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ORIGINAL PAPER

Isotopic studies on detrital zircons of Silurian–Devonian siliciclastic sequences from Argentinean North Patagonia and Sierra de la Ventana regions: comparative provenance

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Abstract The Silurian–Devonian siliciclastic sedimentary units known as Sierra Grande Formation and the upper part of the Ventana Group crop out in the eastern area of the North Patagonian Massif and in the Ventania system, toward the Atlantic border of Argentina. Both sequences show similar stratigraphical characteristics and were deposited in a shallow marine platform paleoenvironment. Previous contributions have provided evidence of an allochthonous Patagonia terrane that amalgamate to Gondwana during the Permian–Triassic. However, other lines of research support a crustal continuity southward, where the Pampean and Famatinian events extend into the northern Patagonia. In either case, the detrital input to the Eo–Mesopaleozoic basins generated along the passive margin tectonic setting should reflect the sedimentary sources. In this contribution, new age data on the sedimentary provenance of these units is provided by U–Pb and Lu–Hf isotopic studies on detrital zircons, using LA-ICP-MS and SHRIMP methodologies. The main sedimentary sources of detrital zircons for both regions are of Cambrian–Ordovician and Neoproterozoic age, while a secondary mode is Mesoproterozoic. Zircons from older cratonic sources (Mesoarchean–Paleoproterozoic ages) are scarcely recorded. The sample from the upper section of the Devonian Lolén Formation (Ventana Group) shows an important change in the sedimentary provenance, with a main mode of Mesoproterozoic detrital zircons. Detrital source areas considering the orogenic cycles known for southwest South America (Famatinian, Pampean–Brasiliano, Mesoproterozoic–'Grenvillian' and Paleoproterozoic–'Transamazonian') are proposed.

Keywords Detrital zircons · U–Pb and Lu–Hf isotopes · Silurian–Devonian · Provenance · Patagonia · Ventania · SW Gondwana

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Introduction

The present work deals with the Silurian–Devonian sedimentary units exposed in the Atlantic margin of Argentina in between 37° 30′–41° 42′ S and 65° 23′–58° 45′W, which partially cover the eastern North Patagonian Massif and the Ventania system. In Fig. 1a and b, the position of the study regions in the context of SW Gondwana is shown, which were about 600–800 km from the paleo-Pacific plate edge.

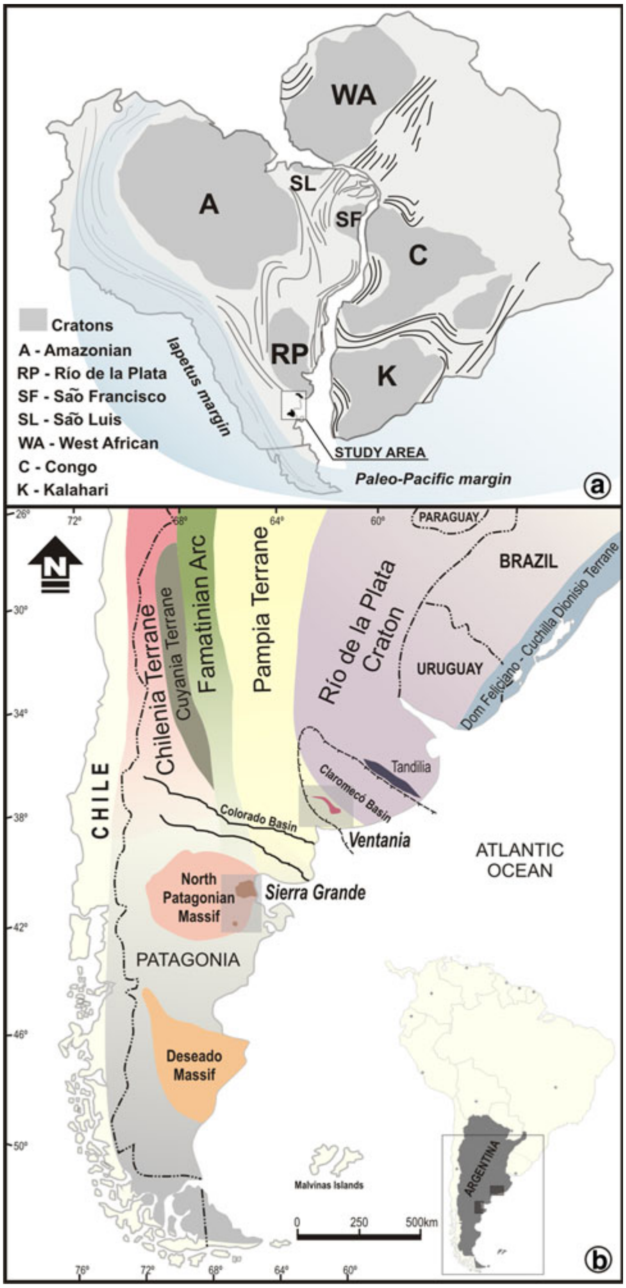


Fig. 1 **a** West Gondwana sketch representation showing the study area in central Argentina. **b** Shows southern South America, with the generalized location of the Río de la Plata craton and the terranes accreted during Neoproterozoic–Upper Paleozoic times (modified after Ramos 1988). The Atlantic location of the Ventania (with the Claromecó basin) and the Sierra Grande studied regions are remarked

In general, the Silurian–Devonian units present comparable lithostratigraphic characteristics and evolution on a shallow marine shelf-type environment. Ramos (1984) and Palma (1989) based on paleontologic and geologic information suggested that Patagonia is an allochthonous terrane to the South American continent, implying that the Paleozoic sedimentary basins would have had separate evolution. On the other hand, Rapalini (1989); Rapalini and Vilas (1991); Dalla Salda et al. (1992); and Pankhurst et al. (2006) among others postulated in different models the continuity of the South American continental crust at least to northern Patagonia, and therefore, the Paleozoic detritus should then reflect the input from a comparable source. In more recent reviews, Ramos (2002, 2008) modified his model proposing the existence of two magmatic arcs; one would have had a western location and would have been active from the Devonian to Middle Carboniferous, whereas the second arc partially overlap in time the other and led to the collision of Patagonia to the southwestern margin of South America in the Permian (Gondwanide orogenic phase).

Gregori et al. (2008) proposed to integrate the directions of compression in mylonitic block movements in the Ventania–North Patagonian areas and the comparison with the Cape Fold Belt in South Africa. These authors concluded that the Pampean and Famatinian rocks that cross the supposed boundary between the North Patagonian massif and central Argentina support the presence of a common continental crust in both areas. Tankard et al. (2009) offer the interpretation of the tectonic evolution of the Cape (and Ventania counterpart) and Karoo basins of South Africa with a subsidence resulted from the vertical motion of rigid basement blocks and intervening crustal faults; after the Neoproterozoic, a suite of small rift basins and their post-rift drape formed at the “releasing stepover model”.

Based on the above-mentioned paleogeographic reconstructions, the main objective that motivated this research was to constrain the sedimentary provenance using isotopic studies on detrital zircons, on the Silurian–Devonian sequences from Sierra Grande and Ventania system (Fig. 1b). Main questions to be resolved are: Were the studied units of both regions developed under a siliciclastic platform conditions with comparable sedimentary sources or they recorded separated tecto-sedimentary histories? The detrital zircon grains, where do they come from? What are their maximum depositional ages? What is their meaning in the paleogeographic evolution?.

Taking into account the geological background knowledge, U–Pb and Lu–Hf isotopic analyses on detrital zircons were undertaken and the major source patterns of the sedimentary units outcropping in both regions were discriminated. The detrital zircon ages provide a discussion on the likely sources of debris, considering the main orogenic cycles recognized within SW Gondwana. By means of the stratigraphic information and known palaeocurrent directions, the potential source areas that would have been exhumed during the development of the depocenters can be estimated. Preliminary isotopic results were anticipated by Uriz et al. (2008a, b).

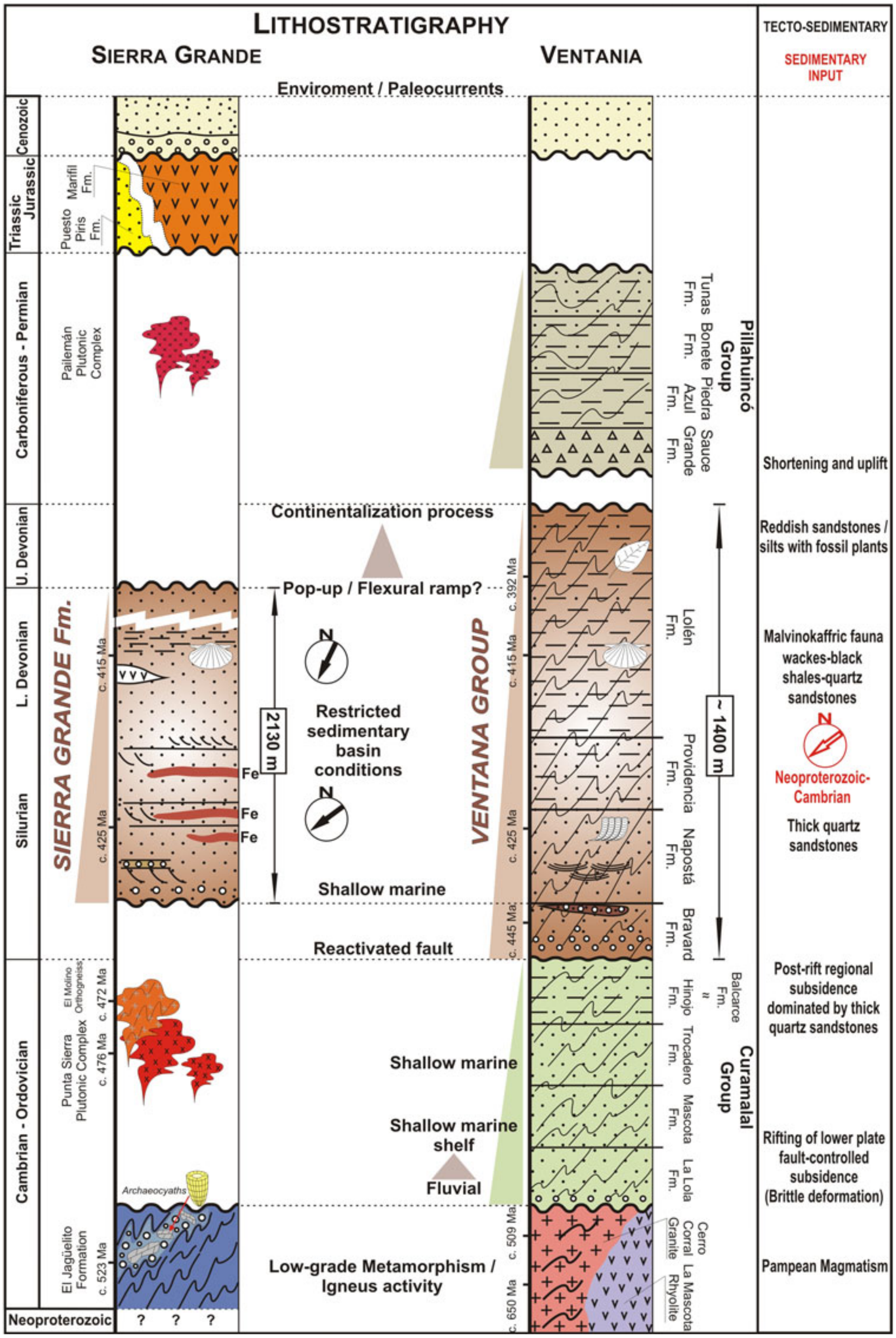


Fig. 2 Comparison of the lithostratigraphy of the study units from Sierra Grande and Ventania regions. Igneous-metamorphic processes, environments, Iron (Fe)-rich beds, tecto-sedimentary events and fining-upward sequences for both regions are shown

Geological setting

Regional aspects

As it is shown in Fig. 1b based on Ramos (1988), the study region is characterized by tectonic terranes collided during different orogenies. (i) The Río de la Plata craton comprises the southernmost Paleoproterozoic ('Transamazonian') basement outcrops in the Tandilia belt, which are covered by Neoproterozoic and Lower Paleozoic sedimentary units. (ii) The Pampia terrane developed mainly during Neoproterozoic to Lower Cambrian times and record the Famatinian magmatic arc. (iii) The Cuyania terrane was accreted during Ordovician, whereas (iv) the Chilenia terrane collided at the end of the Devonian.

The great Patagonia terrane (including the Malvinas plateau) located toward the south has been conventionally considered as the continental region southward of the Río Colorado (Fig. 1b). After Ramos (1984, 1986), a 'cryptic suture' resulted from the closure of an ocean due to southwest-dipping subduction beneath the North Patagonian Massif and it is covered by Mesozoic sedimentary rocks of the Colorado basin (Max et al. 1999). In more recent reviews of the tectonic evolution of Patagonia, Ramos (2002, 2004, 2008) and Pankhurst et al. (2006) include a prior Early Paleozoic collision with the Deseado Massif.

The Sierra Grande region was usually not considered in most Silurian–Devonian reconstructions. However, authors such as Rossello et al. (1997) and more recently von Gosen (2002, 2003, 2009) and Gregori et al. (2008) developed integrated tectonostratigraphic evolution.

The Sierra Grande Formation

It develops in the northeast area of the North Patagonian Massif (Fig. 3), and the best outcrops are found near the eponymous town in the Río Negro province. Many authors, including geologists from mining activities (de Alba 1964; Müller 1965; Stipanicic et al. 1968; Klammer 1964; Braitsch 1965), have studied this Silurian–Lower Devonian unit, which comprises economically interesting ferriferous horizons. A level of detailed knowledge of the Sierra Grande Formation in terms of its mineralogical, sedimentological and structural aspects has been reached through these works as well as from subsequent contributions dealing with different topics (Núñez et al. 1975; Stipanicic and Methol 1980; Zanettini 1981; Avila 1982; Cortés et al. 1984; Ramos and Cortés 1984; Huber-Grünberg 1990; Spalletti et al. 1991; Spalletti 1993; Busteros et al. 1998, among others).

The Sierra Grande Formation (Fig. 3) overlies through an angular unconformity a low-grade metamorphic unit named El Jagüelito Formation assigned to Upper Precambrian to Cambrian age (Pankhurst et al. 2006) and recently a record of Lower Cambrian *Archeocyathids* fossils in carbonate clasts and U–Pb younger detrital zircons ages of c.520 Ma (Naipauer et al. 2010). At the Atlantic coast, the Sierra Grande Formation overlies the Ordovician Punta Sierra Plutonic Complex (Pankhurst et al. 2006; Varela et al. 2008). At the Yacimiento Sur area, a granodioritic Permian body of the Pailemán Plutonic Complex (Varela et al. 1997) intrudes the Sierra Grande Formation, and it is partially covered by younger sedimentary and volcanic units. Pankhurst et al. (2006) have published the first U–Pb SHRIMP data on detrital zircons, from one

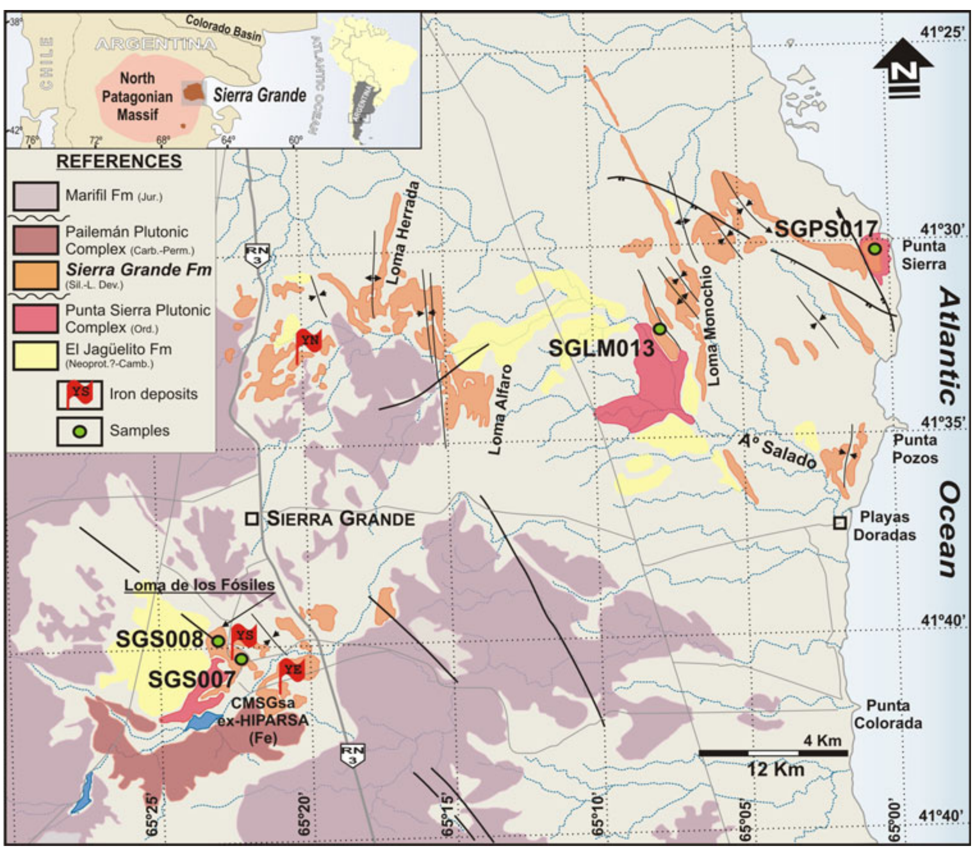


Fig. 3 Geological map showing the outcrops of the Sierra Grande area (based on de Alba 1964; Zanettini 1981; Varela et al. 2008). Iron-rich deposits: *YN* Yacimiento Norte, *YS* Yacimiento Sur, *YE* Yacimiento Este. Sampled localities are showed

sample of the Sierra Grande Formation obtained near the Yacimiento Sur region. Stratigraphical details on the Sierra Grande Formation are presented in the Appendix 1.

Upper part of the Ventana Group

The Ventania system also known as Sierras Australes, outline a structural system with a typical curved ranges string of NW–SE direction. It has been subject of many studies since the beginning of the twentieth century (Keidel 1916; Schiller 1930; Harrington 1947 among others). General geological information is found in Cingolani and Dalla Salda (2000); Dimieri et al. (2005); Massabie et al. (2005). Stratigraphy and evolution of the connected Claromecó basin were described by Lesta and Sylwan (2005) and Ramos and Kostadinoff (2005).

A stable platformal sequence corresponding to the old shallow marine shelf-type basin of Gondwana is preserved in the Ventania system (Fig. 2). Most of the current reconstructions of Gondwana accept that a continuous clastic basin extended from Sierra de la Ventana to the Cape System (Tankard et al. 2009 and references therein). Several lithostratigraphic events were recognized in the Sierra de la Ventana as depicted in Fig. 2. Based on geochemical characteristics and the U–Pb ages of some granites and rhyolites, Rapela et al. (2003) interpreted that a Cambrian rifting event affected the Neoproterozoic basement; sequences of conglomerates and quartzites of up to several hundred meters thick were unconformably deposited between Cambrian and Devonian times (Curamalal and Ventana Groups).

The Ventana Group (Harrington 1970) under study in this paper is part of a Middle Ordovician–Middle Devonian marine siliciclastic sedimentary sequence (Figs. 2, 4) bearing some fossil records. It has a thickness of about 1,300 m and overlies the sublittoral to neritic platformal quartzites of the Curamalal Group, assigned to the Upper Cambrian–Ordovician based on stratigraphic evidence and ichnofossil records (Rodríguez 1988). The Ventana Group is unconformably overlain representing a hiatus, by diamictites of the Gondwanan glaciation and shallow marine and deltaic post-glacial sedimentary rocks of the Pillahuincó Group (Carboniferous to Early Permian). Four lithostratigraphic units were recognized within the Ventana Group, named from base to top: Bravard, Napostá, Providencia and Lolén. Paleocurrent analyses measured on cross-lamination present on some of these mature quartzite sequences indicate a provenance from the northeast (Reinoso 1968) or from east-northeast after Harrington (1970). The study region and the sampling locations are shown in Fig. 4.

Stratigraphical details of the Ventana Group are offered in Appendix 2.

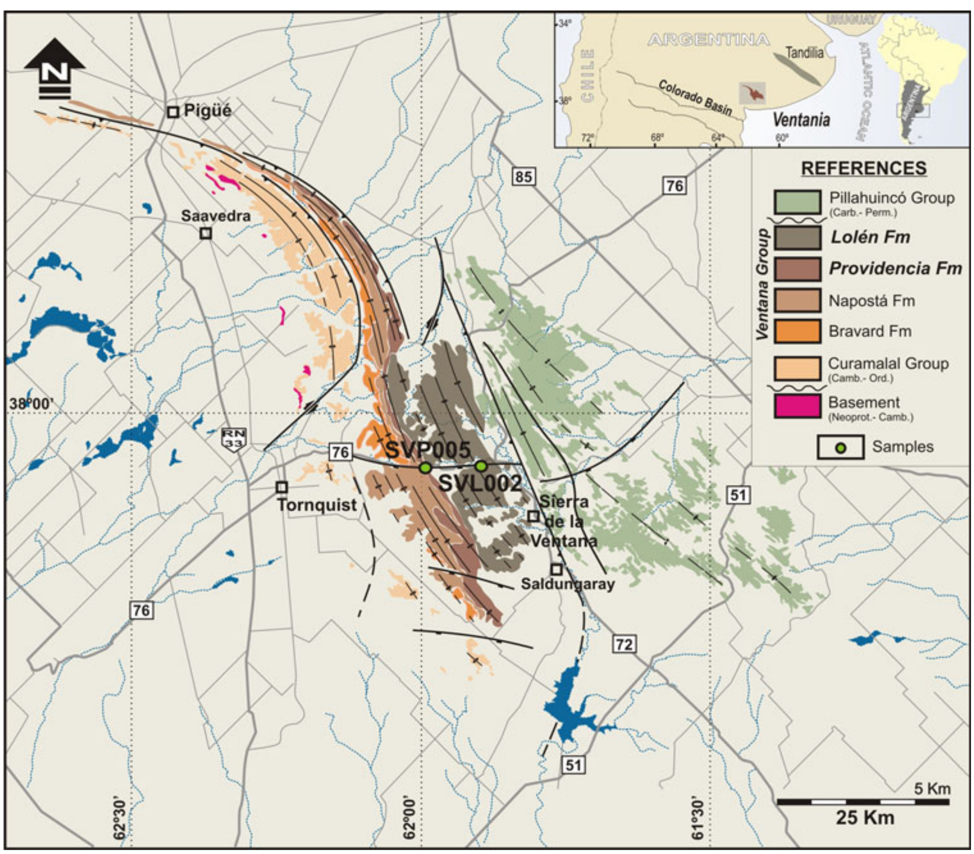


Fig. 4 Geological sketch map showing the outcrops of the Ventania system (based on Harrington 1947; Cobbold et al. 1986; Rossello et al. 1997; Tomezzoli and Cristallini 2004). The locations of the studied samples are remarked

Analytical methods and study samples

The analysis of detrital zircons has been intensively used as an important element to study the mechanisms of growth and recycling of the continental crust along time. It is well known that the zircons can resist multiple processes of erosion, transport and even high-grade metamorphic events, preserving magmatic and metamorphic crystallization ages that can be recorded by the U–Pb system. This method can be combined by the Lu–Hf systematic on the same grain to distinguish magmatic episodes that added juvenile mantle material from those events that merely recycled existing crust (Gerdes and Zeh 2006; Willner et al. 2008). The samples obtained from different levels of the Sierra Grande Formation are the typical quartz-rich sandstones (Fig. 2). The SGPS017 was obtained at the base of the unit, while the SGLM013 was taken from the middle part of the section and SGS007 and 008 from the top. The sample analyzed from the upper part of the Ventana Group is medium-grained quartz-rich sandstone of the top section of the Providencia Formation (SVP005) that was collected at the 76 Road in the area of the "Abra de la Ventana". The sample SVL002 was selected from the upper levels of the Devonian Lolén Formation and consists of quartz–mica-rich sandstone (Fig. 4). In addition, the morphology of detrital zircon grains from samples of the Lolén Formation (SVL002 and 004) and from the Sierra Grande Formation (SGLF026; SGE031) was examined under the scanning electron microscope (JEOL JSM 6360 LV at the Museum of La Plata, Argentina). A total of 378 detrital zircon grains were measured by U–Pb from samples of the Sierra Grande Formation (SGS007, 008, SGLM013, SGPS017). From the Sierra de la Ventana region, one sample from the Providencia Formation (SVP005) and one from the Lolén Formation (SVL002) were studied. The Lu–Hf systematic on 40 zircons that were also dated by U–Pb method was carried out.

In the Appendix 3, we present the laboratory LA-ICP-MS and SHRIMP methodologies.

Results

Typology of zircons

The morphology of zircons can be greatly affected as a result of a long transport or reworking during a sedimentary cycle (Dickinson and Gehrels 2003). The occurrence of zircons with different morphologies in sandstone is indicative of an apparent mixture of the sources of debris. With this approach and taking into account parameters such as size, shape, habit and elongation of the crystals, different zircon populations were observed, appearing with various stages of roundness for similar idiomorphic groups. The populations have been compared with the classification (typology) of igneous zircons after Pupin (1980). A comparative morphological analysis with a summary on zircon grains is shown in Table 1.

Sierra Grande Formation

Based on the analyzed morphological parameters on 55 detrital zircon grains (Fig. 5a, Table 1a), four zircon populations were recognized as follows. *SG group 1*: characterized by short prismatic crystals, with euhedral and rounded to sub-rounded habit but keeping the morphological parameters of the group. They are identified in types as P3-P4-L5-S4 and S23, and they are related to an igneous-plutonic origin. *SG group 2*: they correspond to long euhedral to subhedral prismatic crystals with elongations between >2.7 and <4.5. The recognized crystallographic patterns are P1-P2-P3-P4-G1-R3 and R4, corresponding to igneous-volcanic to sub-volcanic-derived crystals. *SG group 3*: it comprises short prismatic crystals (multifaceted). They show well-developed sub-rounded crystals with complex axial relationships. Zircon types are S13-S14-S18 and S19 and can be related to a metamorphic origin. *SG group 4*: this includes rounded, equidimensional-sized crystals with elongations ranging from 1.1 to 2. Their rounded shapes suggest a long-distance transport and can be linked to ancient zircon cores.

Ventana Group (Lolén Fm)

Morphological studies of detrital zircons of two samples from the Lolén Formation were carried out (Fig. 5b; Table 1b). SVL group 1: the identified forms are related to euhedral to subhedral crystals, appearing in some cases with sub-rounded features but maintaining the general appearance of short prismatic crystals. Typologically are classified as P2-P3-P4-P5-S19-S20 and S25, which may relate to a plutonic origin. SVL group 2: they have euhedral to anhedral forms, with elongations between >2.7 and <3.5. Some grains show crystalline characteristics obliterated by abrasion during transport but maintaining the proportions length/width that characterize the family. The following types are recognized P1-P2-P3-P4 and S1-S6 and are linked to a volcanic to sub-volcanic provenance. SVL group 3: short prismatic crystal sets, which are well-developed crystalline forms, being the predominant sub-rounded crystals, preserving multifaceted aspects and maintaining the proportions of this family. The typologies identified are S2-S7-S13-S14 and S18 and can be related to a metamorphic origin. SVL group 4: it comprises rounded shapes, similar to those form zircon grains from old cores.

Table 1 Summary of comparative morphological analyses on zircon grains from Lolén and Sierra Grande samples

(a) Sierra Grande Formation			
Number of crystals	Broken crystals	Total analyzed	
55	20	35 [n]	
Morphology Of Zircons			
Euhedral	Subhedral	Anhedral	Equidimensional/ rounded
37,1% [13]	22,9% [8]	22,9% [8]	17,1% [6]
Typology Of Zircons			
Features / Groups	Size (length - width) max. - min. (μ)	Length / width max. - min. (μ)	Types (Pupin, 1980)
Group 1 (Plutonic)	193 x 90 to 137 x 70	2.6 - 1.7	P3,P4, L5, S4, S23
Group 2 (Volcanic)	295 x 93 to 175 x 60	4.5 - 2.7	P1, P2, P3, P4, G1, R3, R4
Group 3 (Metamorphic)	265 x 140 to 150 x 140	2.3 - 1.1	S13, S14, S18, S19
Group 4 (Very rounded)	170 x 122 to 115 x 107	2.0 - 1.1	---

(b) Lolén Formation (u. Ventana Group)			
Number of crystals	Broken crystals	Total analyzed	
54	21	33 [n]	
Morphology Of Zircons			
Euhedral	Subhedral	Anhedral	Equidimensional/ rounded
48,5% [16]	18,2% [6]	24,2% [8]	9,1% [3]
Typology Of Zircons			
Features / Groups	Size (length - width) max. - min. (μ)	Length / width max. - min. (μ)	Types (Pupin, 1980)
Group 1 (Plutonic)	291 x 117 to 60 x 28	2.9 - 1.8	P1, P2, P3, P4, P5, S19,S20, S25
Group 2 (Volcanic)	288 x 93 to 136 x 46	3.5 - 2.7	P1, P2, P3, P4, S1, S6
Group 3 (Metamorphic)	298 x 138 to 109 x 63	2.2 - 1.7	S2, S7, S13, S14, S18
Group 4 (Very rounded)	132 x 72 to 107 x 69	1.8 - 1.6	---

U–Pb main populations and age components

Sierra Grande Formation

Three samples were analyzed by U–Pb systematic using LA-ICP-MS equipment (the analytical data and the Concordia diagrams are shown in the electronic supplement). As we depicted in Fig. 6, the sample SGS007 ($n = 27$) showed a main mode of ages at the Neoproterozoic (51.9%), while the Ordovician and Silurian zircon grains represent 14.8%. The Cambrian and Mesoproterozoic ages are presented in 7.4 and 3.7%, respectively; there is only one zircon dated Paleoproterozoic. The sample SGLM013 ($n = 71$) is distinguished by a Cambrian age zircons forming 32.4%. The percentage contributions of the Neoproterozoic that forms the secondary cluster is of 28.3%, while equally well represented are the Mesoproterozoic with 19.7% and the Ordovician with 18.3%. Neoarchean grains are present in 1.4%. In the case of the sample SGPS017 ($n = 72$), the Neoproterozoic detrital zircon grains with a 34.7% are the most significant detritus contribution. Cambrian grains are present in 26.5% and the Ordovician in 20.8%. The Paleoproterozoic detrital zircon grains are present in less than 3%. The younger zircon age reported in this sample is Silurian (1.4%).

Two sandstone samples analyzed by the SHRIMP method (SGS008 and SGLM013) showed an agreement regarding zircon grain ages, with a main source from Ordovician, Cambrian and Neoproterozoic rocks. The following proportions are present: for the sample SGS008 ($n = 52$), 32.7% are Ordovician in age; 28.8% are Cambrian and 23.1% are Neoproterozoic. Sample SGLM013 ($n = 48$) displays a major Neoproterozoic mode with 29.2%, a Cambrian mode with 27.1%, while the Ordovician participates with a 20.8%. The Paleoproterozoic is poorly represented in both samples with 1.9 and 4.2%, respectively. Neoarchean zircon grains are present in a 2.1%.

In Fig. 6, details of the correlation of the frequencies of age recorded for each sample are shown. We also include the obtained SHRIMP data by Pankhurst et al. (2006) and its correspondence with the input of the Neoproterozoic and Mesoproterozoic zircon grains for the samples analyzed here. The difference is the presence of grains younger than c. 500 Ma in all samples analyzed in the present work, which were not recorded in the sample published by those authors.

Upper Ventana Group

A total of 107 zircon grains were analyzed from a quartz-rich and wacke sandstones, corresponding to the Providencia and Lolén Formations, respectively. Analytical data are presented in tables with Concordia diagrams in electronic supplement. The U–Pb data by LA-MC-ICP-MS

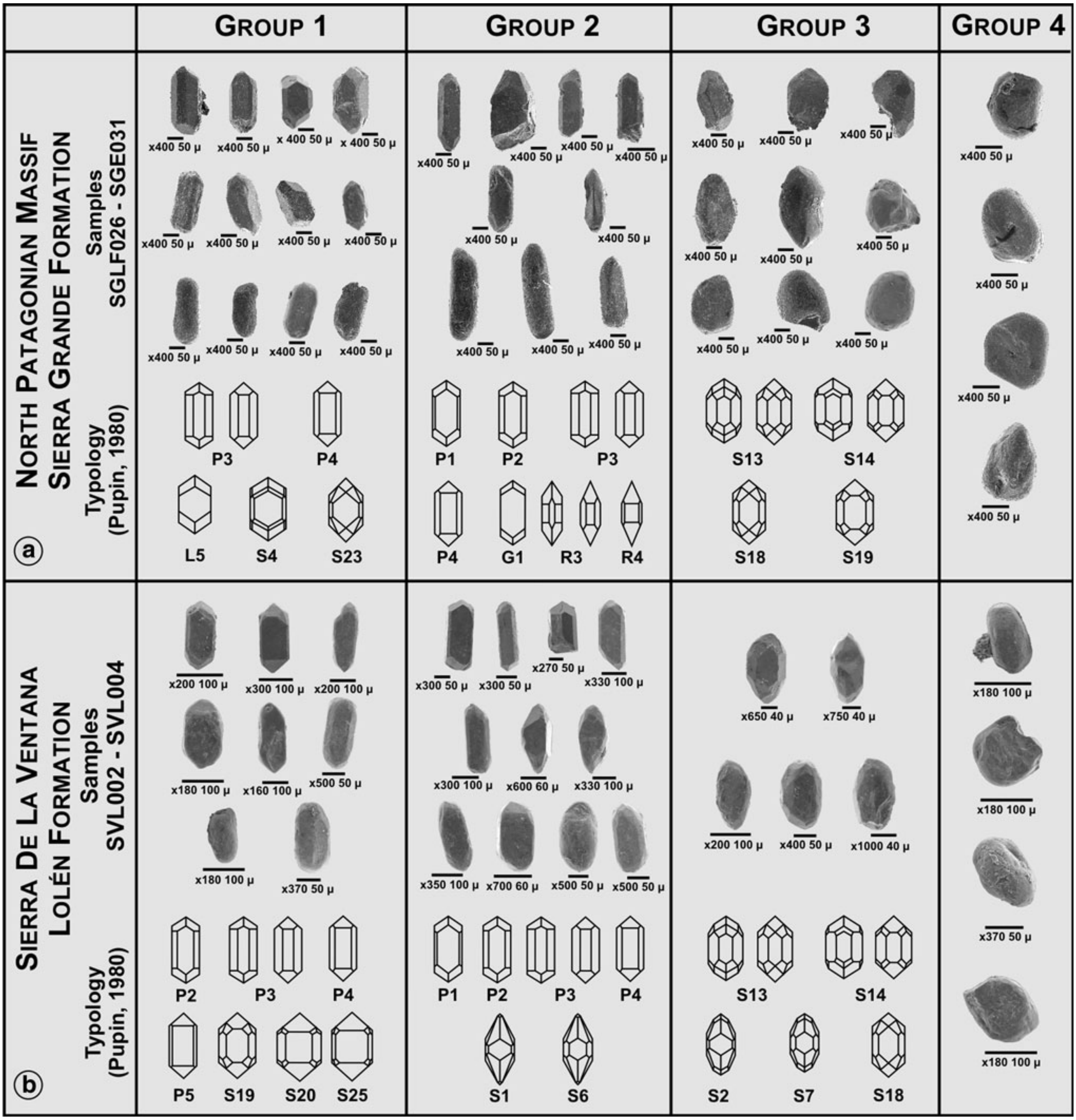


Fig. 5 Electron microscope images of studied zircons from. **a** Sierra Grande Fm and, **b** Lolén Fm samples. Comparative analyses based on morphological zircon grains using the typology characteristics after Pupin (1980)

method ($n = 80$) obtained from detrital zircon grains of the Providencia Formation reveal three major trends (Fig. 7). The most representative cluster comprising 41.3% of total grains is of Cambrian age with main components for the Middle Cambrian. The second cluster (26.3%) is represented by Neoproterozoic ages. The Mesoproterozoic zircon grains constitute 17.5%. Finally, Ordovician grains are present in 5%, and a low participation of elements of Paleoproterozoic (2.5%), Neoarchean (1.3%) and Mesoarchean (1.3%). Results obtained using SHRIMP methodology on the sample of the Lolén Formation SVL002 ($n = 27$) show an important change with respect to all previous samples, especially in the frequency diagram (Fig. 7). Two main modes are present: the Mesoproterozoic 37% and the Ordovician 22.2%, while the Neoproterozoic is represented by 14.8% of detrital zircons and the

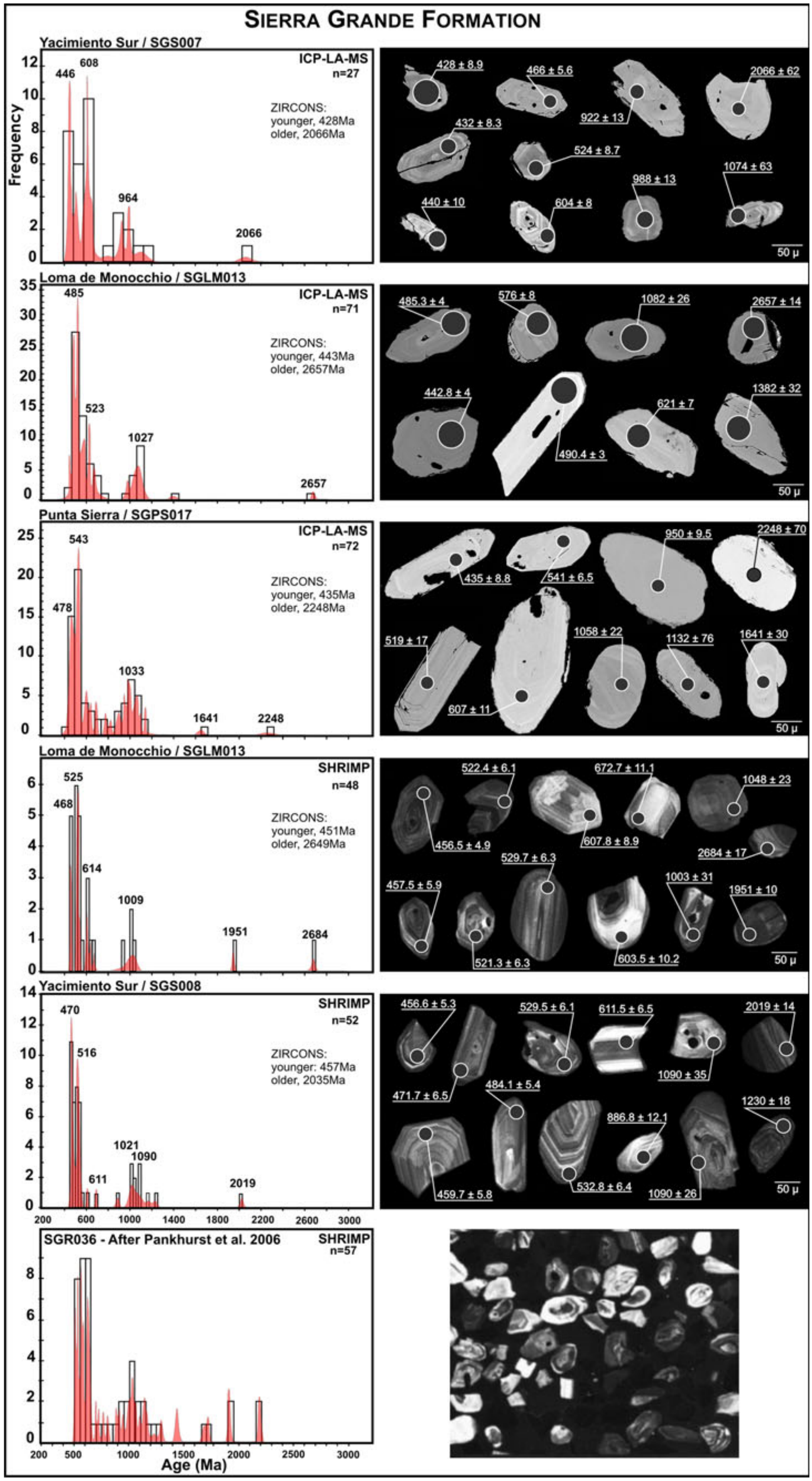


Fig. 6 Frequency histograms and probability curves of detrital zircon ages from Sierra Grande Formation samples obtained by ICP-LA-MS and SHRIMP methodologies. On each sample, the number of analyzed grains and obtained pattern ages was represented. On the right, there are the studied zircon grains by electron microscope or cathodoluminescence images. For comparison, the SGR036 sample was taken from Pankhurst et al. (2006)

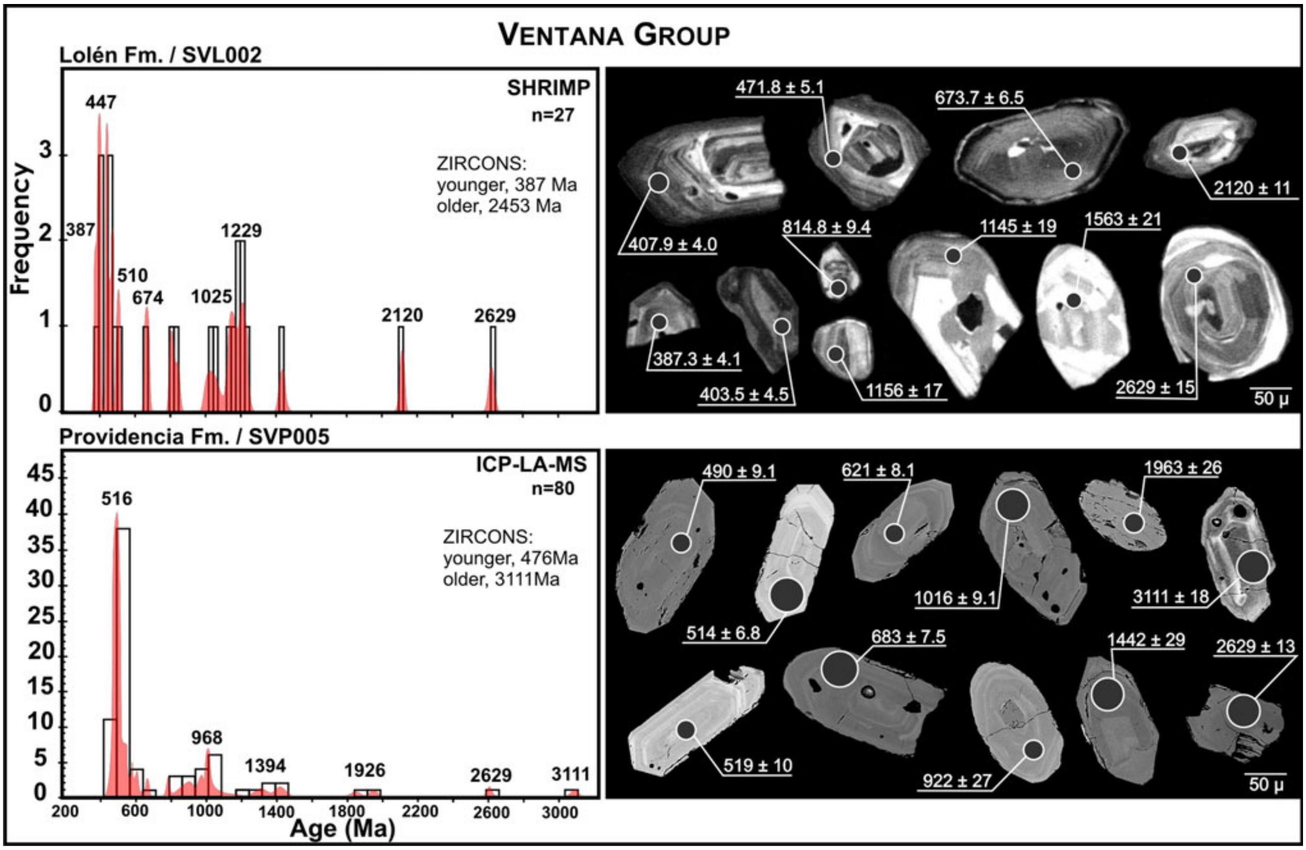


Fig. 7 Frequency histograms and probability curves of detrital zircon ages from Providencia and Lolén Formations obtained by ICP-LA-MS and SHRIMP methodologies. On each sample, the number of analyzed grains and obtained pattern ages was represented. On the right, there are the studied zircon grains by electron microscope or cathodoluminescence images

Devonian by 11.1%. The latter values are of particular interest because they represent the younger zircon ages obtained for the upper levels of the Lolén Formation. The Paleoproterozoic has relatively increased its presence by a record of a 7.4%, while the Cambrian and Silurian clusters are found in 3.7%.

Lu/Hf isotope compositions

We selected for the Sierra Grande Formation 30 zircon grains covering main measured age populations. The Mesoproterozoic analyzed zircons (Table in electronic supplement) show ^{176}Hf/^{177}Hf ratios for $_{\varepsilon}$Hf (t) between 9.46 and −20.46 and T_{DM} model ages between 1,274 and 2,395 Ma. The $_{\varepsilon}$Hf (t) values of Neoproterozoic zircons range between 11.04 and −14.53 and the T_{DM} Hf model ages between 1,072 and 1,767 Ma. Analyses of Hf isotopic composition of Paleoproterozoic–Archean zircons show isotope ratios for $_{\varepsilon}$Hf (t) of 7.07 and −7.87 and T_{DM} Hf model ages of 1,802–2,746 Ma. Finally, the Middle Cambrian to Devonian zircons show isotope ratios with values $_{\varepsilon}$Hf (t) 1.5 and −9.28 and T_{DM} Hf model ages of 1,046–1,506 Ma (Fig. 8).

For the Providencia Formation (Upper Ventana Group) sample, 10 zircon grains were analyzed. Mesoproterozoic grains present ^{176}Hf/^{177}Hf ratio with $_{\varepsilon}$Hf (t) between 12.25 and 15.79 and T_{DM} Hf model ages of 1,200–1,221 Ma. The Neoproterozoic zircons have $_{\varepsilon}$Hf (t) between 6.57 and −6.27. Hf T_{DM} model ages are between 1,125 and 1,495 Ma. The analyzed Upper Cambrian–Ordovician zircons show $_{\varepsilon}$Hf (t) between −0.37 and −4.11 and T_{DM} between 1,107 and 1,272 Ma.

Comments on the isotope results

(a) All samples of the **Sierra Grande Formation** (Fig. 9) record small amount of grains coming from ancient cratonic nuclei, with Archean and Paleoproterozoic zircon ages of up to 7%. In general, the morphology of these zircons is well rounded, with oscillatory zoning and secondary growth. The Mesoproterozoic (essentially the M3 or 'Grenville-age cycle') is present with a variable rate from 7% in samples from the upper part of the sequence to 20% at its bottom. This suggests a decline in the contribution of grains of this age to the sedimentary basin as it

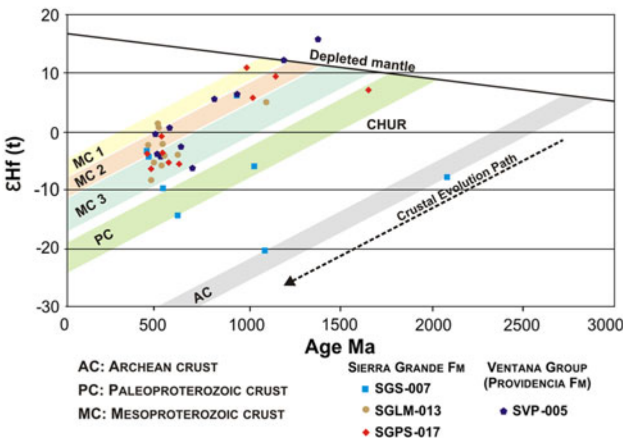
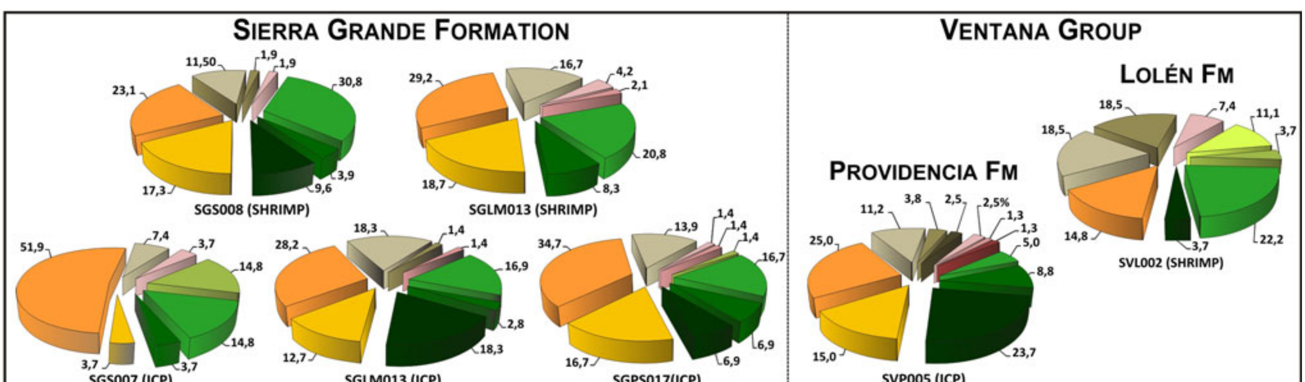


Fig. 8 Comparative $_{\varepsilon}$Hf (t) evolution diagram for single-grain detrital zircons from Sierra Grande and Providencia Formations. The depleted mantle array was calculated using data for MOR basalts (Patchett et al. 1981). The Archean, Paleoproterozoic ('Transamazonian') and mesoproterozoic (M1–M3) crustal evolution paths are remarked

rises in the stratigraphic column. The Neoproterozoic–Lower Cambrian detrital zircon ages (always between 40 and 55%) are assigned to the Pampean cycle (Upper Brasiliano–Pan-African cycles). Ordovician peaks recorded are assigned to the Famatinian cycle, which in all samples represent between 15 and 31%. Silurian aged zircons are more important toward the top of the sequence. These zircon data give the maximum sedimentation age that is consistent with the fossil record.

The samples from the Sierra Grande Formation have similar $_{\varepsilon}$Hf (t) evolution comparing to the analyzed sample of the Ventana Group, with the exception of sample SGS007 (Fig. 8). The group of samples with positive $_{\varepsilon}$Hf values correspond to juvenile (mantle) origin, while samples that are close to the line 0 are interpreted as recycled materials from the crust. A negative data corresponds to zircons from crustal origin. Therefore, 30.8% of analyzed zircons crystallized in juvenile magmatic sources, 5.1% on crustal sources, and 64.1% were derived from a significant crustal recycling with an essentially Mesoproterozoic crust ("Grenvillian").

(b) The **Providencia Formation** (Upper Ventana Group) also records scarce grains from old cratonic nuclei (Fig. 9). Neoproterozoic zircons (25%) and Cambrian grain ages (47%) are present, from which about 40% could be assigned to the Pampean cycle (Upper Brasiliano–Pan-African cycles). Mesoproterozoic zircon ages with a 17.5%, while the M3 or Grenville-age cycle which is mostly. For the Providencia sample, 5% of zircon grains are of Ordovician age. The results indicate that the deposition in the Providencia paleobasin was not older than *c*.476 Ma (youngest zircon),



CYCLES		FAMATINIAN					PAMPEAN-BRASILIANO		SUNSAS "GRENVILLIAN"					
									Mesoproterozoic					
Samples	Number	Dev.	Sil.	Ord.	Upper Camb.	Middle Camb.	Lower Camb.	Neo-prot.	M3	M2	M1	Paleo-prot.	Neo-arch.	Meso-arch.
SGS007-ICP	27		14.8%	14.8%	3.7%		3.7%	51.9%	7.4%			3.7%		
SGS008-SHRIMP	52			30.8%	3.9%	9.6%	17.3%	23.1%	11.5%	1.9%		1.9%		
SGLM013-ICP	71			16.9%	2.8%	18.3%	12.7%	28.2%	18.3%	1.4%			1.4%	
SGLM013-SHRIMP	48			20.8%	8.3%		18.7%	29.2%	16.7%			4.2%	2.1%	
SGPS017-ICP	72		1.4%	16.7%	6.9%	6.9%	16.7%	34.7%	13.9%			1.4%	1.4%	
SVP005-ICP	80			5.0%	8.8%	23.7%	15.0%	25.0%	11.2%	3.8%	2.5%	2.5%	1.3%	1.3%
SVL002-SHRIMP	27	11.1%	3.7%	22.2%		3.7%		14.8%	18.5%	18.5%		7.4%		

Fig. 9 Representation in percentages "pie" diagrams of the main orogenic cycles provenance data: Famatinian, Pampean–Brasiliano, Mesoproterozoic (including "Grenville") and Paleoproterozoic to Archean. Age and system boundaries are presented after the IUGS international stratigraphic Chart 2009

whereas the stratigraphic age could be Silurian based in ichnofossil record. It should be noted that the U–Pb data from detrital zircons for the Providencia Formation here presented have different patterns from the Balcarce Formation samples (Upper Ordovician to Lower Silurian) cropping over the Tandilia region as a last transgression covered the Rio de la Plata craton (Pankhurst et al. 2006; Zimmermann and Spalletti 2009). In this mentioned unit, a clear contribution of Paleoproterozoic zircons from the cratonic basement is presented.

(c) The **Lolén Formation** records Paleoproterozoic ('Transamazonian') detrital zircons (7%), and older grains are absent (Fig. 9). Mesoproterozoic ages (37%) resulted in a considerable percentage of contribution of grains in the basin; half of that percentage can be assigned to the Grenville-age cycle. The Neoproterozoic ages (Upper Brasiliano–Pan-African cycles) has fallen to 15%, which is a notable difference with the Providencia Formation and also with all samples of the Sierra Grande Formation, which recorded an average of 33% of grains of this age. Middle Cambrian-aged zircons are 4%, but instead the Ordovician grains are more abundant (22%) and Silurian-aged zircons are present in 4%. Finally, the 11% of Devonian-aged zircons registered the maximum sedimentation age (*c*.387 Ma) in the Middle Devonian, this set up a part of the Famatinian cycle with a contribution of 41%. After Tankard et al. (2009), this change of input record could be related to the location of Ventania at the margin of the 'Cape basin' during maximum subsidence time. The Lolén Formation was deposited during the "Devonian cycle" recognized within the Paraná basin that appears as a widespread subsidence and accumulation event in separate basin tracts in upper and lower plate settings (Milani 2007; Tankard et al. 2009). These sedimentary conditions with a new lithospheric deflection could also be responsible for the change in the zircon patterns, with exposure of predominantly older source terranes.

Discussion

Paleogeographic aspects

In southern South America and South Africa, the major cratonic elements comprise cratons such as the Río de la Plata, and the Kalahari (or Kaapval) and several smaller crustal fragments, and Mesoproterozoic and Neoproterozoic–Cambrian mobile belts that were involved in the final amalgamation of West Gondwana. Following amalgamation, the proto-Andean Gondwana margin continued to be active with addition of oceanic crust material and remobilization of existing parts of the margin (Ramos 1988; Cawood 2005). In this tectonic scenario, the Silurian–Devonian Ventania–Sierra Grande depocenters were developed over continental crust by rheologic weakening. This tectonic setting resulted in progressive migration of the depocenters and influenced the evolution of fold-belts, adjoining foreland basins and the cratonic interior (Milani 2007).

Main detrital zircon sources

Taking into account the scarce paleocurrent directions recognized in the Sierra Grande and Ventania areas and the comparison with the Cape Supergroup in South Africa (Johnson et al. 2006 and references therein), it is clear that the paleoenvironments were not static, but rather shifted southward and northward several times in line with the marine transgressions and regressions that took place. The age distribution of detrital zircons reflects the ages and approximate proportions of zircons in the source regions. Constrains on provenance of the main detrital zircon sources could be as follows, from older to younger age components (Fig. 10):

Archean to Paleoproterozoic: It is highly likely that the source rocks of the obtained small cluster of zircons are derived from the erosion of the Río de la Plata and/or the Kalahari (Kaapval) cratons. Considering the low percentage of contribution to the Silurian–Devonian basins, the ancient nuclei could have been mainly covered by older units; or the main paleocurrents were in other directions; or they could have different paleogeographic positions, although there is no clear evidence for the later.

Mesoproterozoic: Most important outcrops of Late Mesoproterozoic rocks occur throughout western South America and in the Namaqua-Natal belt in South Africa. The obtained prominent age clusters at 1.0–1.2 Ga in both studied regions reflect the relevance of a Mesoproterozoic event, partially known as Sunsás orogenic belt (Cordani et al. 2000; Schwartz and Gromet 2004; Casquet et al. 2006; Rapela et al. 2007; Adams et al. 2008; Willner et al. 2008; Santos et al. 2008; Ramos 2009, and references therein) or also called Grenvillian-age cycle. The source of detrital zircons could be a belt in Argentina known as Pampia terrane (Fig. 1b) where Escayola et al. (2007) and Leal et al. (2003) among others cited the presence of Mesoproterozoic crust. If the Cuyania terrane with a Mesoproterozoic ('Grenvillian') basement of Laurentian affinity and outcropped at the Pie de Palo, Maz and Umango ranges was accreted to Gondwana during Middle Ordovician time, it could also constitute a source of zircons

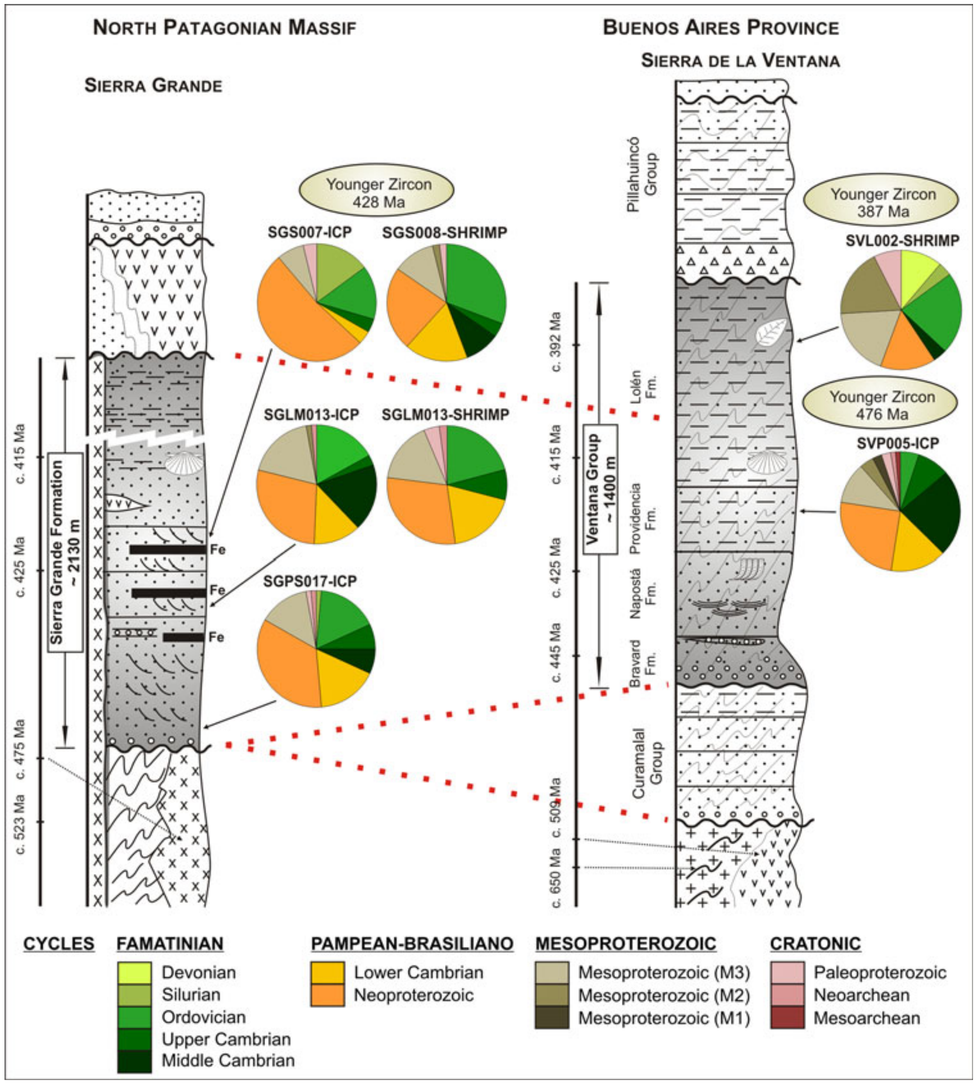


Fig. 10 Stratigraphic sketch columns of the Sierra Grande and Ventania regions with main lithostratigraphic characteristics and showing the obtained U–Pb ages of the studied detrital zircons represented in circular "pie" diagrams. Shaded *red lines* are tentative correlations between both stratigraphical columns. Note that both basement complexes (Varela et al. 1997, 2008; Gregori et al. 2005; Rapela et al.2003; Pankhurst et al. 2006) have different igneous-metamorphic origins but with similar ages and the Curamalal Group in Ventania does not correlate with Sierra Grande region where the iron-rich levels appeared. The Carboniferous–Permian sedimentary record of the Ventania sequence (Pillahuincó Group) with classical Gondwanan glacial diamictites (Lopez Gamundi et al. 2006) does not appear in Sierra Grande region. The Ventania system records more intense folding during the Gondwanide orogeny (von Gosen et al. 1991)

of Mesoproterozoic age. A possible contribution from the Namaqua-Natal belt in South Africa (Robb et al. 1999) and the Malvinas crust (Cingolani and Varela 1976; Thomas et al. 1998) could not be ruled out. Eastward paleocurrents in the Upper Ventana Group–Sierra Grande Formation, which coincides with data from the Cape Supergroup in South Africa (Johnson et al. 2006; Tankard et al. 2009), tend to support such a contribution from the Namaqua-Natal province.

Neoproterozoic to Lower Ordovician: Zircon-bearing rocks of these ages are abundant in southern South America as well as in once-contiguous parts of western Africa and display evidence of uplift and denudation between Silurian–Devonian times. The contribution of zircons of these ages may range from units that make up both the low-grade metamorphic basement of the Sierra Grande Formation as well as the basement of the Ventania system. In a more comprehensive source can be clearly inferred denudation of the Pan-African–Brasiliano belt (Pampean orogeny).

Middle Ordovician–Silurian: Zircon grains of these ages were probably derived from erosion of the igneous rocks that intruded the metamorphic basement of the Sierra Grande Formation. The Punta Sierra Plutonic Complex may have been the source of Ordovician zircons. In other words, the denudation of the Famatinian magmatic rocks could have been an input for the Sierra Grande, Providencia, and Lolén Formations.

Devonian: Zircons of these ages were recorded only in the upper part of the Lolén Formation and could be derived from the final Famatinian magmatic arc ("Achalian Orogenic Cycle", after Sims et al. 1998). Coeval potential rock sources are cited but coming from the southwest: Varela et al. (2005) have obtained Devonian U–Pb ages on granitoids of Patagonia; and Tickyj et al. (2009) registered in Frontal Cordillera of Mendoza a syntectonic Lower Devonian granodiorite.

Comparison of the isotopic data

The U–Pb results (Fig. 11) show a consistency for both regions, with the presence of Neoproterozoic and Cambrian–Ordovician zircon ages as the primary source, while Mesoproterozoic ages appear with a strong presence in all samples but as a secondary cluster. The Early Paleozoic sedimentary rocks of Ellsworth-Whitmore Mountains of Antarctica as a part of the Gondwanide Orogen display the same pattern of age populations that are consistent with a provenance from within Gondwana (Flowerdew et al. 2007). Paleoproterozoic to Neoarchean zircons appear in small quantity in all samples analyzed from both regions. This is relevant information for the Ventania region taking into account the actual close proximity to the Tandilia region as a southern outcrop of the Río de la Plata craton. It is noteworthy that Lower Ordovician–Early Silurian clastic sequences of the Precordillera display a different pattern of detrital zircon ages characterized by a dominantly Mesoproterozoic source, a less abundant Neoproterozoic population, and few Famatinian zircon ages (Abre et al. 2008 and references therein).

Final remarks

1. The U–Pb detrital zircon study provides further documentation of a substantial contribution from Neoproterozoic–Lower Cambrian sources for the Sierra Grande and Providencia Formations. Secondary sedimentary inputs record Middle Cambrian to Silurian and Mesoproterozoic ('Grenvillian') ages. A diminution of Mesoproterozoic zircon age percentages from bottom to top within the Sierra Grande Formation was found.
2. The maximum sedimentation ages (younger zircons dated) are 428 Ma for the Sierra Grande unit and 476 Ma for the Providencia (Upper Ventana Group).
3. Lu–Hf data indicate that zircons from both regions record a significant recycling process with Mesoproterozoic crust, while more than 30% of analyzed zircons crystallized in a juvenile magmatic source.

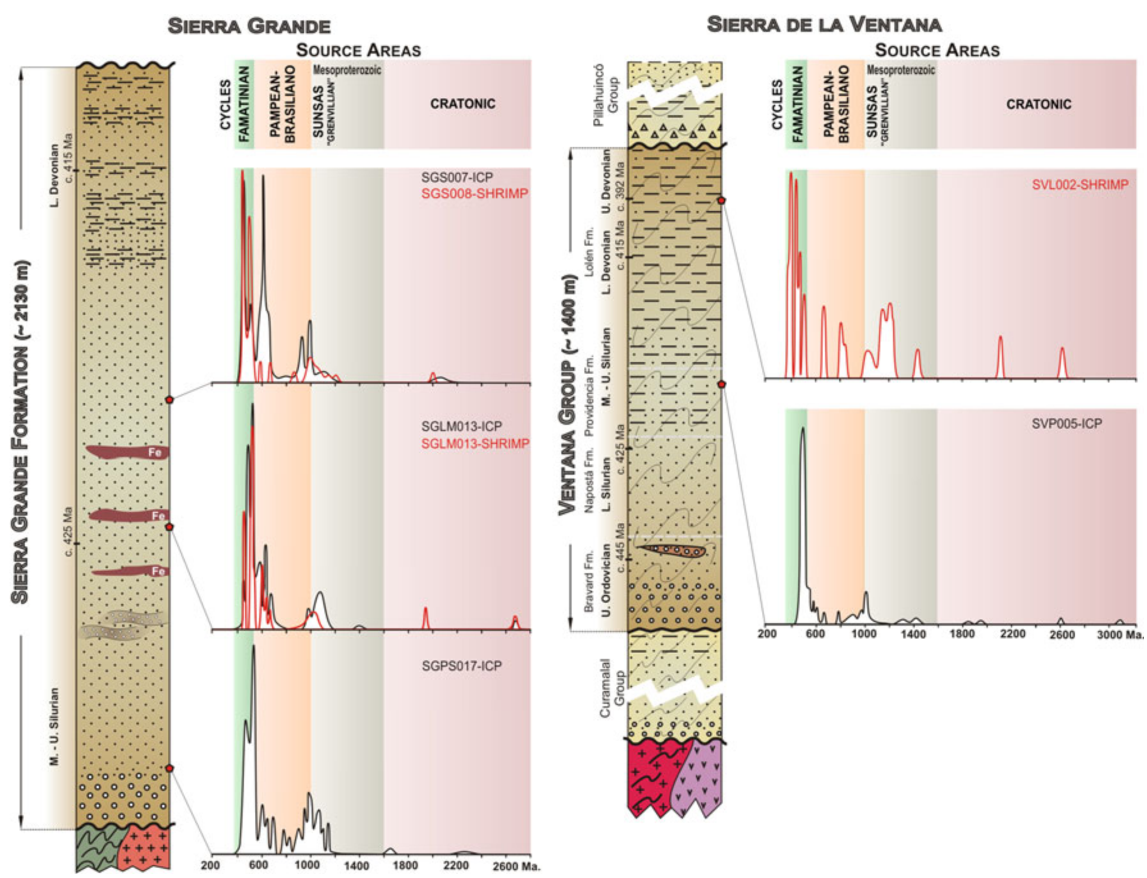


Fig. 11 Synthesis and comparison analysis of the Sierra Grande and Ventana studied samples with frequencies and the main source ages (cycles) recognized: Cratonic, Mesoproterozoic, Brasiliano–Pampean and Famatinian. In *black lines* by ICP-LA and in *red lines* by SHRIMP sample analyses. See "Discussion" in text

4. The Lolén Formation-studied sample of the upper part of the Ventana Group shows a different U–Pb age pattern compared with all other samples. It shows mainly Late Famatinian and Mesoproterozoic detrital zircon clusters and the presence of Neoproterozoic and Paleoproterozoic zircon ages as secondary peaks. This indicates that important changes regarding tectonic history of the depocenter during Middle-Upper Devonian occur. The youngest zircon age is 387 Ma (maximum sedimentation age).
5. A few contributions from Archean to Paleoproterozoic sources were found. This means that the Río de la Plata/Kaapval cratons were not a main source for detritus input to the basins during Silurian–Devonian times.
6. Detrital zircon patterns of both regions suggest that the detritus were derived from Gondwanan sources and from terranes accreted during the Pampean (Brasiliano–Pan-African) and Famatinian orogenic cycles.

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Appendix 1

Sierra Grande Formation

The unit is predominantly composed of mature quartz-rich sandstones interlayered with shales, subordinated conglomerates and the classic oolithic iron horizons. The maximum thickness of the unit is about 2,130 m and was subdivided in three members known, from base to top, as Polke, San Carlos and Herrada (Zanettini 1981, 1999). The most abundant lithological type is light-colored, quartz and mica-rich sandstone. However, iron-rich sandstones and wackes are also present. Cross-stratification and ripple-marks were recognized. The quartz-rich sandstone layers can easily be followed in the mountain landscape, being therefore useful as key-levels. Sandstone and interbedded shale colors vary between white, gray and brown, often associated with red oolithic iron-mineralized horizons. The presence of mica-rich sandstones and wackes become more conspicuous toward the western outcrops, near the "Yacimiento Sur" and Loma de los Fósiles (Fig. 3). Conglomerates and coarse facies sandstones occur in the base of the unit at the eastern Atlantic side of the region. The unit was developed in an open marine environment, with shallow deep shelf areas dominated by processes of waves and storms. Offshore sedimentation was governed by conditions of good weather and storms represented by the heterolithic facies (Huber-Grünberg 1990; Spalletti et al. 1991; Spalletti 1993). The environmental characteristics of shallow water and low rate of sedimentation, warmer paleoclimatic conditions and a general high sea level stage favoured the iron concentrations. The coastline would have developed with NW–SE direction (Spalletti 1993). After Rossello et al. (1997), the tectonic evolution can be considered as part of a large-scale intracontinental deformation in SW Gondwana inboard of an Andean-type compressive margin. This deformation is characterized by transpression combined with overthrusting to the NE and N–S horizontal contraction. Marine invertebrates (brachiopods, gastropods, trilobites, bivalves and conularids) and certain ichnofossils had been recorded mainly at the Loma de los Fósiles and "Yacimiento Este" areas (Müller 1965; Manceñido and Damborenea 1984; Spalletti et al. 1991). The faunistic record assigned a Middle-Upper Silurian to Lower Devonian age to the Sierra Grande Formation where Wenlockian biozones and endemic components related to the Malvinokaffric realm had been also recognized. Furthermore, the stratigraphical position of the Sierra Grande Formation is constrained by the Ordovician isotopic age of the granitoids from the Punta Sierra Plutonic Complex that intrude the Neoproterozoic–Cambrian basement (Varela et al. 2008).

Appendix 2

Upper Ventana Group

The Providencia Formation shows an increase in the amount of fine-grained rocks; although pink and reddish to whitish gray-colored quartz-rich sandstones is still the dominant lithotype. The layers are mainly massive but cross-stratification is also observable along the 300-m-thick sequence. The Silurian age (Rodríguez 1988) for this unit was stratigraphically constrained. The Lolén Formation with a 450- to 600-m-thick (Harrington 1972, 1980), which comprises a variety of more immature lithologies: quartz-rich sandstones, feldspar–quartz-rich and mica-rich sandstones and wackes (Andreis 1964b; Massabie and Rossello 1984), coarse sandstones and conglomerates to fine pebbles are also present in the unit. Fine-grained rock levels are irregularly distributed throughout the sequence and micaceous black shales are partly metamorphosed into slates. Brachiopod molds identified as *Cryptonella* sp. cf. *baini*, *Schellwienella* sp. and others representative of the Malvinokaffric realm were recorded 100 m above the bottom of the unit (Harrington 1972, 1980), allowing to assign these levels to the Lower Devonian (Andreis 1964a), similarly to other Gondwanan regions (Bokkeveld Group in the Cape Fold Belt or Fox Bay Formation in Malvinas). Cingolani et al. (2002) described the first record of fossil plants in upper reddish levels of the unit, recognizing *Haplostigma* sp. and *Haskinsia* cf. *H. colophylla*, suggesting the Middle Devonian age and a shallowing up ('continentalization') sedimentary process.

Appendix 3

Detrital zircon U–Pb and Lu–Hf methodologies

The detrital zircons were obtained after the classical processes of crushing and sieving of about 3–5 kg of each sample. The fractions retained in less than 140-micron mesh were separated using hydraulic processes to obtain heavy minerals pre-concentrates. These pre-concentrates were treated with bromoform ($\delta = 2.89$) to obtain the complete heavy mineral spectra. Methylene iodide ($\delta = 3.32$) was used to obtain a fraction enriched in zircons, followed by an electromagnetic separation with a Frantz Isodynamic equipment when necessary. The final selection of individual crystals was done by handpicking under a binocular microscope. For isotopic dating, all zircon grains were mounted in 2.5-cm-diameter circular epoxy mounts and polished down until the zircons were just revealed. Images of zircons were obtained using the optical microscope (Leica MZ 125) and backscatter electron microscope (JEOL JSM 5800). Zircon grains were dated with a laser ablation microprobe (New Wave UP213) coupled to a MC-ICP-MS (Neptune) at the Laboratorio de Geología Isotópica, Universidade Federal do Río Grande do Sul, Porto Alegre, Brazil. Isotope data were acquired using static mode with spot sizes of 25 and 15 μm. Laser spots for U–Th–Pb selection were guided by internal structures as seen in SEM images of the mounted and polished grains. Laser-induced elemental fractional and instrumental mass discrimination were corrected by the reference zircon GJ-1 (Simon et al. 2004), following the measurement of two GJ-1 analyses to every five-sample zircon spots. The external errors were calculated after propagation error of the GJ-1 mean and the individual sample zircon (or spot). The laser operating conditions were laser output power of 6 J/cm^2 and a shot repetition rate of 10 Hz. The cup configuration of the MC-ICP-MS Neptune was Faradays ^{206}Pb, ^{208}Pb, ^{232}Th, ^{238}U, MIC's ^{202}Hg, ^{204}Hg + ^{204}Pb, ^{207}Pb. The gas input included a coolant flow (Ar) at 15 l/min, an auxiliary flow (Ar) at 0.8 l/min and a carrier flow of 0.75 l/min (Ar) + 0.45 l/min (He); the acquisition was at 50 cycles of 1.048 s. For the interpretation of the detrital zircon ages, only concordant or nearly concordant (less than 10% discordant) data were considered.

U–Pb SHRIMP analyses were undertaken on SHRIMP II and RG of the Research School of Earth Sciences of the Australian National University, Canberra, Australia. Zircon crystals were handpicked, mounted in epoxy resin, ground to half-thickness and polished with 3- and 1-μm diamond paste; a conductive gold-coating was applied just prior to analysis. The grains were photographed in reflected and transmitted lights, and cathodoluminescence (CL) images were produced in a scanning electron microscope in order to investigate the internal structures of the zircon crystals and to characterize different populations as well. SHRIMP analytical procedures followed the methods described in Compston et al. (1984) and Williams (1998). The standard zircon SL13 was used to determinate U concentration, and the U–Pb ratios were referenced to the zircon standard FC1. Raw isotopic data were reduced using the Squid program (Ludwig 2001), and age calculations and Concordia plots were done using both Squid and Isoplot/Ex software (Ludwig 2003). Analyses and ages for individual SHRIMP spots are listed in the data tables and plotted on Concordia diagrams with 1σ uncertainties. Where data are combined to calculate an age, the quoted uncertainties are at 95% confidence level, with uncertainties in the U–Pb standard calibration included in any relevant U–Pb intercept and Concordia age calculations.

The Hf isotope determinations of zircon grains by LA-ICP-MS were performed at the Laboratory for Isotope Geology, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil. A Neptune MC-ICP-MS (Thermo Finnigan) was used to measure Lu, Yb and Hf isotopic signals. The mass spectrometer contains 9 Faraday collectors to detect simultaneously the isotopes required for this methodology. The laser ablation system used in this study was a New Wave Research 213 UV. To obtain further improvements in precision of the Hf isotopic data from zircon material with 40-μm ablation pit size, a N_2 mixing technique was applied (Iizuka and Hirata 2005). In order to optimize the N_2 gas flow rate, the effect of the N_2 gas flow rate on elemental sensitivity was investigated, varying the N_2 gas flow rate using the zircons GJ-1. Signal intensities for three isotopes (^{179}Hf, ^{175}Lu and ^{173}Yb) obtained from zircon standards increased with N_2 gas flow rate. For the corrections in isobaric interferences of Lu and Yb isotopes on mass 176, the isotopes ^{171}Yb, ^{173}Yb and ^{175}Lu were simultaneously monitored during each analysis. The ^{176}Lu and ^{176}Yb were calculated using ^{176}Lu/^{175}Lu of 0.026549 and $^{173}Yb/^{171}Yb$ of 1.123456 (Chu et al. 2002; Thirlwall and Walder 1995). The correction for instrumental mass bias used an exponential law and a $^{179}Hf/^{177}Hf$ value of 0.7325 (Patchett et al. 1981) for correction of Hf isotopic ratios. Data were corrected and normalized following the procedure of the laser ablation analyses, in the excel sheet. Each analysis session has the βHf and βYb factors, and in each zircon analysis, we calculate a new βHf and βYb cycle. The mass bias behavior of Lu was assumed to follow that of Yb. It has been noted before that the Yb interference correction is crucial for precise and accurate $^{176}Hf/^{177}Hf$ obtained by laser ablation analysis (Woodhead et al. 2004).

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