shown amphibole with granoblastic texture. D) Metabasite of the Leones lens (sample FO1922) with fragmental texture composed of chlorite and amphibole. E) Metabasite of the Leones lens (sample FO1922) that show a sigmoidal lens with amphibole showing noticeable foliation. F) Sepentinite of the Traiguanca lens (sample FO16201) with interpenetrative blades of serpentine and microcrystalline aggregates of carbonate dissected by late carbonate veins. Abbreviations are: Cb, carbonate; Mt, magnetite; Chl, chlorite; Atg, antigorite; Lz, lizardite; Ctl, chrysotile; Act, actinolite; Tr, tremolite.

Figure 6. A) Outcrop of the Leones Pluton affected by local shear band foliation. B) Photomicrograph of the garnet-bearing granodiorite (sample F01917). C) Igneous breccia consisting of granitic matrix and dioritic enclaves, resulting from magma mingling. D) Photomicrograph of amphibole-bearing quartzdiorites; amphibole is partially altered to chlorite and epidote. Plagioclase is replaced selectively by sericite. Qz: Quartz, Wm: White mica. Abbreviations are: Qz, quartz; Plg, plagioclase; Amp, amphibole; Gt, garnet..

Figure 7. Back-scattered electron images of serpentinites from the Leones lens (A, B, C, D, E) and the Traiguanca lens (F, G, H). Abbreviations are: Mt, magnetite; Srp, serpentine; Chl, chlorite; Amp, amphibole; Tr, tremolite; Ilm, ilmenite.

Figure 8. (A) Micro-Raman spectroscopy spectrum of serpentine from the Leones and Traiguanca bodies.

Figure 9. Classification minerals from both Traiguanca (FO1621) and Leones (FO1922 and FO1932) bodies. A) Ternary classification diagram (Cr^{3+}-Fe^{3+}-Al^{3+}) for the spinel group. Modified from Gargiulo et al. (2013). B) Classification diagram for chlorite (Zane and Weiss, 1998). C) Classification diagram for calcic-amphibole (Hawthorne et al., 2012). Calculations were made using the excel spreadsheet of Locock (2014).

Figure 10. (A) Classification diagram for metabasites and granitoids using the SiO_2 VS. Nb/Y diagram of Winchester and Floyd (1977). (B) AFM (Na_2O+K_2O-Fe_2O_3-MgO) diagram of Irvine and Baragar (1971).

Figure 11. (A) Chondrite-normalized REE patterns and (B) N-MORB normalized incompatible element patterns for metabasites and ultramafic rocks from the Leones and Traiguanca lenses. Normalizing values are from Sun and McDonough (1989); (C) Th/Yb vs. Nb/Yb diagram (the field of the MORB-OIB mantle array is from Pearce, 2008); Tectonic discrimination diagrams for the metabasites from the Leones and Traiguanca lenses (D) V-Ti/1000 diagram (Shervais, 1982 modified in Pearce (2008), (E) Y/15–La/10–Nb/8 ternary diagram (after Cabanis and Lecolle, 1989) and (F) 2Nb–Zr/4–Y ternary diagram (AI+AII: Whitin-plate alkaline basalt; AII+C: Whitin-plate tholeiitic basalt; B: E-MORB; C+D: Volcanic arc basalt; D: N-MORB;after Meschede, 1986).

Figure 12. (A) ASI diagram of Maniar and Piccoly (1984) and (B) Tectonic discrimination diagrams for the intrusive rocks of the Leones Pluton (Pearce et al. 1984). (C) Chondrite-normalized REE patterns and (D) Incompatible element patterns normalized to primitive Mantle (Sun and McDonough, 1989), for intrusive rocks from Leones Pluton. Syn-COLG: Syn-Collisional Granite; WPG : Whitin Plate Granite; VAG : Volcanic Arc Granite.

Figure 13. (A) Sketch figure illustrating the geodynamic evolution of southwestern Gondwana margin (~46°-47°S present-day coordinates) for mid-late Paleozoic times. See text for explanations. AP: Antarctic Peninsula.

Table Captions

Table 1. Bulk rock chemical composition of studied rocks.

Table 2. Chemical compositions of minerals in tremolite-chlorite schist (sample FO1922) of the Valle Leones.

Table 3. Chemical compositions of minerals in serpentinite (sample FO1932) of the Valle Leones.

Table 4. Chemical compositions of minerals in serpentinite (sample FO1621) of the Valle Traiguanca.

Table 5. Chemical compositions of minerals in garnet-whit mica granodiorite (sample FO1911) of the Leones Pluton.

Highlights

We recognized serpentinites bodies bearing lizardite, antigorite and chrysotile polymorphs.

A marginal basin is proposed with active mid-ocean ridges and spreading centers.

We proposed the Leones Pluton.

Calc-alkaline geochemical affinity to mid-Carboniferous Leones Pluton.

Closure of the basin related to Antarctic Peninsula drift

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: