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ORIGINAL PAPER

Retrowedge-related Carboniferous units and coeval magmatism in the northwestern Neuquén province, Argentina

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Abstract The studied Carboniferous units comprise metasedimentary (Guaraco Norte Formation), pyroclastic (Arroyo del Torreón Formation), and sedimentary (Huaraco Formation) rocks that crop out in the northwestern Neuquén province, Argentina. They form part of the basement of the Neuquén Basin and are mostly coeval with the Late Paleozoic accretionary prism complex of the Coastal Cordillera, south-central Chile. U–Pb SHRIMP dating of detrital zircon yielded a maximum depositional age of 374 Ma (Upper Devonian) for the Guaraco Norte Formation and 389 Ma for the Arroyo del Torreón Formation. Detrital magmatic zircon from the Guaraco Norte Formation are grouped into two main populations of Devonian and Ordovician (Famatinian) ages. In the Arroyo del Torreón Formation, zircon populations are also of Devonian and Ordovician (Famatinian), as well as of Late Neoproterozoic and Mesoproterozoic ages. In both units, there is a conspicuous population of Devonian magmatic zircon grains (from 406 ± 4 Ma to 369 ± 5 Ma), indicative of active magmatism at that time range. The $\varepsilon_{\mathrm{Hf}}$ values of this population range between −2.84 and −0.7, and the TDM-(Hf) are mostly Mesoproterozoic, suggesting that the primary sources of the Devonian magmatism contained small amounts of Mesoproterozoic recycled crustal components. The chemical composition of the Guaraco Norte Formation corresponds to recycled, mature polycyclic sediment of mature continental provenance, pointing to a passive margin with minor inputs from continental margin magmatic rocks. The chemical signature of the Huaraco Formation indicates that a magmatic arc was the main provenance for sediments of this unit, which is consistent with the occurrence of tuff—mostly in the Arroyo del Torreón Formation and very scarcely in the Huaraco Formation—with a volcanic-arc signature, jointly indicating the occurrence of a Carboniferous active arc magmatism during the deposition of the two units. The Guaraco Norte Formation is interpreted to represent passive margin deposits of mostly Lower Carboniferous age (younger than 374 Ma and older than 326 Ma) that precede the onset of the accretionary prism in Chile and extend into the earliest stage of the accretion, in a retrowedge position. The Arroyo del Torreón and Huaraco formations are considered to be retrowedge basin deposits to the early frontal accretionary prism (Eastern Series) of Chile. The presence of volcanism with arc signature in the units provides evidence of a Mississippian magmatic arc that can be correlated with limited exposures of the same age in the Frontal Cordillera (Argentina). The arc would have migrated to the West (Coastal Batholith) during Pennsylvanian–Permian times (coevally with the later basal accretionary prism/Western Series). The source of a conspicuous population of Devonian detrital zircon interpreted to be of magmatic origin in the studied units is discussed in various possible

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geotectonic scenarios, the preferred model being a magmatic arc developed in the Chilenia block, related to a west-dipping subduction beneath Chilenia before and shortly after its collision against Cuyania/Gondwana, at around 390 Ma and not linked to the independent, Devonian–Mississippian arc, developed to the south, in Patagonia.

Keywords Carboniferous retrowedge basin deposits · Mississippian magmatism · Devonian magmatism · U–Pb SHRIMP dating · Hf isotopes · Neuquén province · Argentina

Introduction

Outcrops of pre-Permian Paleozoic rocks (locally referred to as pre-Choiyoi units) forming part of the basement of the Neuquén Basin are scarce. They have been recognized in the nucleus of anticline structures such as in the Chachil Cordillera and compared with the Eastern Series of the accretionary prism complex of the Coastal Cordillera of Chile by Franzese (1995). The presence of accretionary complexes would be indicative of subduction of oceanic crust in the western Gondwana margin in the late Paleozoic, after a period of passive margin stage at 390–340 Ma (Willner et al. 2009). The deposition of the accreted sediments in Chile took place after 344 Ma (Willner et al. 2005, 2008), the accretion starting at 340 Ma (Willner et al. 2009). A change of the accretion mode occurred from frontal to basal before 308 Ma, when also a concomitant retrowedge basin, represented by the Huentelauquen Formation, was developed (Willner et al. 2008).

In this article, we analyze the pre-Choiyoi metasedimentary-sedimentary-pyroclastic units of northwestern Neuquén–Guaraco Norte (Zappettini et al. 1987), Arroyo del Torreón (Méndez et al. 1995), and Huaraco (Zöllner and Amos 1973) formations—as well as the concomitant Carboniferous magmatism, and we discuss their origin and tectonic settings and connection with the Upper Paleozoic accretionary system from Chile.

The aim of this article is to contribute to the knowledge of the architecture of the Late Paleozoic fore-arc/arc system in southern South America through the presentation and interpretation of chemical and isotopic data of previously poorly known units that represent the easternmost and northernmost outcrops of the basement of the Neuquén Basin.

We present a combined U–Pb SHRIMP and Hf-isotope study of single detrital zircon (Guaraco Norte and Arroyo del Torreón formations), as well as whole-rock chemical analyses of the studied units, establishing their ages and main provenances. We address their paleogeographic location interpreted in the context of the crustal evolution of the proto-Pacific margin of southern South America.

Additionally, we analyze the implications of the occurrence of a conspicuous Devonian population of magmatic zircon, focusing on its provenance and on the tectonic setting of the magmatic units exposed at the time of sedimentation of the Guaraco Norte and Arroyo del Torreón formations and discuss their possible relationship with the accretion of the Chilenia terrane in various regional tectonic scenarios.

Geological framework

Rocks of Upper Paleozoic age in the western margin of Gondwana were formed in a period of rapid convergence rates during the continental assembly of this supercontinent; the interaction between the Panthalassic oceanic lithosphere and western Gondwana determined the development, from west to east, of an accretionary prism, a forearc basin, a magmatic arc, and a backarc basin (Charrier et al. 2007).

The continental crust in central Chile and western Argentina, on which the Gondwanan orogeny evolved, has been interpreted to be represented by the Chilenia terrane (Ramos et al. 1984) whose accretion to Gondwana would have occurred at 390 Ma (Willner et al. 2011a). Ramos and Basei (1997), first dated a population of detrital zircon grains of this basement as Mesoproterozoic and interpreted this basement to represent erosional windows, being preserved as roof pendants in the Frontal Cordillera of Argentina (Guarguaraz Complex) and Chile. However, Sm–Nd isochrons of interlayered basaltic sills as well as biostratigraphic constraints of the Guarguaraz Complex (López de Azarevich et al. 2009) and recent age determinations of detrital zircon in this unit (Willner et al. 2008) point to a Late Neoproterozoic to Paleozoic age, with a peak of HP metamorphism at 390 Ma (Willner et al. 2011a, b). The study of the metamorphic evolution of the Paleozoic accretionary complex at this latitude allowed Willner et al. (2009, 2011a) to interpret the Guarguaraz Complex in the context of the collisional scenario between Chilenia and Cuyania/Gondwana.

In this tectonic framework, the late Paleozoic metamorphic rocks located to the west of the Chilenia terrane, south of 33°S, have been interpreted as a coastal accretionary complex, mainly exposed along the Coastal Cordillera of Chile, consisting of a paired belt dominated by siliciclastic metasediments, known as the Western and the Eastern Series (cf. Hervé 1988 and references therein) (Fig. 1). The timing of events in the accretionary prism and its relation with the late Paleozoic Coastal batholith were studied in detail by Willner et al. (2005, 2011) and Glodny et al. (2005, 2006, 2008).

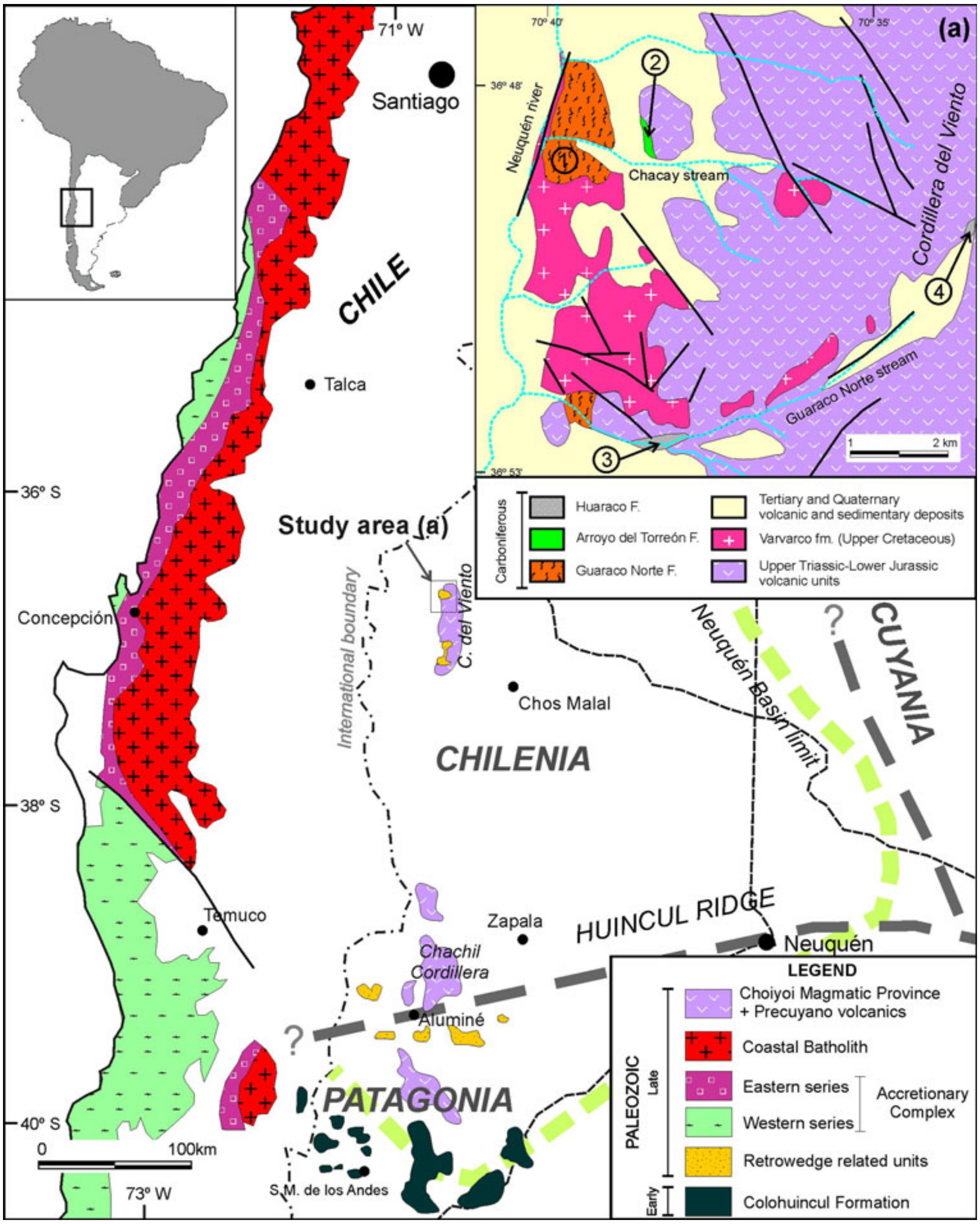


Fig. 1 The study area in the context of the main geological units and tectonic environment during Paleozoic times (modified after Sernageomin 2003; Chernicoff and Zapettini 2004). *a* Geological map of the study area in northern Neuquen province, southwest Argentina. *1–4*: described outcrops-see text for reference

The Eastern Series are characterized by pelitic–arenaceous sequences interpreted as continent-derived, mostly turbidity successions (e.g., Hervé 1988), lacking metabasite intercalations. Metamorphism that overprinted the Eastern Series at around 300 Ma (Willner 2005; Willner et al. 2008), increases to the east and was developed under relatively low P, medium to high T. In the westernmost side of the Chilean Principal Cordillera at ca. 39°30′ to 40°S, similar metasedimentary successions, intruded by Late Carboniferous to Early Permian batholith and referred to as the Trafún Metamorphic Complex, are attributed to the Eastern Series (Martin et al. 1999). In north-central Chile, the depositional age of the Eastern Series is interpreted as being mainly Carboniferous, age constrained by the maximum depositional age (Mississippian) and the age of metamorphism (Willner et al. 2005, 2008 and Willner et al. 2011b). The Eastern Series represent frontal-type accretion, with predominant horizontal shortening at shallow depths (Richter et al. 2007). The change in the accretion mode from frontal (Eastern Series) to basal (Western Series) occurred at around 308 Ma (Willner et al. 2005).

The presence of Silurian fossils in the Eastern Series at 38°S (Tavera 1983) and Devonian trilobites further south (42°15′S; Levi et al. 1966; Fortey et al. 1992) could pertain to preserved sequences that predate the onset of accretion and were incorporated into the accretionary complex.

Recent detrital zircon dating indicates that the maximum depositional ages of most accreted metasedimentary rocks are Mississippian (Willner et al. 2008).

The Western Series comprises metagraywacke, metapelites, metacherts, metabasites with preserved pillow structures and serpentinites (Hervé 1988; Hervé et al. 2007) that correspond to continental margin sediments mixed with slices of upper oceanic crust. Between 39°30′S and 42°S, exhalative iron formations, massive sulfides (Oyarzún et al. 1986; Collao et al. 1990), tourmalinites and intercalations of spessartine quartzites (Willner et al. 2001) are part of the Western Series. Metamorphic grade was developed under high P/T ratios, with peak conditions attained at 292–319 Ma in north-central Chile (Willner 2005). In south-central Chile, basal accretion has been dated at 249 ± 5 Ma (Glodny et al. 2005). In the eastern part of the Western Series, blocks with a blueschist facies overprint (Kato and Godoy 1995) constitute the earliest and deepest subducted material incorporated into the developing accretionary system, being time markers for the onset of subduction mass flow in the Coastal Cordillera accretionary prism at around 340 Ma (Willner et al. 2004). This section represents basal-type accretion, that is, subhorizontal flattening in deeper levels of the accretionary prism (Richter et al. 2007).

In Argentina, metamorphic units from the basement of the Neuquén Basin can be grouped into units that crop out south of 39°50′S, namely Colohuincul Formation and Metamorfitas Rio Limay (Cingolani et al. 2011b) and those exposed to the north, in nucleus of brachianticlinal structures, and grouped in the Piedra Santa (Leanza 1990) and the Guaraco Norte (Zappettini et al. 1987) formations. The first group have lower Paleozoic protoliths, considering available U–Pb ages of intrusive units in the Colohuincul Formation (401 ± 4 Ma; Pankhurst et al. 2006) and U–Pb ages of metamorphic titanites from the Metamorfitas Rio Limay (380 ± 2 Ma; Lucassen et al. 2004).

In the northern group, the Piedra Santa Formation (renamed as Piedra Santa Complex and correlated with the Eastern Series of the accretionary complex of Chile by Franzese (1995) consists of a low- to medium-grade metasedimentary sequence including metapelite and metagraywacke and minor mafic volcanic intercalations. Its metamorphic grade increases westward, reaching a high grade with associated migmatites (Vattuone de Ponti 1988). A maximum depositional age at 364 Ma was determined by Ramos et al. (2010). Older K–Ar ages in schists from this unit yielded 372–311 Ma and were considered to reflect the age of a regional metamorphic event (Franzese 1995).

At Cordillera del Viento, northern Neuquén, the oldest basement unit is the Guaraco Norte Formation, that consists of a low-grade metasedimentary sequence exposed in the northwestern part of this region and correlated to the Piedra Santa Complex (Zappettini et al. 1987; Cingolani et al. 2011b). It is unconformably covered by tuff and volcanic sandstone attributed to the Arroyo del Torreón Formation (Zappettini and Dalponte 2009) whose main outcrops were originally recognized in the Andacollo district by Zöllner and Amos (1955), where the total thickness was calculated at 1,500 m. The U–Pb SHRIMP age of zircon from a rhyodacitic lava flow interbedded in the tuff yielded 327.9 ± 2 Ma (Suárez et al. 2008).

The following unit in the stratigraphy (from bottom to top) is the Huaraco Formation, a Carboniferous sedimentary sequence that precedes the Choiyoi magmatism and covers the Arroyo del Torreón volcanic rocks, cropping out in the Andacollo region (Zöllner and Amos 1955; Stoll 1957). The sequence consists of sandstone and pelite to shale. Its upper section contains a *Rhacopteris Flora* and *Brachiopoda* molds. Total thickness was calculated at 700 m. A 100 m thick sequence crops out in the middle section of the Guaraco Norte stream.

Subduction and related arc magmatism in the western margin of Gondwana is recorded since at least the Cambrian, and up to Upper Paleozoic times, although Willner et al. (2009), advocate for the absence of evidence for both subduction and magmatism during the Devonian and Early Mississippian (390–340 Ma), which point to the presence of a passive margin at those times related to the prior collision of Chilenia. Between 33°S and 40°S, the accretionary prism exposures in Chile are flanked on their eastern side by the Pennsylvanian–Permian Coastal Batholith with reported ages ranging between 308 ± 15 and 257 ± 1 Ma (Hervé et al. 1988; Gana and Tosdal 1996; Martin et al. 1997; Lucassen et al. 2004; Willner et al. 2005). In the Andacollo region of Argentina, the magmatic units of this age are represented by the Huinganco Complex (Llambías et al. 2007) that includes La Premia Formation volcanic rocks (281.8 ± 2.1 Ma; Suárez et al. 2008) and the Huinganco granite (dated at 283,4 ± 1 Ma; Sato et al. 2008) and, further south by the Chachil Complex (Leanza 1990), where the oldest age determined reaches the Pennsylvanian (315 ± 1.5 Ma Re–Os age on molybdenite from La Voluntad porphyry Cu deposit, Garrido et al. 2008) (Fig. 1).

The studied units

Guaraco Norte Formation

The first mention of low-grade metamorphic rocks in northern Neuquén was made by Groeber (1929), who described small outcrops in the northern shore of the Varvarco Campos lake. The Guaraco Norte Formation was defined by Zappettini et al. (1987) to include the latter and another outcrop in the Guaraco Norte stream valley, at 36°52′S. Further findings were made later in the Chacay stream valley, to the north of the town of Varvarco (Zanettini 2001), at 36°48′S (location 1, in Fig. 1).

The sequences derive from sedimentary rocks and are composed of micaceous and quartzitic schists. The quartzitic schist displays alternating bands of quartz-rich and mica-rich layers, with albite and K-feldspar as minor components. The micaceous schist is composed of biotite, sericite, chlorite, white mica, and quartz. Accessory minerals are zircon, apatite, and pyrite. Locally, black shale has been recognized at the Guaraco Norte stream outcrop as well as fine-grained metaquarzite in the Chacay stream outcrop.

The rocks were metamorphosed and fully recrystallized under greenschist grade and display a conspicuous schistosity (S_1) with NNW trending, parallel to subparallel to bedding (S_0). Biotite follows S_1 foliation. The S_1 surfaces are cut by incipient shearing. Post-kinematic andalusite, diopside, and hornblende were formed in relation to Cretaceous-Paleocene granodiorite intrusions (Varvarco Formation).

Arroyo del Torreón Formation

The unit was formally defined in the Andacollo district (Méndez et al. 1995), to the south of the study area, to describe a unit mapped by Zöllner and Amos (1955) and Stoll (1957) and informally named as "*Tobas Inferiores*". Together with the Huaraco Formation, it constitutes the Andacollo Group (Digregorio 1972, emend. Llambías et al. 2007).

At Andacollo, it consists of stratified gray to reddish tuff of dacitic composition varying locally to rhyodacitic to andesitic compositions. Interbedded layers of metasandstone and slate, as well as thin rhyodacitic intercalations, have been identified at this location. Cleavage oblique to the stratification and locally incipient schistosity is noticeable and indicative of very low-grade metamorphism. Tuff is porphyroblastic, with crystalloclasts up to 5 mm composed mainly of quartz and plagioclase, as well as lithic fragments comprising sandstone and andesite, in a feldspathic matrix totally altered to chlorite, sericite, epidote, and silica.

Only one small outcrop has been identified in the study area (location 2, in Fig. 1). It consists of tuffaceous layers of yellow to green colors, interbedded with sandstone and affected by low-grade metamorphism. Lithoclasts, crystalloclasts of feldspar and the matrix are almost totally replaced by micas. Chlorite, tourmaline, sphene, zircon, and opaque minerals are common. Micaceous minerals consist of white mica and Fe-rich chlorite. Quartz ribbons are developed and show an incipient granoblastic texture; the clay matrix was also recrystallized to sericite. Pleochroic pale-orange euhedral hexagonal crystals of tourmaline, aligned to the incipient schistosity, are interpreted to be metamorphic in origin and would imply boron availability probably released by metamorphic breakdown of detrital minerals, for example, illite and/or feldspar.

Huaraco Formation

The unit was defined by Zöllner and Amos (1973) to describe a marine to continental sedimentary sequence that crops out in the Andacollo district and together with the Arroyo del Torreón Formation, it constitutes the Andacollo Group. It includes shale, claystone, siltstone, sandstone, and lenses of conglomeratic sandstone and tuff. Black shale is dominant in the lower section of the unit; it is finely grained with angular quartz grains in an incipiently recrystallized matrix with sericite and chlorite. Toward the top of the sequence sandstone prevails, locally grading to greenish brown to yellow siltstone; it is well stratified and consists of quartz clasts, sericite, minor amounts of detrital zircon, and tourmaline as well as volcanic and sedimentary lithoclasts. Cement consists of chlorite, sericite, and calcite. Quartz grains exhibit microgranulation and evidence of deformation.

Tuff occurs as thin lenses consisting of crystalloclasts of quartz, oligoclase, orthoclase, and minor biotite. The matrix and the crystalloclasts are altered to sericite, calcite, ankerite, chlorite, and clays. The sequence includes fossils indicative of a shallow marine to littoral environment at Andacollo; toward the top, the sequence includes fluvial conglomeratic deposits. The *Brachiopoda* and *Rhacopteris* flora of the unit are indicative of Pennsylvanian age (Amos 1972).

Rocks attributed to the Huaraco Formation have been identified in the Guaraco Norte valley, where the main outcrop (location 3, in Fig. 1) is a 100 m thick sequence of gray to green sandstone and siltstone, intruded and unconformably covered by Triassic volcanic rocks. They are constituted by finely grained quartz in a matrix consisting of clays, sericite, minor chlorite, opaque minerals, and scarce zircon; they show schistosity parallel to bedding and an incipient cleavage developed oblique to S_0–S_1 surfaces that are sparsely distributed due to the predominance of psammitic layers.

A second outcrop has been identified in the study area (location 4, in Fig. 1) at the headwaters of the Guaraco Norte stream. Here, the sequence is gray to black colored, and otherwise similar to the outcrop described immediately before; the preponderance of clay size minerals originates a conspicuous cleavage and crenulation that masks the original bedding.

Geochemistry

Provenance and sedimentary processes related to sedimentary sequences can be traced using their geochemical signature, although the relationship between sediments and their source region is a complex function of chemical changes that accompany weathering, transportation, and depositional processes. However, major elements (e.g., Bhatia and Crook 1986) as well as trace elements such as Th, Sc, Zr, and REE (McLennan 1989; McLennan et al. 1993), preserve characteristics of the source rocks in the sedimentary record (as long as the composition of the rock is not appreciably affected by diagenesis, metamorphism or other alteration processes). Consequently, a number of chemical analyses were carried out on the Guaraco Norte and Huaraco formations to contribute to the identification of their provenance and tectonic setting (Table 1). Methodology is given in the "Appendix". In the diagrams, samples from the Piedra Santa Complex, considered equivalent to the Guaraco Norte Formation, were also plotted for comparison, using data from Vattuone de Ponti (1988) and Gallegos and Vattuone (2010).

Chemical analyses of the meta-tuff from the Arroyo del Torreón Formation were also carried out with a view to characterize this magmatism and to compare it with the signature of the magmatic source of the sediments (Guaraco Norte and Huaraco formations).

In Table 1, the high LOI values represent H_2O+, SO_3 and CO_2. Thermogravimetric studies of all samples allowed to identify the presence of H_2O+ included as hydration water owing to incomplete loss of water adsorbed in both smectite and glass (in tuff), together with the actual hydroxyl water in both phases. SO_3 is present as gypsum and CO_2 as Mg and Ca carbonates of secondary origin. In such cases, major elements were recalculated to 100 % in order to establish their correct proportions, and these figures were used in the major elements discrimination diagrams that follow.

Discriminant function parameters based on major elements (Roser and Korsch 1986) from analyzed samples of the studied units indicate that the Guaraco Norte Formation as well as the Piedra Santa Complex are composed mainly of polycyclic quartzose sediments from a mature continental provenance, whereas the Huaraco Formation was primarily sourced by igneous rocks with felsic to mafic igneous components (Fig. 2a). This is consistent with the occurrence of tuff -mostly in the Arroyo del Torreón Formation and very scarcely in the Huaraco Formation—with a magmatic arc signature. The SiO_2 content and the K_2O/Na_2O of the Guaraco Norte and Huaraco formations point to a mixed source with magmatic arc rocks formed in an active continental margin as well as preexisting sedimentary units related to a passive margin (Fig. 2b).

Using the $Zr/15*Al_2O_3/300*TiO_2$ diagram of Garcia et al. (1994), samples from the Guaraco Norte Formation and the equivalent Piedra Santa Complex fall in the immature sandstone + common shale fields. The TiO_2/Ni ratios (Floyd et al. 1989) indicate for both units a felsic magmatic origin.

Trace elements from the Guaraco Norte and Huaraco formations, such as the V/Cr ratio (Dill et al. 1988) and U/Th ratios (Nath et al. 1997) provide useful information on the paleoxygenation conditions of deposition. V/Cr ratios above 2 point to anoxic conditions, whereas values below 2 suggest more oxidizing conditions (Jones and Manning 1994); ratios from analyzed samples vary between 0.99 and 1.75 (Fig. 2c), implying an oxic depositional environment; low Cu/Zn ratios is in agreement with this oxic environment (Hallberg 1976). U/Th ratios below 1.25 suggest oxic conditions of deposition, whereas values above 1.25 indicate suboxic and anoxic conditions; values for the studied (meta-) sedimentary units range between 0–18 and 0.27, also consistent with an oxic depositional environment.

The chemical composition of the Arroyo del Torreón Formation in the Th–Hf–Ta discrimination diagram (Wood 1980) (Fig. 2d), indicates a volcanic-arc setting, confirmed in the Rb-(Y + Nb) diagram (Pearce et al. 1984) (Fig. 2e) where tuff plots in the volcanic-arc field. The Piedra Santa Complex metaigneous samples (data from Gallegos and Vattuone 2010), as well as those of the metasedimentary units (with important input from magmatic rocks), also plot in the volcanic-arc field (Fig. 2d, e).

Trace element ratios of the analyzed samples from both the (meta)-sedimentary and (meta)-volcanic units mostly overlap with the average present-day global arc rocks (Tatsumi and Eggins 1995) as shown in Fig. 2f.

The REE contents of the Guaraco Norte Formation, Piedra Santa Complex, and Huaraco Formation have been plotted normalized to Chondrite (Fig. 2g). Considering that the main factor that controls REE contents in clastic sediments is their provenance (e.g., McLennan 1989), then the patterns could be interpreted as being consistent to that of the source. The patterns of both the metasedimentary rocks from Guaraco Norte Formation (+Piedra Santa Complex) and sandstone from Huaraco Formation as well as those of the meta-tuff from Arroyo del Torreón Formation show an overall uniform enrichment in light rare earth elements and marked negative Eu anomalies resulting from igneous processes; they point to an arc setting, compatible with the presence of an active margin field, discussed in the following sections. Negative Eu anomalies, $Eu/Eu^* = Eu/(Sm^*Gd)^{0.5}$, range from 0.18 to 0.22 for the meta-tuff, 0.20 for the metasedimentary rocks and 0.15–0.22 for the sandstone.

Whole-rock multiple trace element data normalized to continental crust (Fig. 2h) show depletions in Ba and Sr as

Table 1 Major and trace element data of samples from basement units of the Cordillera del Viento, northwestern Neuquén province, Argentina

Sample		ZD-58	ZD-59	ZD-60	ZD-61	ZD-193	ZD-62	ZD-81	ZD-185	ZD-219
Location		Chacay stream	Chacay stream	Chacay stream	Chacay stream	Chacay stream	Chacay stream	Andacollo	Huaraco N stream	Huaraco N stream
Rock type		Meta-tuff	Meta-tuff	Meta-tuff	Meta-tuff	Meta-tuff	Quartzitic schist	Sandstone	Meta-sandstone	Sandstone
Unit		AT	AT	AT	AT	AT	GN	H*	H	H
Location		36 48 17.6	36 48 17.7	36 48 17.8	36 48 17.9	36 48 51.1	36 48 38.6	37 10 10.7	36 49 19.9	36 52 35.9
		70 38 34.2	70 38 34.2	70 38 34.3	70 38 34.3	70 38 14.9	70 40 10.4	70 38 30.9	70 33 05.1	70 38 02.8
SiO_2	%	63.06	65.1	65.15	52.86	64.82	72.76	58.25	57.58	60.09
Al_2O_3	%	19.29	18.93	16.8	25.77	18.53	12.18	16.81	22.57	19.19
Fe_2O_3	%	4.96	4.51	5.67	5.72	4.81	5.48	7.37	6.8	7.46
MnO	%	0.008	0.035	0.046	0.057	0.049	0.058	0.226	0.097	0.17
MgO	%	0.81	0.76	1.12	0.97	1.43	2.43	3.71	1.93	2.29
CaO	%	0.06	0.08	0.24	0.24	0.05	1.08	6.37	0.15	0.27
Na_2O	%	0.28	0.33	0.74	0.99	0.72	1.19	1.2	0.46	1.15
K_2O	%	4.66	4.34	3.74	5.19	3.9	2.23	0.96	4.69	3.82
TiO_2	%	0.91	0.8	0.71	0.96	0.75	0.7	0.89	0.89	0.85
P_2O_5	%	0.07	0.05	0.07	0.06	0.04	0.11	0.16	0.17	0.19
Cr2O3	%	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.01
V_2O_5	%	0.04	0.028	0.031	0.027	0.043	0.019	0.045	0.034	0.031
CO_2	%	2.08	1.94	1.90	2.13	1.73	0.00	0.64	2.29	1.92
SO_3	%	0.60	0.59	0.82	1.76	0.37	0.00	<0.01	<0.01	<0.01
H_2O-	%	0.00	0.00	0.00	0.00	0.00	0.00	0.33	0.15	0.13
H_2O+	%	2.52	1.86	1.55	2.78	2.03	0.86	2.18	2.17	1.82
LOI	%	*5.20*	*4.38*	*4.27*	*6.67*	*4.14*	*0.86*	*3.14*	*4.61*	*3.86*
Totals		99.35	99.36	98.60	99.53	99.29	99.11	99.15	100.00	99.38
Ag	ppm	1	0.9	0.6	1.1	0.6	1.2	<0.5	0.5	0.7
As	ppm	315	473	403	416	165	17	<5	19	107
Ba	ppm	1,270	1,070	875	1,190	897	362	121	652	867
Bi	ppm	0.5	1.2	<0.4	<0.4	0.4	<0.4	1.8	<0.4	0.5
Co	ppm	12	13	19	18	16	71	35	10	21
Cr	ppm	100	80	90	80	90	120	160	110	100
Cs	ppm	5.1	4.6	6.9	6.3	4.2	3.5	2.2	12.5	7
Cu	ppm	50	50	70	50	50	< 10	100	20	30
Ga	ppm	25	26	24	32	26	16	22	31	27
Ge	ppm	2	2	3	2	2	2	2	2	2
Hf	ppm	5	4.4	3.6	7	3.9	9	3.7	4.6	4.3
In	ppm	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mo	ppm	9	9	<2	<2	10	<2	<2	<2	<2
Nb	ppm	16	15	12	15	14	11	7	19	17
Ni	ppm	<20	<20	<20	30	<20	40	20	30	50
Pb	ppm	83	255	128	130	20	34	17	< 5	21
Rb	ppm	204	190	178	224	179	104	60	237	172
Sb	ppm	1.6	2.8	2.1	0.6	<0.5	<0.5	<0.5	<0.5	<0.5
Sn	ppm	5	5	4	6	5	2	5	7	5
Sr	ppm	43	61	50	37	39	51	79	67	64
Ta	ppm	1.4	1.2	1	1.3	1.2	1.5	0.6	1.7	1.4
Th	ppm	13.7	12.4	9.7	14.4	12	11.5	5.9	17.7	13.6
Tl	ppm	1.5	1.4	1.3	1.6	1.4	0.6	0.4	1.5	0.9

Table 1 continued

Sample		ZD-58	ZD-59	ZD-60	ZD-61	ZD-193	ZD-62	ZD-81	ZD-185	ZD-219
Location		Chacay stream	Chacay stream	Chacay stream	Chacay stream	Chacay stream	Chacay stream	Andacollo	Huaraco N stream	Huaraco N stream
Rock type		Meta-tuff	Meta-tuff	Meta-tuff	Meta-tuff	Meta-tuff	Quartzitic schist	Sandstone	Meta-sandstone	Sandstone
Unit		AT	AT	AT	AT	AT	GN	H*	H	H
Location		36 48 17.6	36 48 17.7	36 48 17.8	36 48 17.9	36 48 51.1	36 48 38.6	37 10 10.7	36 49 19.9	36 52 35.9
		70 38 34.2	70 38 34.2	70 38 34.3	70 38 34.3	70 38 14.9	70 40 10.4	70 38 30.9	70 33 05.1	70 38 02.8
U	ppm	5.6	4.2	2.7	3.9	5	2.7	1.6	3.1	2.7
V	ppm	190	164	166	153	236	119	257	192	169
W	ppm	74	65	58	52	91	415	113	19	33
Y	ppm	31	34	41	51	24	26	28	30	35
Zn	ppm	390	870	560	730	430	110	210	60	300
Zr	ppm	191	179	137	263	151	347	140	166	163
La	ppm	40.9	39.2	37.4	46.6	32	35.7	19.4	41.3	41.7
Ce	ppm	86	81.1	65.6	97	65.1	74.9	41.6	81.8	86.4
Pr	ppm	10.3	10.4	9.02	12.3	8.1	8.55	5.21	10.1	10.2
Nd	ppm	38.8	40.9	35.7	48.9	30.8	32.4	21.5	37.1	38.4
Sm	ppm	8.1	8.7	7.2	10.1	6.4	6.3	5	7.1	7.7
Eu	ppm	1.27	1.64	1.49	1.69	1.14	1.13	1.09	0.93	1.3
Gd	ppm	6.5	6.9	6.5	8.8	5.2	5.1	4.9	5.5	6.4
Tb	ppm	1.1	1.1	1.1	1.5	0.8	0.8	0.9	0.9	1.1
Dy	ppm	6.2	6.5	6.7	9.3	4.7	4.8	5.3	5.7	6.4
Ho	ppm	1.2	1.3	1.4	2	0.9	1	1	1.2	1.3
Er	ppm	3.4	3.8	4	5.7	2.7	2.8	3	3.5	3.6
Tm	ppm	0.55	0.6	0.62	0.91	0.42	0.43	0.46	0.54	0.55
Yb	ppm	3.7	4.1	4.1	6.1	2.9	2.9	3	3.7	3.6
Lu	ppm	0.57	0.66	0.67	0.98	0.49	0.48	0.48	0.59	0.56

Values in italics are the sum of CO_2, SO_3, H_2O- and H_2O+ already taken into account for the calculated totals

AT: Arroyo del Torreón Formation; GN: Guaraco Norte Formation; H: Huaraco Formation; H*: Huaraco Formation at Andacollo locality. LOI represents the sum of CO_2, SO_3, H_2O- and H_2O+

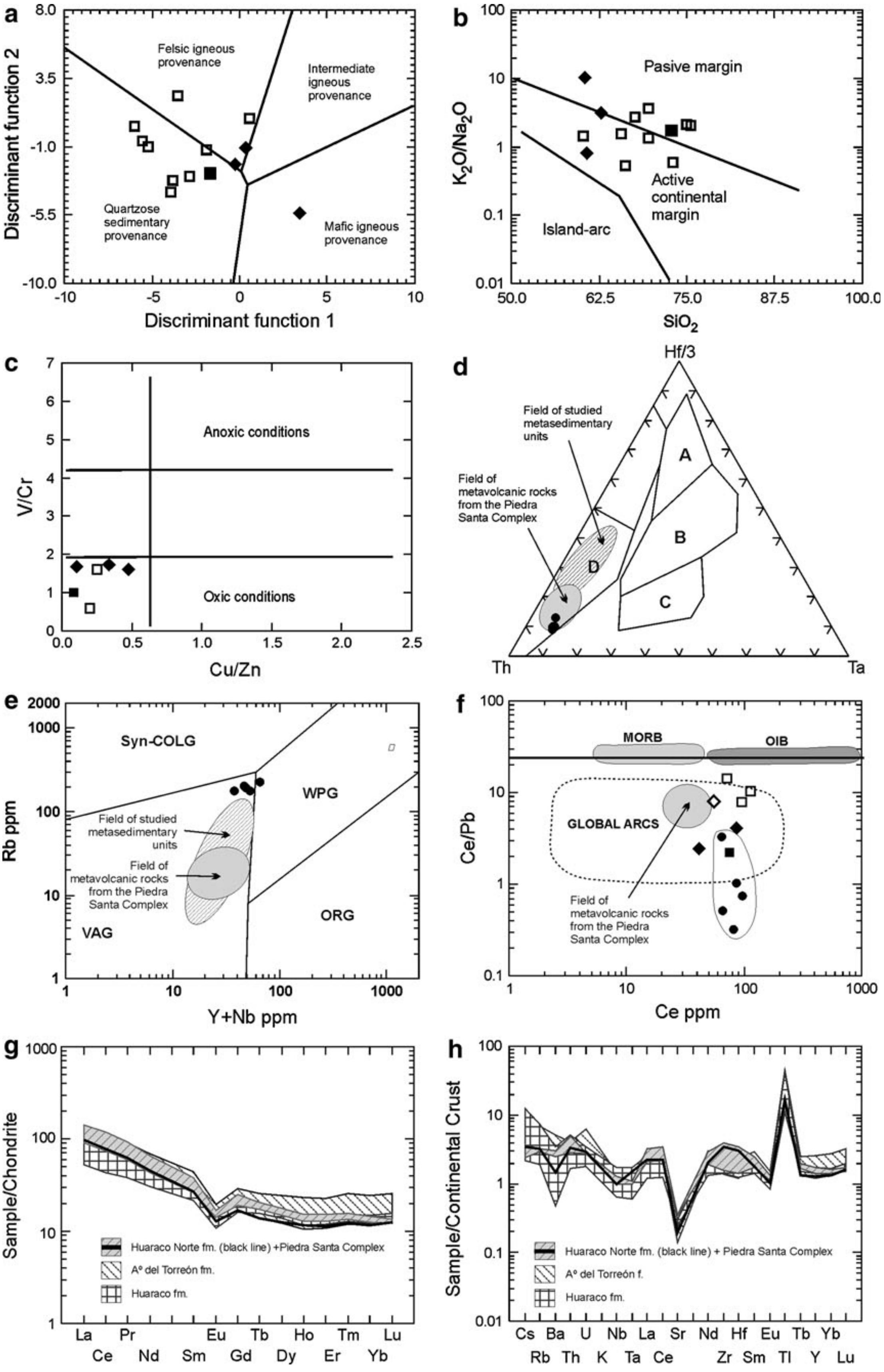
well as enrichment in Cs, Th–U, Ce, Zr–Hf, and Tl. Patterns for (meta-) sedimentary and (meta-) volcanic rocks are very similar.

Summarizing, these data indicate that the occurrence of active arc magmatism during the deposition of the Arroyo del Torreón, Huaraco and, at least partially, the Guaraco Norte formations and the equivalent Piedra Santa Complex (i.e., Carboniferous).

Geochronological data

The combination of U–Pb SHRIMP and Hf isotopic determinations for individual zircon grains provides not only the age but also the nature and source of the host magma, whether crustal or juvenile (mantle derived), and model age (T_{DM}) of the provenance.

Fig. 2 Geochemical data for Guaraco Norte Formation, Piedra Santa Complex and Huaraco Formation plotted in (**a**) the discriminant function diagram of Roser and Korsch (1988) showing: the discriminant functions employed are: $f1 = -1.773{*}TiO_2 + 0.607{*}Al_2O_3 + 0.76{*}Fe_2O_3 - 1.5{*}MgO + 0.616{*}CaO + 0.509{*}Na_2O - 1.22{*}K_2O - 9.09$ and $f2 = 0.445{*}TiO_2 + 0.07{*}Al_2O_3 - 0.25{*}Fe_2O_3 - 1.142{*}MgO + 0.438{*}CaO + 1.475{*}Na_2O + 1.426{*}K_2O - 6.861$; **b** log ($K_2O/Na_2O$) versus SiO_2 diagram of Roser and Korsch (1986); **c** (V/Cr–Cu/Zn plot (from Jones and Manning (1994) and Hallberg 1976) showing the oxic conditions field for the Huaraco F. samples. **d** The Th–Hf–Ta discrimination diagram for basic to silicic lavas from Wood (1980); **e** the Rb—(Yb + Nb) discrimination diagram for acid igneous rocks from Pearce et al. 1984): VAG: Volcanic-arc granites (and volcanic equivalents); **f** (Ce/Pb)—Ce plot (Tatsumi and Eggins 1995) for (meta) tuff and (meta) sediments, showing the global arcs field; **g** chondrite normalized rare earth elements plot for (meta) sediments and (meta) tuff; **h** multielement diagram for (meta) sediments and (meta) tuff normalized to continental crust (Taylor and McLennan 1985). References: solid square: Guaraco Norte F.; empty square: Piedra Santa Complex; solid diamond: Huaraco F. in the study area; empty diamond: Huaraco Fm. at Andacollo; solid circle: Arroyo del Torreón F ▶


a
Discriminant function 2
Discriminant function 1
8.0
3.5
-1.0
-5.5
-10.0
-10
-5
0
5
10
Felsic igneous provenance
Intermediate igneous provenance
Quartzose sedimentary provenance
Mafic igneous provenance
b
K_2O/Na_2O
SiO_2
100
10
1
0.1
0.01
50.0
62.5
75.0
87.5
100.0
Pasive margin
Active continental margin
Island-arc
c
V/Cr
Cu/Zn
Anoxic conditions
Oxic conditions
0.0
0.5
1.0
1.5
2.0
2.5
d
Hf/3
Th
Ta
A
B
C
D
Field of studied metasedimentary units
Field of metavolcanic rocks from the Piedra Santa Complex
e
Rb ppm
Y+Nb ppm
2000
1000
100
10
1
Syn-COLG
WPG
VAG
ORG
Field of studied metasedimentary units
Field of metavolcanic rocks from the Piedra Santa Complex
f
Ce/Pb
Ce ppm
MORB
OIB
GLOBAL ARCS
Field of metavolcanic rocks from the Piedra Santa Complex
g
Sample/Chondrite
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Huaraco Norte fm. (black line) +Piedra Santa Complex
Aº del Torreón fm.
Huaraco fm.
h
Sample/Continental Crust
Cs Rb Ba Th U K Nb Ta La Ce Sr Nd Zr Hf Sm Eu Ti Tb Y Yb Lu
Huaraco Norte fm. (black line) + Piedra Santa Complex
Aº del Torreón f.
Huaraco fm.

This integrated analysis, applied to suites of detrital zircon, gives a more distinctive, and more easily interpreted, picture of crustal evolution in the provenance area than age data alone (e.g., Veevers et al. 2006, and references therein). U–Pb isotopes allow determining crystallization ages of analyzed zircon and Lu–Hf isotopes provide crust formation ages for the igneous source of the dated grains (e.g., Amelin et al. 1999). Hf isotopes allow distinguishing juvenile, essentially mantle-derived crust of a given age, from contemporary crust derived from remelting of older crust. Methodology is given as an "Appendix".

Guaraco Norte Formation

Sample ZD62-946 of the Guaraco Norte Formation presents a large number of Devonian (47 %) and Ordovician (40 %) zircon grains, in addition to Cambrian (6 %) and Late Mesoproterozoic (Stenian; 6 %) grains (Table 2; Fig. 3a).

Zircon does not show overgrowth rims and the external morphology points to an igneous origin (Hoskin and Schaltegger (2003). It is also noticeable that the zircon grains have their crystalline faces preserved (cf. BSE images Fig. 3b), which would be indicative of restricted transport. The Th/U ratios of zircon grains vary from 0.12 to 2.11 and U content is up to 1,593 ppm; this would also indicate that most of the grains have a magmatic origin (Rubatto 2002). Two grains (e.8-1 and e.12-1) dated at 406 and 456 Ma, respectively, show very low Th/U ratios (0.01 and 0.005) and are interpreted as metamorphic.

The Devonian zircon range from 369 ± 5 Ma to 406 ± 4 Ma. Hafnium isotope determinations (Table 3) on the Devonian zircon yielded moderately to slightly negative (−2.84 to −0.70) epsilon Hf values, and model ages ranging from 1,384 to 1,513 Ma (mostly Middle Mesoproterozoic = Ecstasian).

The Ordovician zircon grains range 449 ± 5–458 ± 5 Ma. Hafnium isotope determinations on this population also yielded moderately to slightly negative epsilon Hf values (−4.04 to −0.34), though averaging more negative values than the Devonian zircon. Hafnium model ages range from 1,427 to 1,655 Ma (Late Paleoproterozoic = Statherian to Early Mesoproterozoic = Calymmian), that is, about 100 Ma older than the TDM-Hf of the Devonian zircon.

The single Mesoproterozoic grain is 1,015 ± 15 Ma. The Hafnium isotope determination on this zircon yielded a pronounced positive epsilon Hf value of +8.28, and a TDM-Hf of 1,330 Ma (Middle Mesoproterozoic = Ecstasian).

The age of the youngest detrital zircon is 369 ± 5 Ma (Upper Devonian)—epsilon Hf −2.84; TDM-Hf 1,513 Ma—, which corresponds to the maximum age for the onset of sedimentation, indicating that deposition was probably mainly Mississippian (considering the age of the overlying Arroyo del Torreón Formation, see below).

Provenance of the Devonian zircon could be an inconspicuous Devonian magmatic arc (see "Discussion", below), whereas the Ordovician zircon could derive from Famatinian sources. In addition, the predominance of slightly negative $\varepsilon_{\mathrm{Hf}}$ (T) values in the Devonian detrital zircon suggests that their primary sources contained small amounts of older recycled crustal components (of Middle Mesoproterozoic age). In contrast, the more negative $\varepsilon_{\mathrm{Hf}}$ (T) values in the Ordovician detrital zircon would indicate that their primary sources contained larger amounts of older recycled crustal components (of Late Paleoproterozoic to Early Mesoproterozoic age).

Arroyo del Torreón Formation

The youngest detrital zircon age of the Arroyo del Torreón Formation is 383 ± 6 Ma (Devonian: 6 % of grains), similarly to that of the Guaraco Norte Formation. Also, both units contain Lower Paleozoic grains (Arroyo del Torreón Formation: 6 % Cambrian, 19 % Ordovician). In addition, the Arroyo del Torreón Formation contains Middle Neoproterozoic (Cryogenian or "Brasiliano age"; 25 %), Early Neoproterozoic (Tonian; 13 %), Late Mesoproterozoic (Stenian; 13 %), Middle Mesoproterozoic (Ecstasian; 6 %), and Late Paleoproterozoic (Statherian; 6 %) grains (Table 2; Fig. 3c).

Depositional age is bound to be Carboniferous, as indicated by the intercalation of rhyodacitic flows dated at ca. 327.9 ± 2 Ma (U–Pb SHRIMP age; Suárez et al. 2008) and identified at the main outcrops of this unit, to the south of the study area, consistent with the age of the youngest zircon. Recently, U–Pb SHRIMP crystallization age was reported by Hervé et al. (2010) for a rhyolite belonging to the Andacollo Group from southern Cordillera del Viento, at ca. 326 Ma, confirming the age given by Suárez et al. (2008). It should be noted that the unit is covered by the Huaraco Formation of Pennsylvanian age (Amos 1972).

Similarly to zircon from the Guaraco Norte Formation, zircon from the Arroyo del Torreón Formation does not show overgrowth rims but, contrary to the former unit, zircon grains from the Arroyo del Torreón Formation have their crystalline faces less well preserved, the older grains being well rounded, possibly indicating a long distance transportation (Fig. 3d). The Th/U ratios of the zircon vary from 0.02 to 0.86 (all but one grain >0.1) and U content is up to 1,494 ppm; this would point to a magmatic origin for all grains (Rubatto 2002).

Table 2 U–Pb–Th isotopic data from units of the basement of Cordillera del Viento

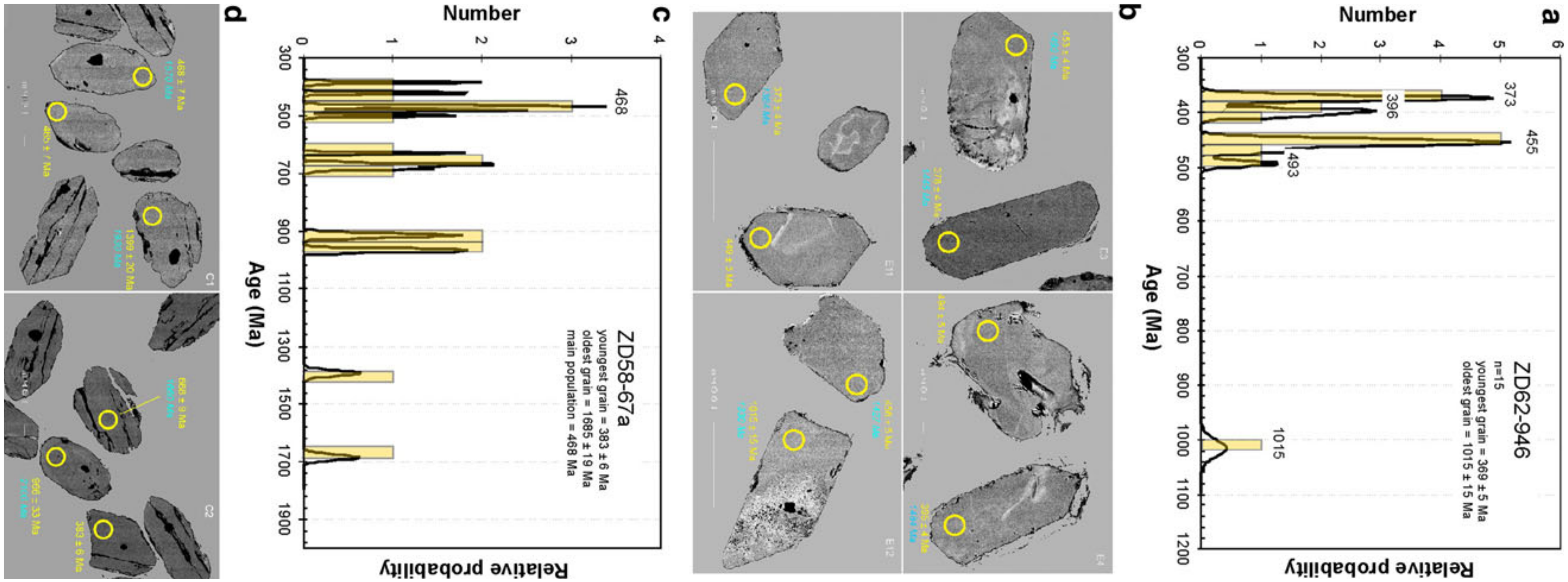
Spot	U (ppm)	Th (ppm)	Th (U)	^{206}Pb (ppm)	4f^{206} (%)	Isotopic ratios					Ages		
						^{207}Pb/^{206}Pb	^{238}U/^{206}Pb	^{206}Pb/^{238}U	^{207}Pb/^{235}U	^{208}Pb/^{232}Th	^{207}Pb/^{206}Pb	^{206}Pb/^{238}U	Disc. (%)
ZD62-946, paraschist. Guaraco Norte Formation													
e.1-1	160	69	0.45	8	0.21	0.05474 ± 3.89	16.9672 ± 1.37	0.4449 ± 4.13	0.0589 ± 1.37	0.0179 ± 3.99	402 ± 87	369 ± 5	8
e.2-1	1,035	221	0.22	53	0.05	0.05515 ± 1.26	16.7702 ± 1.07	0.4534 ± 1.65	0.0596 ± 1.07	0.0181 ± 2.35	418 ± 28	373 ± 4	11
e.2-2	123	45	0.38	8	0.22	0.05388 ± 3.07	13.6677 ± 1.40	0.5435 ± 3.37	0.0732 ± 1.40	0.0225 ± 3.33	366 ± 69	455 ± 6	−24
e.3-1	1,593	388	0.25	100	0.08	0.05627 ± 0.90	13.7446 ± 0.99	0.5644 ± 1.34	0.0728 ± 0.99	0.0207 ± 2.09	463 ± 20	453 ± 4	2
e.3-2	594	279	0.48	31	0.29	0.05282 ± 2.28	16.5578 ± 1.08	0.4398 ± 2.52	0.0604 ± 1.08	0.0179 ± 3.08	321 ± 52	378 ± 4	−18
e.4-1	579	345	0.62	31	−0.12	0.05704 ± 1.51	15.8176 ± 1.07	0.4972 ± 1.85	0.0632 ± 1.07	0.0217 ± 2.32	493 ± 33	395 ± 4	20
e.4-2	691	1,408	2.11	47	0.03	0.05650 ± 1.20	12.5652 ± 1.04	0.6200 ± 1.59	0.0796 ± 1.04	0.0239 ± 1.17	472 ± 26	494 ± 5	−5
e.6-1	477	227	0.49	30	0.00	0.05670 ± 1.33	13.5805 ± 1.09	0.5757 ± 1.72	0.0736 ± 1.09	0.0225 ± 1.59	480 ± 29	458 ± 5	5
e.7-1	379	75	0.21	21	0.03	0.05503 ± 2.13	15.6997 ± 1.13	0.4833 ± 2.41	0.0637 ± 1.13	0.0205 ± 3.66	413 ± 48	398 ± 4	4
e.8-1	1,580	17	0.01	88	−0.02	0.05425 ± 0.80	15.3758 ± 0.99	0.4864 ± 1.27	0.0650 ± 0.99	0.0237 ± 7.76	381 ± 18	406 ± 4	−7
e.8-2	559	270	0.50	36	0.13	0.05723 ± 1.33	13.1911 ± 1.07	0.5982 ± 1.71	0.0758 ± 1.07	0.0217 ± 2.44	500 ± 29	471 ± 5	6
e.11-1	484	316	0.67	25	−0.14	0.05558 ± 1.81	16.8095 ± 1.10	0.4559 ± 2.12	0.0595 ± 1.10	0.0180 ± 1.75	435 ± 40	373 ± 4	14
e.11-2	429	51	0.12	27	0.25	0.05479 ± 1.80	13.8784 ± 1.11	0.5443 ± 2.11	0.0721 ± 1.11	0.0198 ± 5.16	404 ± 40	449 ± 5	−11
e.12-1	378	2	0.005	24	0.16	0.05594 ± 2.32	13.6459 ± 1.13	0.5652 ± 2.58	0.0733 ± 1.13	– ± –	450 ± 52	456 ± 5	−1
e.12-2	510	166	0.34	82	0.06	0.07305 ± 0.76	5.3325 ± 1.05	1.8888 ± 1.30	0.1875 ± 1.05	0.0551 ± 1.69	1,015 ± 15	1,108 ± 11	−9
ZD58-67a, meta-tuff. Arroyo del Torreón Formation													
c.1-1	372	45	0.12	24	0.29	0.05480 ± 2.55	13.3624 ± 1.51	0.5655 ± 2.96	0.0748 ± 1.51	0.0280 ± 5.85	404 ± 57	465 ± 7	−15
c.1-2	267	121	0.47	55	0.06	0.08875 ± 1.07	4.1468 ± 1.54	2.9510 ± 1.88	0.2412 ± 1.54	0.0708 ± 1.96	1399 ± 20	1,393 ± 19	0
c.1-3	580	195	0.35	38	0.30	0.05605 ± 2.39	13.2943 ± 1.44	0.5813 ± 2.79	0.0752 ± 1.44	0.0223 ± 3.35	454 ± 53	468 ± 7	−3
c.2-1	179	144	0.83	9	0.32	0.05472 ± 3.35	16.3236 ± 1.65	0.4622 ± 3.73	0.0613 ± 1.65	0.0189 ± 2.73	401 ± 75	383 ± 6	4
c.2-2	443	156	0.36	58	0.07	0.07130 ± 1.64	6.5525 ± 1.45	1.5004 ± 2.19	0.1526 ± 1.45	0.0573 ± 1.89	966 ± 33	916 ± 12	5
c.2-3	731	422	0.60	69	0.06	0.06024 ± 1.10	9.1600 ± 1.39	0.9068 ± 1.78	0.1092 ± 1.39	0.0333 ± 1.91	612 ± 24	668 ± 9	−9
c.3-1	71	36	0.53	7	3.23	0.06152 ± 12.3	9.1322 ± 2.13	0.9289 ± 12.5	0.1095 ± 2.13	0.0349 ± 11.9	658 ± 263	670 ± 14	−2
c.3-2	543	9	0.02	38	0.32	0.05634 ± 2.10	12.4458 ± 1.51	0.6241 ± 2.58	0.0803 ± 1.51	0.0351 ± 29.1	466 ± 46	498 ± 7	−7
c.4-1	131	55	0.43	17	0.64	0.06730 ± 3.71	6.5776 ± 1.73	1.4108 ± 4.09	0.1520 ± 1.73	0.0442 ± 5.04	847 ± 77	912 ± 15	−8
c.5-1	785	375	0.49	46	0.53	0.05480 ± 2.33	14.8214 ± 1.41	0.5098 ± 2.72	0.0675 ± 1.41	0.0202 ± 3.28	404 ± 52	421 ± 6	−4
d.1-1	162	106	0.67	42	0.07	0.10332 ± 1.24	3.3477 ± 1.32	4.2555 ± 1.81	0.2987 ± 1.32	0.0848 ± 1.92	1,685 ± 23	1,685 ± 20	0
d.3-1	683	201	0.30	95	0.08	0.07476 ± 0.82	6.1543 ± 1.06	1.6749 ± 1.34	0.1625 ± 1.06	0.0513 ± 1.50	1,062 ± 17	971 ± 10	9
d.4-1	1,397	375	0.28	193	0.07	0.07304 ± 0.62	6.2100 ± 1.01	1.6217 ± 1.18	0.1610 ± 1.01	0.0466 ± 1.37	1,015 ± 13	963 ± 9	5
d.5-1	176	62	0.36	17	−0.10	0.06921 ± 1.85	8.9398 ± 1.44	1.0675 ± 2.35	0.1119 ± 1.44	0.0527 ± 2.23	905 ± 38	684 ± 9	24

Table 2 continued

Spot	U (ppm)	Th (ppm)	Th (U)	^{206}Pb (ppm)	4f^{206} (%)	Isotopic ratios					Ages		Disc. (%)
						^{207}Pb/^{206}Pb	^{238}U/^{206}Pb	^{206}Pb/^{238}U	^{207}Pb/^{235}U	^{208}Pb/^{232}Th	^{207}Pb/^{206}Pb	^{206}Pb/^{238}U	
d.6-1	1,494	389	0.27	100	0.00	0.05669 ± 0.85	12.8885 ± 1.01	0.6065 ± 1.32	0.0776 ± 1.01	0.0232 ± 1.67	480 ± 19	482 ± 5	0
d.9-1	1,052	589	0.58	93	0.08	0.06023 ± 1.09	9.7726 ± 1.02	0.8497 ± 1.50	0.1023 ± 1.02	0.0321 ± 1.37	612 ± 24	628 ± 6	−3

Isotopic ratios errors in %. All Pb in ratios are radiogenic component, all corrected for ^{204}Pb. disc. = discordance, as 100–100{t[^{206}Pb/^{238}U]/t[^{207}Pb/^{206}Pb]} 4f206 = (common ^{206}Pb)/(total measured ^{206}Pb) based on measured ^{204}Pb

Uncertainties are 1σ; n.a. = not analyzed (very high Th content)



◀**Fig. 3** **a** Cumulative probability plot of 206Pb–238U isotopic ages of detrital zircon (*n* = 15) from the Guaraco Norte Formation, sampled at Chacay valley. Youngest grain: 369 ± 5 Ma. The minimum age is considered the maximum possible sedimentation age. **b** Back-scattered image of zircon from sample ZD62-946. The SHRIMP spots indicate U–Pb age (*upper number*) and Hf model age (*lower number, in italic*). **c** Cumulative probability plot of 206Pb–238U isotopic ages of detrital zircon (*n* = 16) from the Arroyo del Torreón Formation, sampled at Chacay valley. Youngest grain: 383 ± 6 Ma. The minimum age is considered the maximum possible sedimentation age. **d** Back-scattered image of zircon from sample ZD58-67a. The SHRIMP spots indicate U–Pb age (*upper number*) and Hf model age (*lower number*, *in italic*)

The Ordovician zircon grains range 465 ± 7 Ma–482 ± 5 Ma. Hafnium isotope determinations (Table 3) on a zircon dated at ca. 468 Ma yielded a moderately negative epsilon Hf value (−1.49) and a model age of 1,507 Ma (Lower Mesoproterozoic = Calymmian, that is, within the range of model ages obtained for the Ordovician zircon of the Huaraco Formation). Hafnium isotope determinations on a Cambrian zircon dated at ca. 498 ± 7 Ma yielded a negative epsilon Hf value of −4.42 and a model age of 1,710 Ma (Late Paleoproterozoic = Statherian). These Lower Paleozoic grains could derive from recycled late Pampean to Famatinian sources.

Middle Neoproterozoic (Cryogenian or "Brasiliano age") zircon grains range 628 ± 6 Ma to 684 ± 9 Ma. Hafnium isotope determinations indicate the presence of two types of zircon of similar age but of contrasting origin, that is, a grain dated at ca. 668 Ma yielded a very slightly negative epsilon Hf value (−0.25) and TDM-Hf of 1,587 Ma (Lower Mesoproterozoic = Calymmian), whereas a grain dated at ca. 670 Ma yielded a strongly negative epsilon Hf value (−9.76) and TDM-Hf of 2,167 Ma (Middle Paleoproterozoic = Rhyacian or "Transamazonian age"). In the first case, the slightly negative $\varepsilon_{\mathrm{Hf}}$ (T) value would suggest that the primary sources of this zircon contained small amounts of older recycled crustal components of ca. 1,587 Ma and a predominant juvenile Brasiliano-age component (juvenile arc?, extensional magmatism related to Rodinia rifting?). In the second case, the strongly negative $\varepsilon_{\mathrm{Hf}}$ (T) value would point to primary sources that contained larger amounts of older recycled crustal components of ca 2,167 Ma (Transamazonian crust?).

Early Neoproterozoic (Tonian) zircon grains range 912 ± 15 Ma–916 ± 12 Ma. Hafnium isotope determinations on the grain dated at ca. 916 Ma yielded a negative epsilon Hf value of −4.09 and a model age of 2,015 Ma (Middle Paleoproterozoic = Orosirian).

Hafnium isotope determinations on a Middle Mesoproterozoic (Ecstasian) zircon dated at ca. 1,399 ± 20 Ma yielded a positive epsilon Hf value of +4.88 and a model age of 1,838 Ma (Middle Paleoproterozoic = Orosirian).

Discussion

Age, provenance, and tectonic setting of the Guaraco Norte, Arroyo del Torreón and Huaraco Formations

The age of the youngest detrital zircon of the Guaraco Norte Formation is 369 ± 5 Ma (Upper Devonian)—epsilon Hf −2.84; TDM-Hf 1,513 Ma—, which corresponds to the maximum age for the onset of sedimentation, consistent with a Carboniferous depositional age for this unit. The age of 328 Ma for a volcanic flow interbedded in the overlying Arroyo de Torreón Formation constrains the depositional age of the Guaraco Norte Formation to the Lower to Middle Mississippian. Most of the detrital zircon grains of the Guaraco Norte Formation derive from magmatic units, dominantly Devonian and Ordovician (plus minor Cambrian and late Mesoproterozoic). Hf-isotope determinations suggest that the primary sources of the Devonian zircon contained small amounts of older recycled crustal components (of Middle Mesoproterozoic age), in contrast to the primary sources of the Ordovician zircon, which contained larger amounts of older recycled crustal components (of Late Paleoproterozoic to Early Mesoproterozoic age). The Hf model ages of the analyzed Devonian and Ordovician zircon are within the range of both the Nd-(e.g., Rapela et al. 1998) and Hf-(e.g., Chernicoff et al. 2012) model ages available for the Pampia terrane, as well as within the range of the Nd model ages reported for the Cuyania (e.g., Sato et al. 2004; Naipauer et al. 2005; Abre et al. 2006) and Chilenia (Lucassen et al. 2004) terranes, which would not preclude any of these terranes as direct or indirect sources for the Devonian and Ordovician zircon. Hence, the model ages per se would seem to be insufficient to unequivocally assign the derivation of these zircon grains.

The Mesoproterozoic zircon from the Guaraco Norte Formation dated at 1,015 ± 15 Ma has $\varepsilon_{\mathrm{Hf}}$ (T) +8.28 and TDM-Hf: 1,330 Ma could have been sourced from the Ediacaran-Lower Cambrian Guarguaraz Complex that contains a predominant Mesoproterozoic population of juvenile character. Provenance could also be directly the Cuyania and/or Chilenia basement at the collisional zone (cf. Alvarez et al. 2011), or even the Pampia terrane, whose basement is bound to be, at least partly, of Mesoproterozoic age (cf. Casquet et al. 2006; Miller et al. 2011) and juvenile nature (Chernicoff et al. 2012).

All of the zircon grains of the Arroyo del Torreón Formation were also derived from magmatic units, the youngest, but not predominant, being Devonian (383 ± 6 Ma). This maximum depositional age is coherent with that of 327.9 ± 2 Ma obtained in a rhyodacitic flow interbedded in the unit (Suárez et al. 2008), therefore indicating a Carboniferous depositional age. Most important sources are Brasiliano (Middle Neoproterozoic: two types derived from two contrasting primary sources, that is, juvenile Brasiliano and reworked Transamazonian) and Middle Mesoproterozoic (juvenile); otherwise, there are Ordovician (reworked from Early Mesoproterozoic), and minor Cambrian (reworked from Late Paleoproterozoic), Tonian (reworked from Middle Paleoproterozoic), and Late Paleoproterozoic sources.

The provenance of the zircon dated at ca. 1,015 and ca. 1,062 Ma could be either the underlying Guaraco Norte Formation (and equivalent units) or the coeval source regions thereof.

A Middle Mesoproterozoic (Ecstasian) zircon from the Arroyo del Torreón Formation, dated at ca. 1,399 ± 20 Ma, yielded a positive epsilon Hf value of +4.88 and a model age of 1,838 Ma (Middle Paleoproterozoic = Orosirian). The provenance of this zircon could be either the Guarguaraz Complex or directly Cuyania and/or Chilenia. The latter terranes are also considered to have shed Mesoproterozoic–Early Neoproterozoic detrital zircon to the sedimentary protolith of the Piedra Santa Complex (Ramos et al. 2010; see also Geological Framework, above).

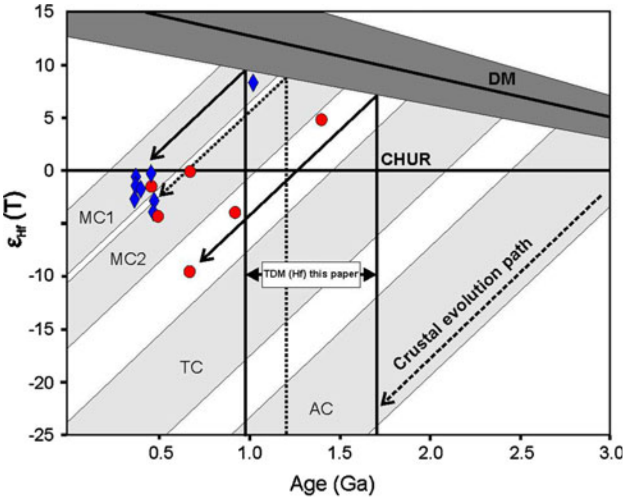


Fig. 4 Comparative ε_{Hf} (T) evolution diagram for single detrital grains from the Guaraco Norte Fm. (*solid diamond*) and Arroyo del Torreón Fm (*solid circ*le). For comparison, the depleted mantle array and crustal evolution trends of zircon (*shaded areas*) from Willner et al. (2008) are indicated: AC Archean crust; TC Transamazonian crust; MC1 and MC2 late and early Mesoproterozoic crust respectively

The comparative ε_{Hf} (T) evolution diagram for single detrital magmatic zircon grains from Guaraco Norte and Arroyo del Torreón formations (Fig. 4) shows that both populations have mainly negative ε_{Hf} (T) values that plot, respectively, in two trends: in a late Mesoproterozoic trend (Stenian) evolving from a relatively young juvenile crust formed mostly at ca. 1 Ga coeval to a Sunsás orogeny, and

Table 3 Lu–Hf data of zircon from units of the basement of Cordillera del Viento

Spot	Age* Ma	^{176}Hf/^{177}Hf	Error 1σ	^{176}Lu/^{177}Hf	^{176}Yb/^{177}Hf	^{176}Hf/^{177}Hf	Epsilon Hf	Error 1σ	T_{DM} (Ma)	T_{DM} Crustal	Hf $_{CHUR}$ (t)	Hf $_{DM}$ (t)
ZD62-946, paraschist. Guaraco Norte Formation												
e.1-1	369	0.282471	±0.000007	0.002343	0.122307	0.282454	−2.84	±0.24	1,107	1,513	0.282535	0.282976
e.3-1	453	0.282452	±0.000009	0.001435	0.072124	0.282439	−1.46	±0.30	1,107	1,493	0.282481	0.282914
e.3-2	378	0.282489	±0.000008	0.000858	0.045712	0.282483	−1.63	±0.29	104	1,446	0.282529	0.282970
e.4-1	395	0.28247	±0.000010	0.001287	0.071569	0.282460	−2.04	±0.33	1,078	1,484	0.282518	0.282957
e.6-1	458	0.282378	±0.000009	0.001675	0.085331	0.282363	−4.04	±0.33	1,216	1,655	0.282477	0.282910
e.7-1	398	0.282477	±0.000008	0.001220	0.066627	0.282468	−1.71	±0.26	1,066	1,466	0.282516	0.282955
e.8-2	471	0.282414	±0.000014	0.002851	0.164058	0.282388	−2.86	±0.49	1,204	1,594	0.282469	0.282900
e.11-1	373	0.282518	±0.000010	0.000730	0.039358	0.282513	−0.70	±0.35	997	1,384	0.282532	0.282974
e.12-1	456	0.282471	±0.000008	0.000218	0.009189	0.282469	−0.34	±0.27	1,046	1,427	0.282479	0.282912
e.12-2	1,015	0.282368	±0.000009	0.000983	0.056297	0.282349	8.28	±0.30	1,207	1,330	0.282115	0.282491
ZD58-67a, meta-tuff. Arroyo del Torreón Formation												
c.1-2	1,399	0.282061	±0.000022	0.002191	0.076516	0.282001	4.88	±0.77	1,674	1,838	0.281863	0.282200
c.1-3	468	0.28244	±0.000016	0.001223	0.056635	0.282429	−1.49	±0.56	1,117	1,507	0.282471	0.282903
c.2-2	916	0.282088	±0.000013	0.001304	0.047561	0.282065	−4.09	±0.46	1,598	2,015	0.282180	0.282566
c.2-3	668	0.28235	±0.000013	0.001215	0.049750	0.282334	−0.25	±0.46	1,239	1,587	0.282341	0.282753
c.3-1	670	0.282081	±0.000013	0.001158	0.039574	0.282066	−9.76	±0.46	1,601	2,167	0.282341	0.282753
c.3-2	498	0.28235	±0.000015	0.002435	0.072822	0.282326	−4.42	±0.53	1,281	1,710	0.282451	0.282880

* Ages are U–Pb SHRIMP ages; Isotopic ratios errors are absolute (1σ); ^{176}Lu decay constant (1.93 × 10^{-11} year^{-1}) according to Blichert-Toft et al. (1997)

in a late Paleoproterozoic (Statherian) to early Mesoproterozoic trend (Calymnian) at ca. 1.67 Ga coeval to a Rio Negro-Juruena orogeny. The distribution of the analyzed population of zircon overlap the fields MC1 + MC2 determined by Willner et al. (2008) in the coastal accretionary system from Chile. Coincidentally with the latter authors' view, generation by partial melting of a Mesoproterozoic crust appears most likely.

Geochemical data indicate that the Guaraco Norte Formation as well as the equivalent Piedra Santa Complex, outcropping further south of the study area, consist mainly of polycyclic quartzose sediment of mature continental provenance, whereas the Huaraco Formation was primarily sourced from igneous rocks with felsic to mafic igneous components. In the Piedra Santa Complex, with numerous outcrops and much thicker exposures than the Guaraco Norte Formation, metaigneous intercalations have been identified (Vattuone de Ponti 1988; Gallegos and Vattuone 2010) of original basaltic to andesitic composition, with arc signature. Both Guaraco Norte (+Piedra Santa Complex) and Huaraco formations point to a mixed source with magmatic arc rocks formed in an active continental margin as well as preexisting sedimentary units related to a passive margin. This is consistent with the presence of the conspicuous population in both units of detrital Devonian magmatic zircon. Trace elements for sediments and tuff of all the analyzed units have similar distribution in multielement and rare earth elements diagrams pointing to magmatic arc sources.

The occurrence of tuff—mostly in the Arroyo del Torreón Formation and very scarcely in the Huaraco Formation—as well as rhyodacitic interbedded lava flows, with an arc signature, point to the presence of an active magmatism during the Mississippian in the retrowedge area, that represents the southern extension (at Cordillera del Viento) of a magmatic arc poorly defined, mainly exposed in Frontal Cordillera (Fig. 5a) with ages between 341 ± 17 and 311 ± 15 Ma (Llambías 1999). The 315 ± 1.5 Ma age of the La Voluntad porphyry Cu (Garrido et al. 2008) would be related to this magmatic belt. Detrital magmatic zircon of this age identified within the Coastal Cordillera of central Chile (Willner et al. 2008) would point to this belt as a main source.

Provenance of Devonian magmatic zircon grains

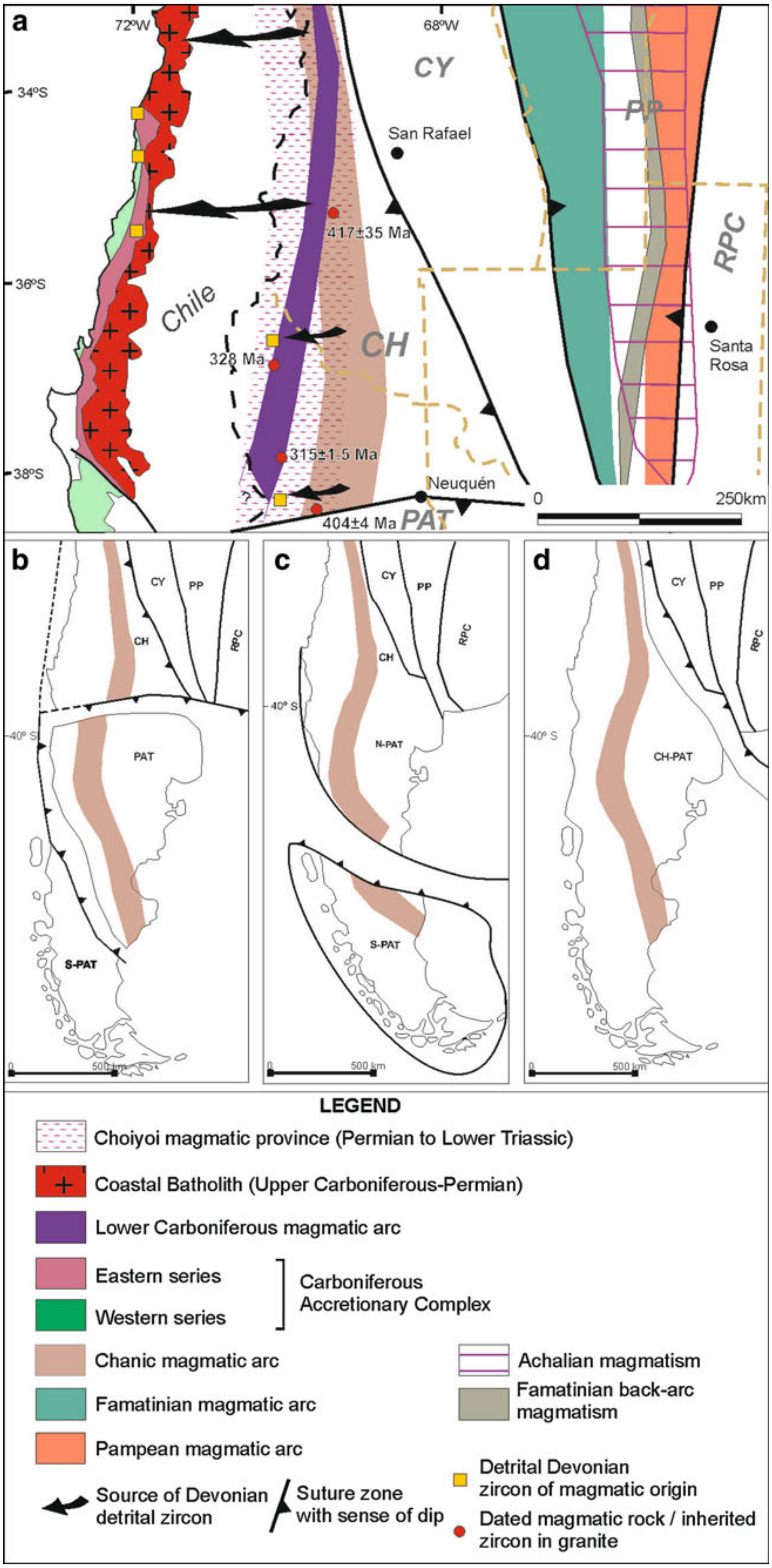
The conspicuous presence of Devonian detrital zircon of magmatic origin in the studied units (364–410 Ma), mainly in the Guaraco Norte Formation, points to a source exposed and subject to erosion during the Carboniferous; considering the low number of dated zircon grains, the significant peak of the Devonian ages obtained could indicate that this source was proximal. A zircon population of this age is not restricted to the units from Cordillera del Viento, but also has been identified in other Paleozoic units such as within the Coastal Cordillera of central Chile, with ages ranging between 365 and 414 Ma (Willner et al. 2008). Sagripanti et al. (2011) have recently identified a prominent Devonian population (414 to 361 Ma, with maximum peaks at ca. 365 and 375 Ma) in samples from Pampa de Carrizalito (Neuquén Basin), closely to the east of our study area, interpreting them as sourced from the Northern Patagonian Andean basement where magmatism of such age has been identified by Varela et al. (2005) and Pankhurst et al. (2006), and discarding an Achalian provenance.

Devonian magmatism is known to occur in different regions within Argentina, the most prominent being A-type granitoids often referred to as Achalian magmatism from Sierras Pampeanas (cf. Sims et al. 1998; Dahlquist et al. 2006, 2010; Toselli et al. 2010), and the magmatic arc from northern Patagonia (I type granitoids) forming a NNW–SSE belt that traverses most of the Patagonian region (Varela et al. 2005; Pankhurst et al. 2006; Ramos 2008). This magmatism in both regions extends into Mississippian in accordance to the ages provided, *for example* by Linares and González (1990), Pankhurst et al. (2003, 2006), Dahlquist et al. (2006) and Grosse et al. (2008).

A third region to consider is restricted to the area comprised by the Chilenia terrane, with minor occurrence of Devonian plutons. Tickyj et al. (2009) have recently reported a preliminary dating of the Pampa de los Avestruces Granodiorite (Frontal Cordillera, Mendoza) as Lower Devonian (U–Pb LAM-ICP-MS method; no numerical age provided), identifying its calc-alkaline signature attributed to an arc setting (Tickyj 2011). Furthermore, Cingolani et al. (2011a) have indicated an age of 400 ± 3 Ma for the Rodeo de la Bordalesa calc-alkaline tonalite (San Rafael Block, Mendoza). The identification of inherited magmatic zircon cores of ca. 400 Ma in the Lower Jurassic volcanic rocks in the Huincul Ridge area of Neuquén (Schiuma and Llambías 2008) provides further evidence for the occurrence of magmatism by Devonian times. Recently, Heredia et al. (2012), analyzing the geodynamic evolution of the basement of the Frontal Cordillera, have described volcanic clasts in the Vellecitos beds unit and interpreted them as sourced from an active Devonian volcanic area in the Chilenia terrane.

The analyzed Devonian source could represent the southern extension of a pre- to syn-collisional magmatism related to the accretion of the Chilenia terrane against Cuyania (Gondwana). Most common geotectonic models (cf. Ramos 2004; Willner et al. 2011a) consider an eastward dipping subduction beneath Cuyania, but the lack of Devonian magmatism in the latter terrane and the location of the scarcely recorded Devonian magmatic plutons

Fig. 5 **a** Proposed geotectonic context for the Carboniferous retrowedge-related units from Neuquén. Pampean to Upper Paleozoic magmatism are indicated in order to explain source materials. Sutures with sense of dip, detrital zircon with Devonian ages (from Willner et al. 2008; Hervé et al. 2010; this article) and active/passive margins during the Devonian are also presented. Sutures modified after Chernicoff and Zapettini (2004). **b**–**d** The Devonian magmatic belt in the context of different geotectonic scenarios. References: RPC: Rio de la Plata Craton; PP: Pampia; CY: Cuyania; CH: Chilenia; PP: Pampia terrane; PAT: Patagonia; N-PAT: Northern Patagonia (North Patagonian Massif); S-PAT: Southern Patagonia (Deseado Massif)



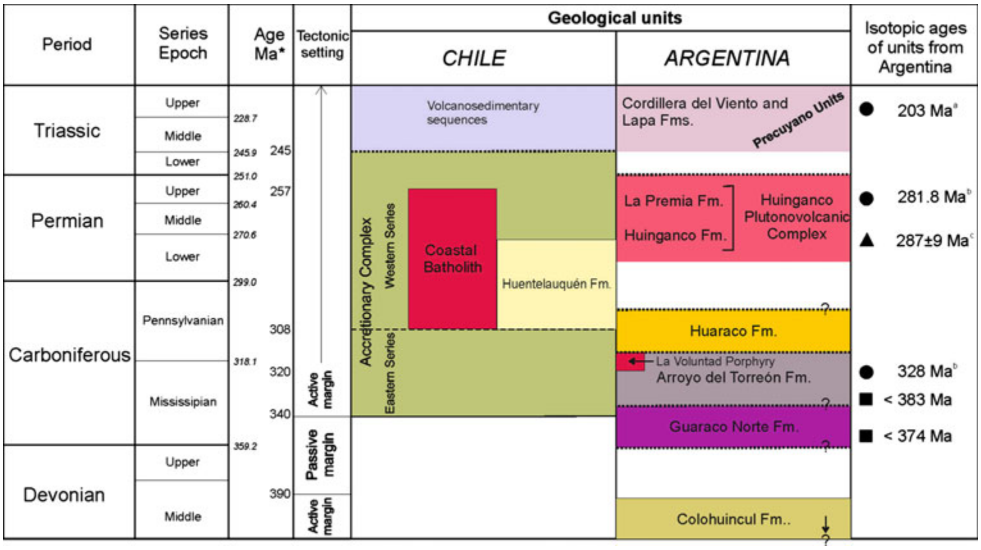


Fig. 6 Stratigraphic chart summarizing the analyzed units from Argentina and their correlation to the units from Chile. Data from Chile after Willner et al. (2005, 2008); Glodny et al. (2005, 2008). Note that basal accretion—Western Series—lasted to approximately 224 Ma in north-central Chile (Willner et al. 2005). Data from Argentina: this article and **a** Schiuma and Llambías (2008b). Suárez et al. (2008); Suárez and De la Cruz (1997)

mentioned previously, as well as the other indirect evidence discussed in this article, would point to a westward dipping subduction of oceanic crust beneath Chilenia (see Fig. 5a), as proposed by Benedetto and Astini (1993), Méndez et al. (1995), Astini et al. (1995), Davis et al. (1999), Gerbi et al. (2002) and, recently, through a detailed stratigraphic, structural and petrological study, by Heredia et al. (2012).

Alternatively, Devonian magmatism in this same region could have been extensional and therefore could have heralded the Mississippian (ca. 334 Ma) bimodal volcanism of southern Puna (Martina 2009; Martina et al. 2010). Recent U–Pb SHRIMP dating of the volcaniclastic Punta del Agua Formation (western depocenter of Paganzo Basin) carried out by Ezpeleta et al. (2009) has permitted to identify the youngest zircon grains at ca. 337 Ma and interpret them as autochthonous and related to recycling of the andesitic and dacitic flows in the same unit.

It is worth mentioning that the possibility that Devonian detrital zircon contained in the Carboniferous accretionary complex had been sourced from the A-type Achalian granites is unlikely since, by the time of deposition of the Guaraco Norte sediments, the western part of Gondwana herein considered, was topographically separated from the region known as Sierras Pampeanas by the Famatinian Orogen and, later as a consequence of the accretion of Chilenia against Cuyania, by the barrier constituted by the Proto-Precordillera orographic belt (cf. Fig. 5a); by the time of deposition of Mississippian sequences, the erosion of the above-mentioned belt would not have yet exposed the Achalian granites. The other possible source, that is, the northern Patagonian Cordillera, is also discarded, since Patagonia is considered to have been separated from Gondwana during the Devonian at least up to the Pennsylvanian (e.g., Rapalini 2005; Ramos 2008 and references therein), precluding it to be a source area during the Carboniferous.

The possible geotectonic scenarios for the connection of the proposed Devonian magmatic arc with the Devonian belt defined further south, in the Patagonian region, are summarized in Fig. 5b–d.

The first and herein preferred setting, considering an allochthonous Patagonia (cf. Ramos 1984, 1986), is presented in Fig. 5b. In this model, the Devonian belt in this latter terrane is interpreted as related to an east-dipping subduction beneath Patagonia sensu stricto, that is, preceding the Carboniferous accretion of the Southern Patagonian terrane (Ramos 2008 and references therein) thus being unrelated to the belt located in Chilenia. An alternative scenario (Fig. 5c) would agree with that originally proposed by Frutos et al. (1975), Gallagher (1990) and lately by Pankhurst et al. (2006), where Devonian granitoids present in the Somuncura Massif (northern Patagonia) would represent arc-type magmatism resulting from the NE-dipping subduction preceding the accretion of the Deseado Massif (Southern Patagonia). This scenario fails to explain the Devonian arc magmatism exposed in the Deseado Massif as well as its extension into Chilenia. Yet another alternative scenario (Fig. 5d) would involve a single block formed by Patagonia + Chilenia as proposed by Martínez (1980), Valencio and Vilas (1985), and lately by Tomezzoli (2011). Accordingly, Patagonia + Chilenia would have started to collide with southwestern Gondwana by Middle Devonian; subduction would dip uniformly west (north of 38–39°S) to southwest (south of 38–39°S) along the Gondwana margin, Patagonia-Chilenia being the upper plate with a passive western margin.

Conclusions

The late Paleozoic Guaraco Norte, Arroyo del Torreón and Huaraco formations from northwest Neuquén, Argentina, were formed closely related with the onset and development of the late Paleozoic accretionary prism of Chile. The detrital zircon ages and their isotopic signatures, combined with the analysis of their geochemical signature provide useful information for establishing and constraining their tectonic setting.

In the stratigraphic chart of Fig. 6, a synthesis of the units analyzed, their regional correlations, as well as their ages of deposition are presented.

The Guaraco Norte Formation (and the equivalent Piedra Santa Complex) would represent passive margin deposits of mostly Mississippian age (younger than 374 Ma and older than 326 Ma) that predates the onset of the accretionary prism in Chile; the sedimentation of this unit is interpreted to have extended into the earliest stage of the accretion, in a retrowedge position, since the equivalent Piedra Santa Complex unit includes, in its much thicker exposures, metaigneous intercalations with arc signature. In this context, the unconformity that separates the Guaraco Norte and the younger Arroyo del Torreón formations, as well as their differing metamorphic grades, indicate the occurrence of a pronounced tectonic activity in a short period of time, during this early stage of sedimentation.

The conspicuous presence of a detrital magmatic zircon population of Devonian age and the chemical arc signature of the Guaraco Norte (and the equivalent Piedra Santa Complex) point to the presence of a magmatic arc of this age exposed and subject to erosion as a main source for this unit; the preserved shape of this zircon population being indicative of short distance transportation. This arc would have been developed in the Chilenia terrane, and related to a possibly west-dipping subduction beneath Chilenia before and shortly after its collision against Cuyania/Gondwana. The extensive superposition of the Pennsylvanian to Triassic magmatism represented by the Choiyoi Group along the same axis would be responsible for the dismembering and obliteration of the Devonian arc that could remain as relics that require a detailed mapping and dating to track its exposures.

The Arroyo del Torreón Formation, with ages ranging from Mississippian to Lower Pennsylvanian, and the Huaraco Formation (of Pennsylvanian age), represent retrowedge basins to the early frontal accretionary prism (Eastern Series) of Chile. The tuff and associated lava flows of the Arroyo del Torreón Formation and the rare tuff of the Huaraco Formation as well as their geochemical signature indicate the presence of a magmatic arc in the retrowedge, suggesting the occurrence of a continuously active magmatism during the deposition of both units, coeval with frontal accretion in the west (Eastern Series).

The Mississipian arc magmatism is interpreted to be related to the onset of an active margin in western Gondwana that switched from a passive margin at Mississippian times (Willner et al. 2008). This arc would have later migrated to the west, constituting de Coastal Batholith of Pennsylvanian to Permian age, in present-day Chilean territory. In this context, the Early Permian Huinganco Plutonovolcanic Complex at Cordillera del Viento (Llambías et al. 2007) represents postectonic magmatism (Ramos et al. 2011) related to the San Rafael orogeny associated to a shallowing of the subducted plate.

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Appendix: Description of methods

Chemical analysis of unaltered and homogeneous samples includes the following: major elements were analyzed by XRF and trace element determinations were performed by ICP/MS, both at Activation Laboratories Ltd. of Canada. For high LOI values, quantitative analyses were made by thermogravimetry, using a TA instrument model SDT Q600 at SEGEMAR laboratories.

U–Pb analyses were carried out at Curtin University of Technology, Perth, and the Hf isotopic analyses at Macquarie University, Sydney.

Samples ZD62-946 (Guaraco Norte Formation, metasandstone collected at point 1, Fig. 1) and ZD58-67a (Arroyo del Torreón Formation, meta-tuff collected at point 2, Fig. 1) have been crushed, milled, sieved, and washed to remove very fine material (clay and silt sizes). The 60–250 mesh fractions were treated with heavy liquids (to remove light minerals) and magnetic separator (to concentrate the less magnetic minerals such as zircon). Zircon was handpicked and organized in an epoxy mount, which was polished and carbon-coated for SEM (Scanning Electron Microscope) study. Back-scattered images (BSE) were taken using a JEOL6400 SEM at the Center for Microscopy and Microanalyses at University of Western Australia. Images of zircon are critical for identifying internal features such as core and rims and to help avoiding areas with high common lead content (inclusions, fractures, and metamict areas). Epoxy mount (UWA 05–85) was gold coated for SHRIMP analyses. The SHRIMP analytical spot was about 25 μm in diameter and four or five LA scans were used for each spot-analysis. Both ^{206}Pb/^{238}U and

^{207}Pb/^{206}Pb ages are presented in Table 2 but ^{206}Pb/^{238}U ages are used for the ages in cumulative plots and for individual grains except for Mesoproterozoic grains c.1–1., d.1–1, and e.12–2. The uncertainties of individual ages are quoted at 1σ, whereas the final ages and those used in the plots are calculated at 2σ level (about 95 % confidence). SHRIMP data were reduced using SQUID software (Ludwig 2001) and plots are prepared using ISOPLOT/Ex (Ludwig 2003).

Hf-isotope analyses reported here were carried out in situ using a New Wave Research LUV213 laser-ablation microprobe, attached to a Nu Plasma multicollector ICPMS at GEMOC Key Center, Macquarie University, Sydney. Most analyses are carried out with a beam diameter of about 40 µm, a 10 Hz repetition rate, and energies of 0.6–1.3 mJ/pulse. Typical ablation times are 30–120 s, resulting in pits 20–40 µm deep. The analytical spots of Hf-isotope analyses were located in the same site of the previous U–Pb SHRIMP analyses. Isobaric interferences of ^{176}Lu and ^{176}Yb on ^{176}Hf were corrected by the Nu Plasma because the mass bias of the instrument is independent of mass over the mass range considered. Interference of ^{176}Lu on ^{176}Hf is corrected by measuring the intensity of the interference-free ^{175}Lu isotope and using ^{176}Lu/^{175}Lu $= 0.02669$ to calculate the intensity of ^{176}Lu. Similarly, the interference of ^{176}Yb on ^{176}Hf is corrected by measuring the interference-free ^{172}Yb isotope and using ^{176}Yb/^{172}Yb to calculate the intensity of ^{176}Yb. The spiking of JMC475 Hf standard is used to determine the value of ^{176}Yb/^{172}Yb (0.5865) required to yield the value of ^{176}Hf/^{177}Hf obtained on the pure Hf solution.

The ^{176}Lu decay constant used to calculate initial ^{176}Hf/^{177}Hf, $\varepsilon_{\mathrm{Hf}}$ values, and model age is $1.983 \times 10{-}11$ (Bizzarro et al. 2003). Typical uncertainties on single ^{176}Lu/^{177}Hf analyses are about 1 epsilon unit (±0.001–0.002 %) incorporating both spatial variation of Lu/Hf and analytical uncertainties. Hf data are given in Table 3. $\varepsilon_{\mathrm{Hf}}$ values, also summarized in Table 3, were calculated at the ^{206}Pb/^{238}U age of each grain (T). For grains c.1-2 and e.12-2, the $\varepsilon_{\mathrm{Hf}}$ is calculated at the ^{207}Pb/^{206}Pb age.

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