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NEW INSIGHTS ON THE INTERPRETATION OF THE PROVENANCE AND EVOLUTION OF THE SILURIAN UNITS IN THE CENTRAL PRECORDILLERA, ARGENTINA.

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ABSTRACT

In the central region of the Precordillera, San Juan Province, Silurian silicoclastic sedimentites of the Los Espejos Formation crop out in the Jáchal River area. To the south of this region, an equivalent unit is recognized in the San Juan River area (Tambolar Formation). Both units present similar lithological characteristics, however, it has not yet been defined if they share source areas of detrital contributions. On the other hand, for the Jáchal River sector, it is proposed to establish if there were changes in the regions from where the sub-basin received sediment contributions during the Devonian, which can be seen reflected in the detrital zircon contribution patterns of the overlying unit (Talacasto Formation). The present work is part of a series of studies tending to determine the nature and provenance of the Silurian-Devonian sequences of the Central Precordillera. On this occasion, detrital zircon patterns of the detrital sources of the Los Espejos Formation are analysed and compared with the information obtained for the Silurian Tambolar Formation

(San Juan River area) and the overlying Devonian Talacasto and Punta Negra formations (Jáchal and San Juan rivers areas). To characterize and compare the studied units, different methodologies were applied, namely sedimentary petrography, heavy minerals studies, and morphological and isotopic analyses of detrital zircons. The analysis of thin sections allowed determining textural and compositional parameters. Through the predominance of detrital minerals, it was possible to establish that the studied units are composed of quartzite-type rocks coming from mature areas, with low percentages of lithic components and abundant opaque heavy minerals of the hematite group. The study of heavy minerals, especially morphological and typological parameters of detrital zircons, allowed to establish recycled and plutonic sources as main modes, as well as the changes that occurred during the basin filling dynamics for Silurian and Devonian times. On the other hand, U-Pb isotopic analysis in detrital zircons indicate that the Pampean-Brasiliano orogenic cycle composes the main source of detritus with ages between 511 and 816 Ma. In second place are the Mesoproterozoic ages, represented by the interval from 1000 to 1350 Ma. The youngest detrital ages show a maximum sedimentation age of 478.5 ± 4.4 Ma (Tremadocian), indicating that younger sources of contribution correspond to the Famatinian Orogen. The Kolmogorov-Smirnoff test revealed that the studied Silurian-Devonian units have similar patterns of sedimentary contributions, which suggests that the sources of provenance were common in both regions and remained active throughout the entire time interval, without significant changes.

Keywords: U-Pb geochronology; Lu-Hf isotopes; detrital zircons provenance; Los Espejos Formation; Cuyania terrane; South West Gondwana.

1. INTRODUCTION

The Paleozoic sequences of the Argentinian Precordillera have been extensively studied from different approaches, mainly sedimentological and paleontological (Arnol et al., 2022 and references therein). The pioneering works to the understanding of sedimentary provenance in the area correspond to Loske (1992, 1994 and 1995) and Kury (1993), who approach different methodologies applied to units of the San Juan and Mendoza provinces. However, analysis of sedimentary provenance evolution are still scarce due to the great exposures of sequences that form part of the Precordillera (Keller, 1999). The Precordillera, as a geological province, was divided into three sub-provinces according to their structural and stratigraphic characteristics: Eastern, Central and Western (Baldis, 1970; Baldis et al., 1981; Ortiz and Zambrano, 1981; Fig. 1). Contributions regarding the sedimentary provenance of exposed lower Paleozoic units of the Eastern Precordillera have been provided by Naipauer et al. (2010) and Abre et al. (2012), given the petrographic, geochemical and isotopic information. Through different methodological approaches, the basal unit of the Tucunuco Group (La Chilca Formation) of the Central Precordillera was analyzed by Abre et al. (2012), while the Gualilán Group and the Tambolar Formation were recently studied by Arnol et al. (2020, 2022). Regarding the Western Precordillera, Abre et al. (2012) studied the Ordovician units, while Giunta et al. (2022) recently provided new information of the Ordovician to Devonian units. Finally, in the Mendoza Precordillera, Cingolani et al. (2013) provided U-Pb ages of the Devonian Villavicencio Formation, while Wenger et al. (under review) performed a more complete provenance analysis of this unit.

This contribution aims to improve the knowledge of the characteristics of the Silurian successions exposed in the Central Precordillera, particularly in the Jáchal River area, combining different methodologies in order to elucidate the evolution of the sedimentary basin, the provenance of the detrital sources and their relationship with the overlying Devonian succession.

2. GEOLOGICAL SETTING AND STRATIGRAPHY

The Precordillera is part of the so-called Cuyania terrane (Ramos et al., 1986), for which a Laurentian origin has been attributed (Ramos et al., 1986; Astini et al., 1995; among others) and that would have collided with the western edge of Gondwana during the Middle Ordovician (Vujovich et al., 2004). The collision produced an abrupt increase in the subsidence (drowning) of the platform that was developing at that time. This event was recorded by a gradual transition from shallow carbonate facies to dysoxic and anoxic facies (Astini, 1992; Astini et al., 1995).

In the Central Precordillera, Silurian-Devonian silicoclastic marine sequences crop out, which lie on the Ordovician carbonate platform. During Silurian times, the Central Precordillera recorded the Tucunuco Group (Cuerda, 1969), which includes, from base to top, the La Chilca and Los Espejos formations. The Silurian sequence crops out from the north of Jáchal River to Sierra de la Deheza, being its type locality in the Cerro La Chilca (Cuerda, 1965). This group has its maximum thickness to the north of the basin, where it reaches 600 meters and is mainly composed of psamo-pelitic strata (Sánchez et al., 1991), being arranged in erosive unconformity on the carbonate platform.

After the drowning of the carbonate platform known as the San Juan Formation, Silurian sedimentites of the La Chilca Formation are exposed in erosive discordance, mainly composed of psamo-pelitic strata (Astini, 1992; Astini et al., 1995). The La Chilca Formation is lithologically characterized by a ca. 20 cm thick basal conglomerate composed of chert clasts, followed by laminated dark beds with abundant graptofauna. Upwards, the deposits become thicker, with a rhythmic deposition, increasing the sand-pelite ratio in the upper part and observing that the sand strata coalesce towards the northern sector of the basin, increasing its thickness (Astini and Maretto, 1996), which does not exceed 200 meters. The temporal range goes from the Hirnantian to the Llandoverian (Cuerda et al., 1988; Lenz et al., 2003). For its part, the Los Espejos Formation is characterized by the occurrence of a ferruginous basal conglomerate, covered by green and purple shales that alternate with silt up beds, followed by shales and olive-green sandy shales, finely stratified and with the presence of graptolites, tentaculites, brachiopods and trilobites. The sand content increases to the top, forming a coarsening- and thickening-upward strata arrangement. They also contain levels of tabular coquinas of autochthonous or para-autochthonous origin. The unit is usually covered by amalgamated sandstones sequences in the North and Central sections. The shales are strongly bioturbated, recording the *Cruziana* ichnofacies. The maximum thickness reached in the northern sector of the basin (Cerro del Fuerte and Loma de Los Piojos area) is around 500 meters, while towards the south does not exceed 25 meters (Astini and Maretto, 1996; Benedetto et al., 1996).

Towards the south, in the San Juan River section, equivalent deposits of the Tambolar Formation (Bracaccini, 1949; Heim, 1952) crop out, being its type section in Portezuelo del Tambolar, on the old road that linked the San Juan and Calingasta localities. For this region, Arnol et al. (2022) highlighted that the unit is characterized by having a high percentage of rounding of its detrital zircons, although the original characteristics are not obliterated. A domain of zircons derived from plutonic sources is observed over the metamorphic ones, where the most representative ages are Neoproterozoic, followed by Mesoproterozoic ages. The presence of Famatinian ages, as well as the low and null proportions of Paleoproterozoic and Archean ages, respectively, are conspicuous for this unit.

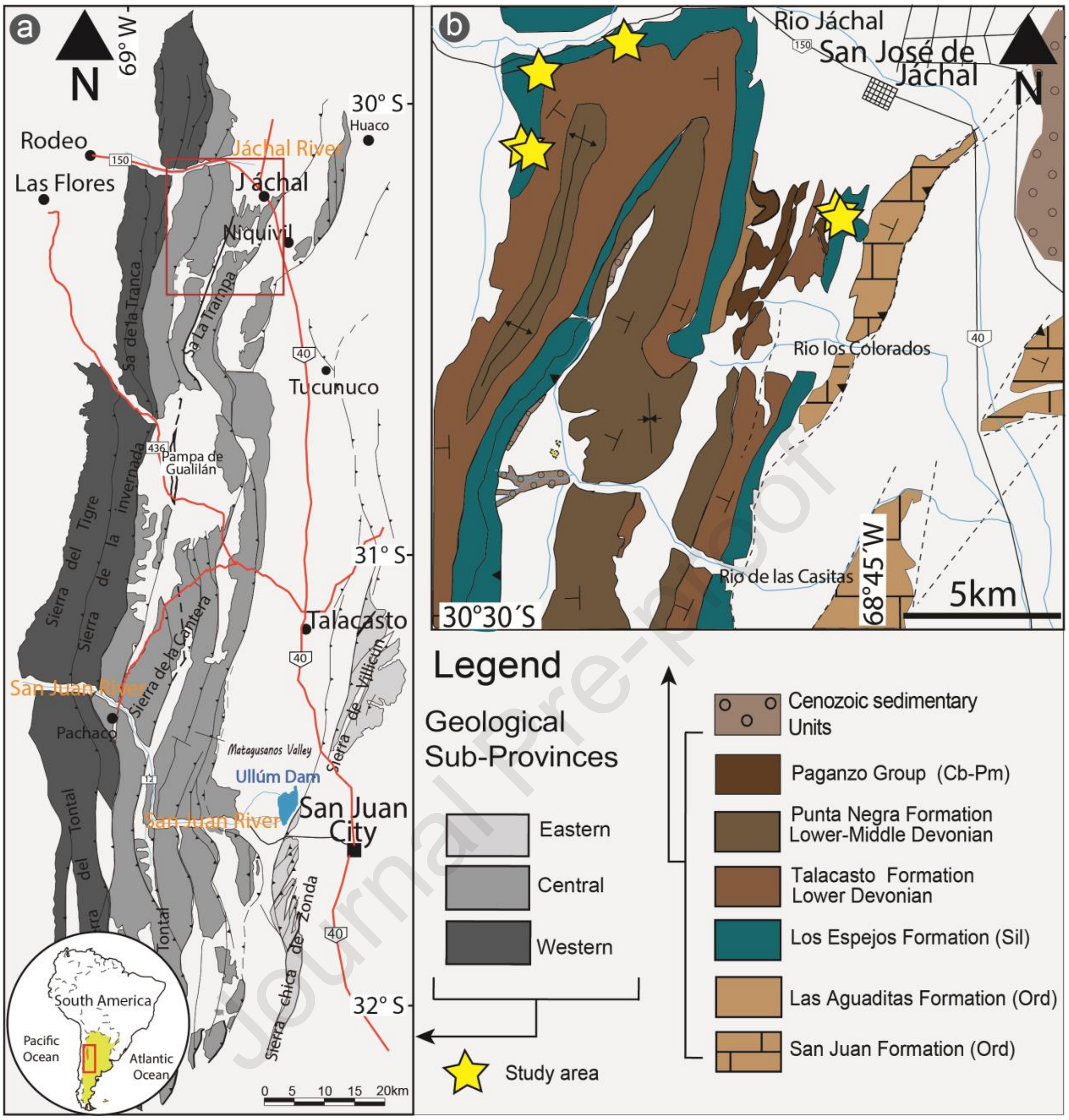


Figure 1. a) Tectonic subdivision of the San Juan Precordillera. **b)** Detailed map of the area studied in this work. Sampling locations represented as yellow stars. Modified from Astini (1992) and Arnol et al. (2020, 2022).

3. SAMPLING AND METHODOLOGY

The Los Espejos Formation was studied in two different sections, near the San José de Jáchal locality. In order to obtain relevant information regarding each section, petrographical, morphological (detrital zircon), geochronological (U-Pb) and isotopic (Lu-Hf) studies were carried out (Table 1).

Table 1 Coordinates and analysis carried out on samples studied in this work.

Sample	Latitud	Longitud	Methodology
16LE12	30°17'49.69"S	68°46'21.49"W	Petrography
16LE13	30°17'49.26"S	68°46'18.76"W	Petrography
16LE22	30°15'30.84"S	68°56'14.79"W	Petrography
16LE25	30°15'35.42"S	68°56'9.32"W	Petrography
16LE26	30°13'11.96"S	68°55'15.77"W	Petrography
16LE29	30°12'35.25"S	68°53'7.95"W	Petrography, Zr morphology, U-Pb and Lu-Hf

3.1 Petrography

Six thin sections of sandstones were studied under the microscope and quantitatively analyzed with a Swift-type point counter. Using the traditional method of Gazzi-Dickinson, 400 points were counted (Ingersoll et al., 1984). Classic procedures for petrographic classification of rocks were followed, applying the schemes proposed by Garzanti (2016). The ternary diagrams of Dickinson et al (1983) were used for the sedimentary provenance studies. The results were integrated with data from the same or equivalent units published in previous works. The populations represented in each triangle include detrital grains, except for micas, opaque minerals, chlorite, heavy minerals and carbonate grains. Chert was counted as a sedimentary lithic clast. Petrographic assessment (textural and optical characteristics of minerals as well as paragenetic associations) allows establishing the tectonic sedimentary environment using classic discrimination diagrams.

3.2 Detrital zircon analysis

Sample 16LE29 was processed by physical methods (crushing, milling, and sieving) to collect heavy minerals by classical concentration methodologies. The zircon grains were identified and hand-picked under the binocular microscope (ZEISS Stemi 2000-C model). Morphological and typological studies on the zircon crystals were carried out with a Scanning Electron Microscope (JEOL JSM 6360 LV) at the *Museo de La Plata* according to the procedures applied by Gärtner et al. (2013) to determine the main morphological populations and the preliminary provenance of the detrital sources (Dickinson and Gehrels, 2003). The Pupin (1980) classification was used to expand the interpretations of euhedral zircons. The morphological parameters identified on zircons were compared with the data presented by Arnol et al. (2020) and Cretacotta (2022) for Silurian-Devonian sequences of the San Juan Precordillera.

Selected zircon grains were mounted in epoxy resin and their internal structures were exposed by polishing for cathodoluminescence imagery and dating. The U-Pb and Lu-Hf data were obtained at the Centro de Pesquisas Geocronológicas (CPGeo) of the Universidade de São Paulo, Brazil, with a Thermo Fisher Neptune LA multicollector ICP-MS equipped with a 193 Photon laser system.

3.2.1 U-Pb analysis

Each analysis was composed of 40 sequential measurements (of approx. 1s of integration each) in the ICP-MS "Neptune", 10 with the laser off (to obtain the instrumental blank) and 30 under the ablation of the excimer laser "Analyte Excite". 7 isotope signals were measured simultaneously, 4 in Faraday cups (of greater amplitude): ^{206}Pb, ^{208}Pb, ^{232}Th, ^{238}U and 3 in MICs ("Multiple Ion Counters" of greater sensitivity): ^{202}Pb, ^{204}Pb and ^{207}Pb. At the end of each measurement sequence, the mean value of the instrumental blank is immediately subtracted from each of the seven isotope signals. The signal of the isotope ^{235}U is not measured but obtained mathematically, dividing the signal ^{238}U by the relative abundance 238/235 (= 137.88). The participation of Hg (of the carrier gas) in signal ^{204}Pb was discounted by subtracting from it the quotient: signal ^{202}Pb / relative abundance 202/204 (= 4.355). Using the ratios: $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ and $^{208}Pb/^{232}Th$ as age estimates and the Stacey-Kramers (1975) formulas, the relative abundances (variables with geological age) were calculated: 206/204, 207/204 and 208/204. The "common Pb" (non-radiogenic) fraction of the isotopes: 206, 207 and 208 is then discounted by subtracting the 204 from each of them multiplied by their respective relative abundance: 206/204, 207/204 and 208/204. Analysis of the GJ-1 standard were redone every 10 minutes to correct errors and/or variations in the instrument of subsequent samples. The comparison between tabulated and measured GJ-1 values provides: The (multiplicative) coefficients used to convert the three total signals: Pb (204 + 206 + 207 + 208), Th (232) and U (235 + 238) in ppm. The fractionation correction factors of the four ratios: 206/238, 207/235, 207/206 and 208/232 before these were finally used to calculate the (respective) ages. All the LA-ICP-MS U-Pb zircon data are shown in the supplementary material.

3.2.2 Lu-Hf analysis

Each Lu-Hf analysis consists of 40 sequential measurements performed in the ICP-MS: 10 with the laser off (measurement of instrumental blank) and 30 with the laser on (laser ablation on GJ-82C and 91500 standards, or the analyse). Each measurement lasts approximately 1 second. Eight isotopes were measured simultaneously using only Faraday cups: 172, 173, 174, 175, 176, 177, 178, and 180. At the end of each sequence of measurements, the value of the instrumental blank is subtracted from each of the eight isotope signals. Abundance values published by the IUPAC (https://ciaaw.org/pubs/TICE-2009.pdf) were then used to calculate the isotopic ratios between the Yb (172, 173, 174, 176), Lu (175, 176), and Hf (176, 177, 178, 180) signals. Signals 172, 173, and (part of) 174 were used to calculate the fractionation coefficient of Yb (βYb) using exponential law. Signals 180, 178, 177, and (part of) 174 were used to calculate the fractionation coefficient of Hf (βHf) also using exponential law. As Lu does not have enough isotopes to allow self-correction, the fractionation coefficient of Lu is assumed to be: βLu = βHf. The 176Hf/177Hf ratio can then be readily obtained after subtracting the two interferences: 176Yb (estimated via βYb) and 176Lu (estimated via βLu) from the 176 total signal. Before and after the analysis, blanks and zircon standards GJ-82C and 91500 were measured. The analyses of the standards were repeated at regular intervals in order to correct the errors and/or variations of the equipment in the following measurements. Liu et al. (2010) reported an 176Hf/177Hf value of 0.282015 ± 0.000025 for the GJ-82C standard, while Woodhead and

Hergt (2005) reported an 176Hf/177Hf value of 0.282306 ± 0.000006 for the 91500 standard. The 176Hf/177Hf values obtained for these standards at the CPGeo during the analysis period were 0.282015 ± 0.000025 (GJ-82C) and 0.282054 ± 0.000020 (91500). The parameters εHf and T_{DM} are then finally calculated using the formulas of Yang et al. (2007). All the LA-ICP-MS Lu-Hf zircon data are shown in the supplementary material.

4. RESULTS

4.1 Petrography

Given that the analyzed samples show similarities according to their petrographic characteristics, a general description is provided for characterize them.

The Los Espejos Formation is represented by medium-grained rocks, with a moderate selection of its components inferred from their subangular to angular edges. These rocks are mainly composed of monocrystalline quartz grains, mostly with undulose extinction, with sutured edges between crystals, triple junctions and, in some cases, with embayments. Polycrystalline quartz is of small size and is found in low proportion, making it difficult to identify. Plagioclase constitutes a secondary detrital component, with subangular crystals slightly altered to carbonates at its edges and showing the classic polysynthetic twinning. Potassium feldspar is totally altered to carbonates forming a pseudomatrix. Micas are scarce. Muscovite appears as disperse detritus, while biotite occupy holes left by other minerals and is sometimes deformed. Accessory minerals include small concentrations of magnetite and hematite forming mantles (Fig. 2). In the opaque minerals concentrations, abundant translucent heavy minerals are present, with zircon, apatite and rutile as the main minerals. The cement is composed by illitic clay on the one hand, surrounding the crystals of the aforementioned minerals and forming an incomplete ring, while on the other hand, carbonate cement is observed replacing feldspars, both partially (K-feldspar and plagioclase) and completely (K-feldspar). It is defined as a macrosparitic cement that in some sectors behaves like a poikilotropic. A third type of cement is composed of a light brownish sericite filling the rock pores.

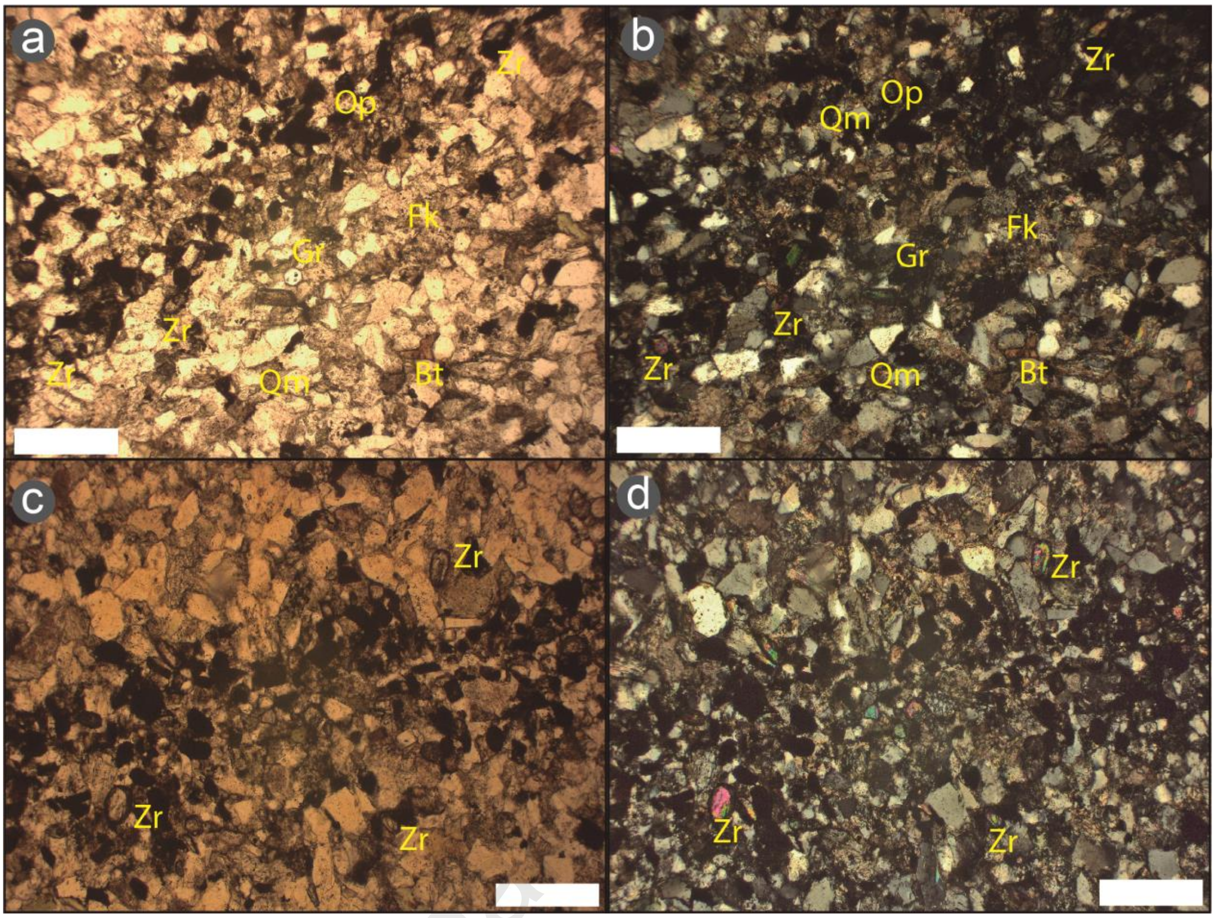
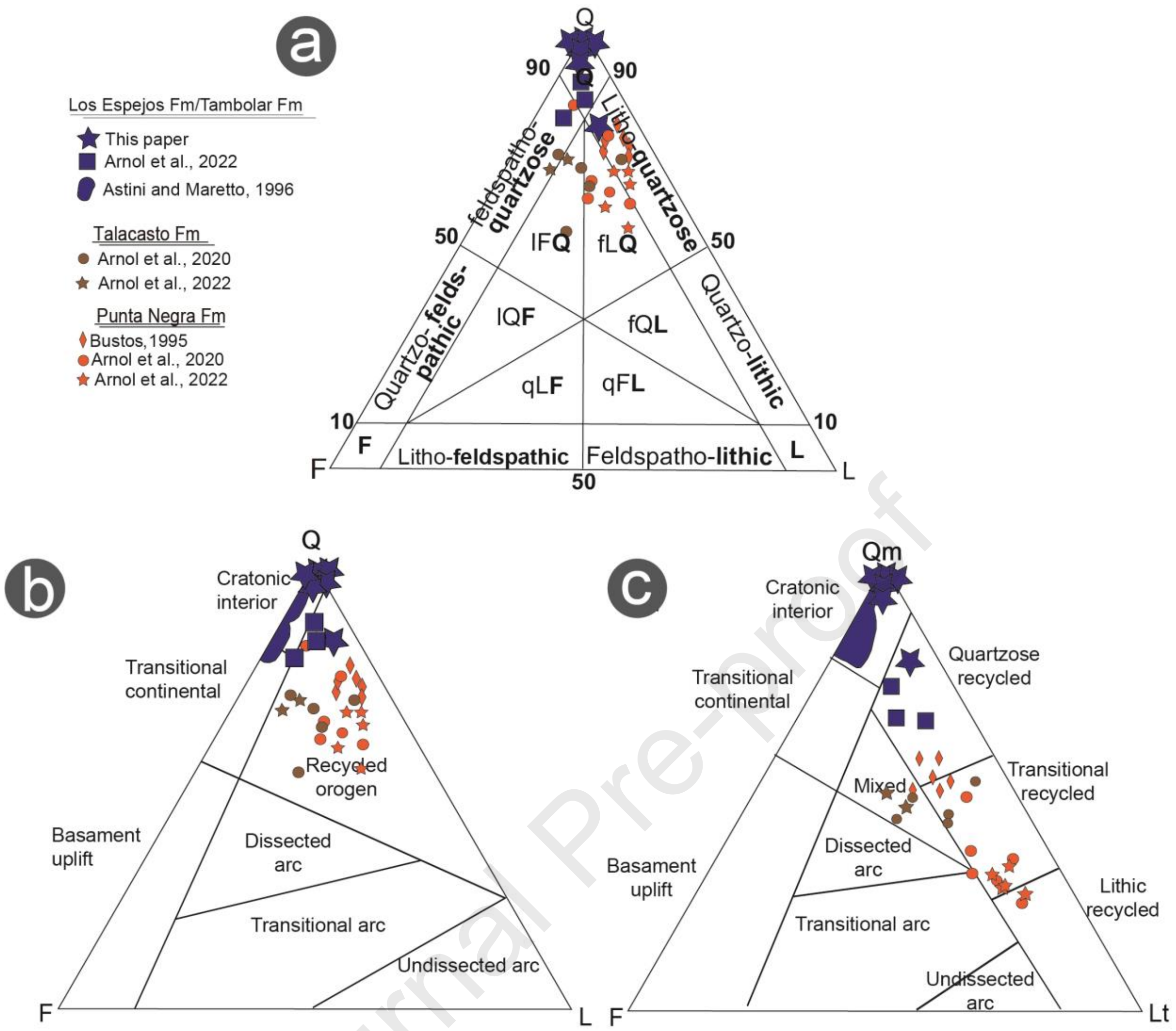


Figure 2. Microphotographs of the Los Espejos Formation samples. Scale bar: 200 micrometers. Detail of the mantles where opaque and heavy minerals are concentrated. The rest of the elements are difficult to visualize because of the small grain size. Qm: monocrystalline quartz, Fk: K-feldspar, Bt: biotite, Gr: garnet, Zr: zircon, Op: opaque mineral. a, c) with parallel nicols. b, d) with crossed nicols.

According to the diagram of Garzanti (2016), the studied samples mainly fall in the quartzose field, except for one sample which falls in the Litho-quartzose field (Fig. 3a). The same samples mainly fall in the cratonic interior fields of the QFL (Fig. 3b) and QmFLt (Fig. 3c) diagrams of Dickinson et al. (1983), except for one sample which falls in the quartzose recycled field of the last diagram.

251 

252 **Figure 3. a)** Ternary diagrams of lithological classification according to Garzanti (2016). **b, c)**
253 Provenance diagrams of Dickinson et al. (1983). Q: quartzose, F: Feldspathic; L: lithic; lF**Q**:
254 litho-feldspatho-quartzose; lQ**F**: litho-quartzo-feldspathic; fL**Q**: feldspatho-litho-quartzose;
255 fQ**L**: feldspatho-quartzo-lithic; qF**L**: quartzo-feldspatho-lithic; qL**F**: quartzo-litho-feldspathic.

256 *4.2 Morphological analysis of zircons*

257 Forty-six photographs of detrital zircons were analyzed, of which 7 are euhedral grains, 19
258 subhedral and 20 anhedral (Fig. 4).

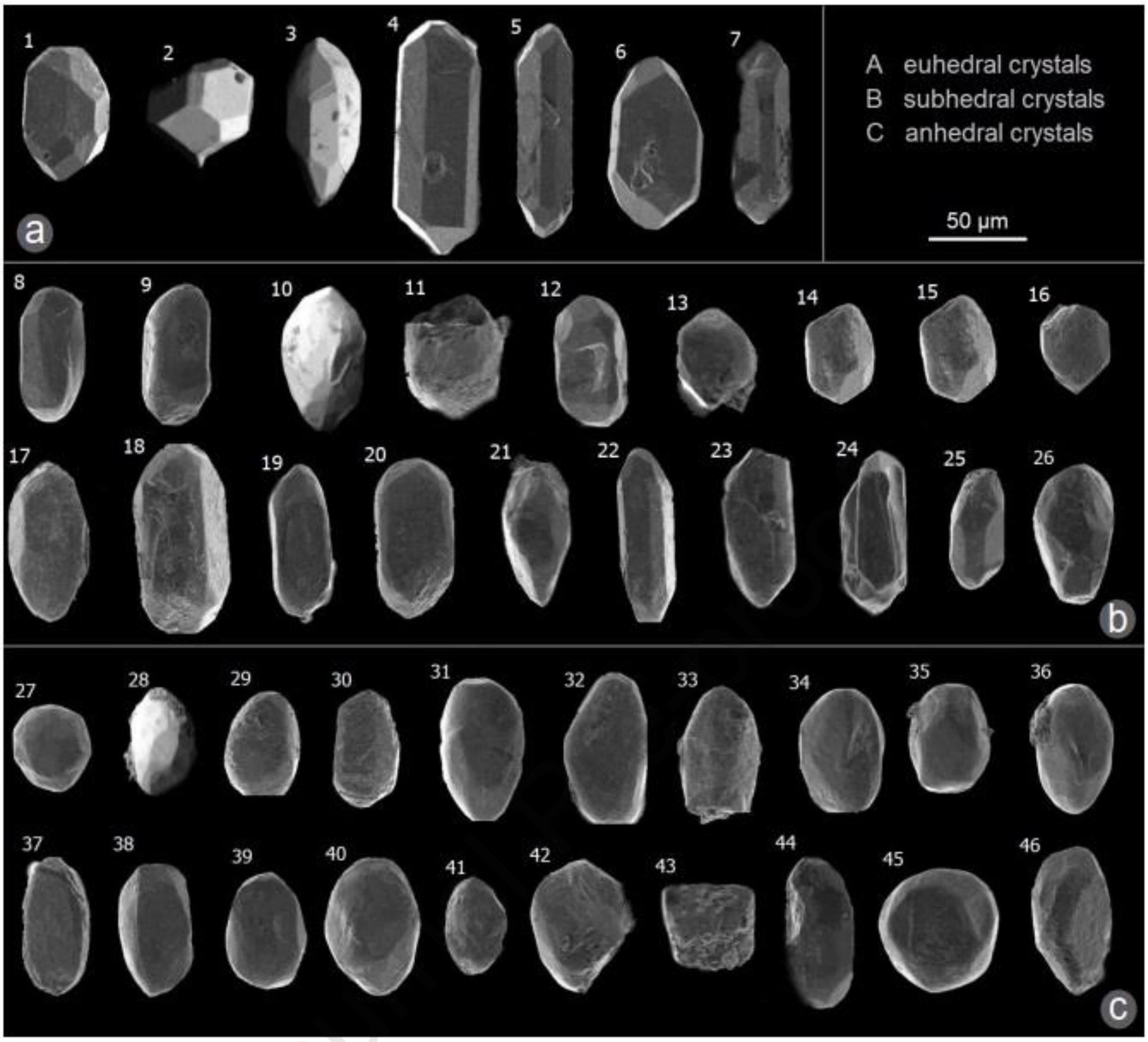


Figure 4. Detrital zircons from sample 16LE29 (Los Espejos Formation) labeled from 1 to 46. See text for information.

The size of the crystals is between 43.4 µm (n.43) and 131.9 µm (n.22) long, and between 37.0 µm (n.25) and 60.4 µm (n.40) wide (Fig. 4b, c).

The relationship between the length and width of the crystals is shown in Figure 5a, being crystal n.5 (Fig. 4a) the one with the greatest elongation, with 3.94 and corresponding to the long-prismatic class, and crystal n.43 (Fig. 4c) the one with lowest elongation, with 1.10 and corresponding to the short-stubby class.

The degree of crystals roundness is variable, ranging from completely unrounded to completely rounded (classes 1 to 10 in the classification of Schneiderhöhn, 1954), with classes 1, 2, 4 and 7 predominating over the rest (Fig. 5b). In this way, three main groups are recognized in the studied sample, suggesting different sources of contribution or degrees of transport.

Following the classification proposed by Mitterer (2001), three groups of zircons were defined according to their habit: stubby, stalky and prismatic. Taking into account their elongation, 61% are stalky, 28% stubby and 11% prismatic (Fig. 5c).

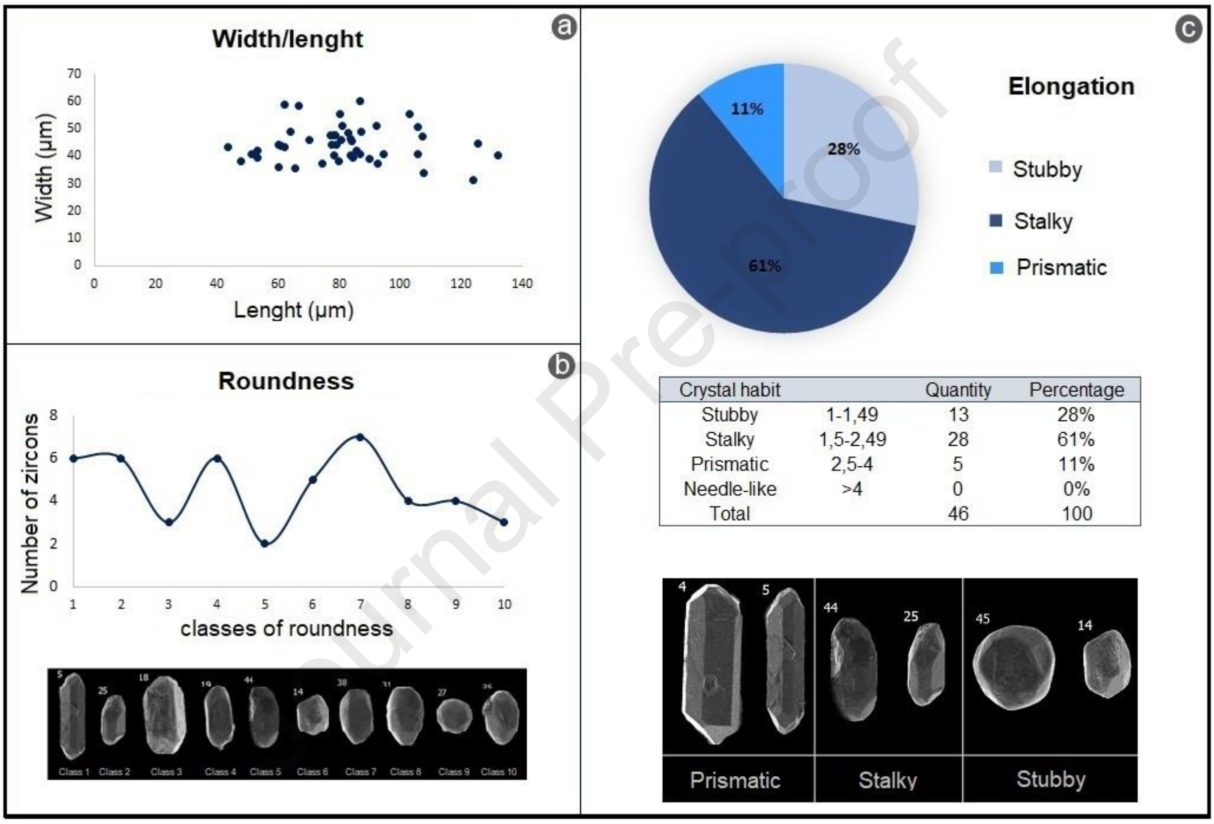


Figure 5. a) Length/width ratio of crystals. **b)** Number of zircons for each rounding class (Schneiderhöhn, 1954) with examples from the studied sample. **c)** Percentage of crystals for each elongation class (Mitterer, 2001) with examples from the studied sample.

The predominant surface features are collision marks and fractures. The crystals were classified following the work and classifications proposed by Gärtner et al. (2013 and references therein). In this way, it was recognized that these features are present in 45% of zircons, belonging the euhedral crystals to classes 1 and 2, and the subhedral and anhedral crystals to the four classes. In addition, 15% of zircons have fractures, with 4% and 11% of fractures parallel and perpendicular, respectively, to the *c* axis. Finally, only 3 zircons have visible cracks (n.20, 23 and 31; Fig. 4b, c).

Of the total zircon crystals analyzed, only 32% could be classified according Pupin (1980) because they preserved their crystalline faces. The crystals show a predominance of group P, accompanied by some crystals with morphotypes S, R, and D that could be associated with two feldspars granites.

4.3 U-Pb analysis in detrital zircons

To achieve a better understanding of the distribution of the recorded ages, they were grouped according to recognized orogenic cycles. The analysis of 87 detrital zircon grains reveals a polimodal trend (Fig. 6a). The main mode is represented by ages belonging to the Pampean-Brasiliano orogenic cycle (42.5%), of which 26.4% ages correspond to the Neoproterozoic and 16.1% to the early Cambrian. The Grenvillian orogenic cycle is represented by 28.7% grains with ages between 1354 and 1014 Ma (Ectasian-Stenian). The Famatinian orogenic cycle is represented by 16.1% grains with ages between 507 and 474 Ma (late Cambrian-Devonian). Famatinian ages are distributed as follows: 3.6% in the middle Cambrian, 5.7% in the late Cambrian and 6.8% in the Ordovician. Although a Devonian age (400 Ma) was recorded, this value was not considered in the percentage calculation due to its high common Pb (> 34%) and lack of concordance. The Paleoproterozoic and Archean are represented by 10.3% (2078 - 1624 Ma) and 2.4% (2642 - 2523 Ma) grains, respectively, and constitute the oldest ages (Fig. 6a, b).

From the peaks of ages generated by the youngest zircons, the maximum sedimentation age of this sample was calculated, giving a value of 478.5 ± 4.4 Ma (Tremadocian; Fig. 6c). This age is not consistent with the fossil record of the unit, corresponding to the Afro-South American fauna, mainly assigned to the upper Silurian, but would be indicating an important contribution from Ordovician sources at the time of deposition of the unit in the study region. Figure 6d shows the cathodoluminescence images of the analyzed zircons, where it can be seen that most of them present a concentric internal zonation, which allows them to be interpreted as plutonic zircons.

These U-Pb data have been subjected to the Kolmogorov-Smirnoff statistical analysis (K-S test), providing objective information of the degree of correlation between the different detrital zircon populations of the compared samples (Table 2).

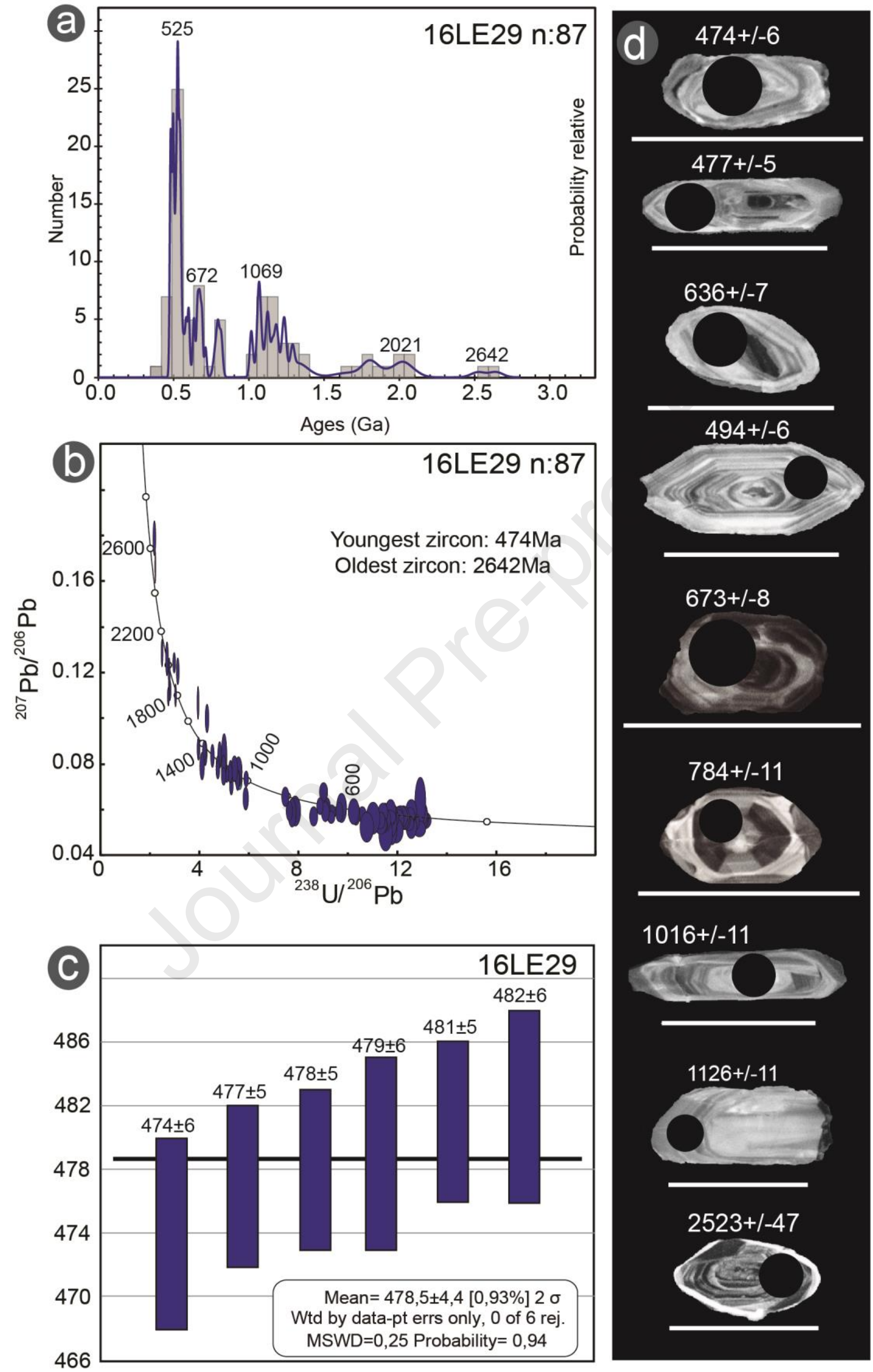
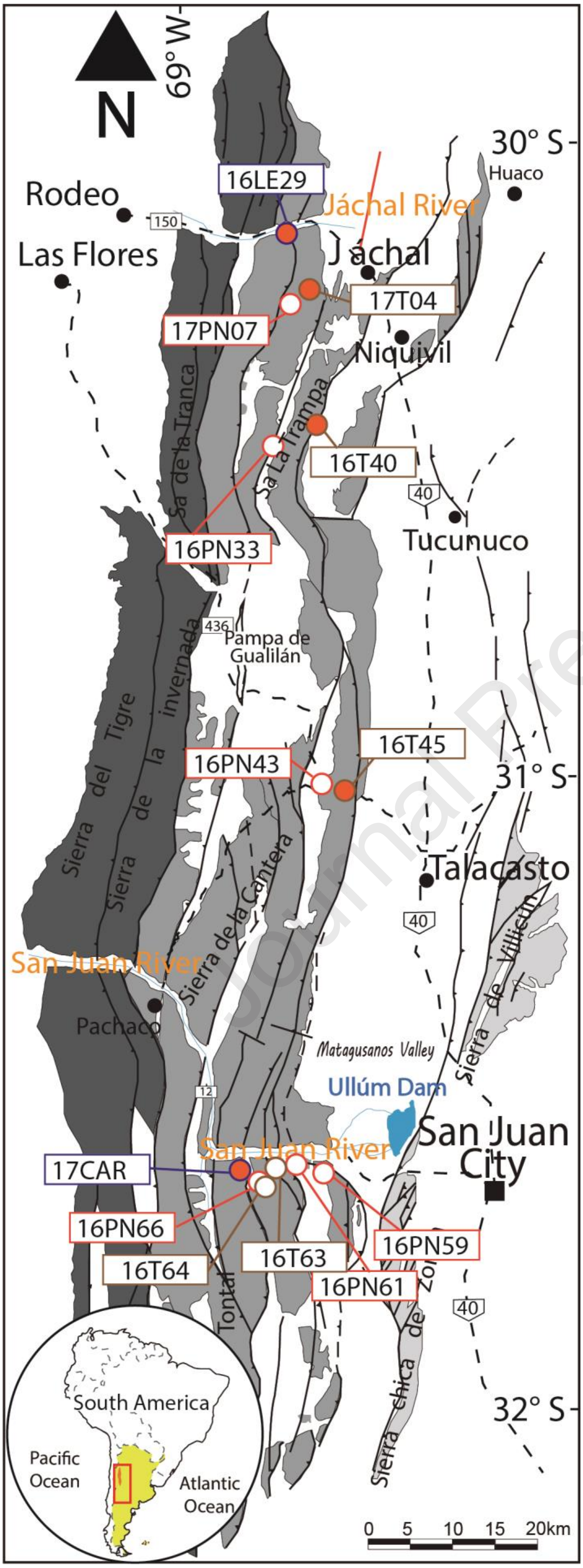


Figure 6. a) Relative probability diagram with U-Pb ages in detrital zircons for sample 16LE29 from the Los Espejos Formation. **b)** Tera-Wasserburg diagram. a and b were

generated with the programme Isoplot/Ex (Ludwig, 2008). **c)** Maximum sedimentation age (MSA) of sample 16LE29. **d)** Selected cathodoluminescence (CL) images, scale: 100 µm.

The Kolmogorov-Smirnov statistical test was performed comparing the Los Espejos Formation with one sample of the Tambolar Formation (Arnol et al., 2022). In addition, Silurian samples were compared with eleven samples of the Devonian Gualilán Group (Fig. 7; Arnol et al., 2020, 2022). From the K-S test (Table 2), a good correlation is observed between Silurian samples, despite the fact they belong to very distant sectors / areas. In Table 2 it is important to note that sample 16LE29 record a high correlation grade with samples of the Talacasto Formation, mainly with those of the Northern region and whit some samples of the Central region (Fig. 7). On the other hand, the Punta Negra Formation does not show any correlation (Fig. 7 and Table 2).

334 

N
69° W
30° S
31° S
32° S
Rodeo
150
Las Flores
16LE29
Jáchal River
Huaco
Jáchal
17T04
17PN07
Niquivil
Sa de la Tranca
Sa La Trampa
16T40
40
16PN33
Tucunuco
436
Pampa de Gualilán
Sierra del Tigre
Sierra de la invernada
16T45
16PN43
Sierra de la Cantera
Talacasto
40
San Juan River
Pachaco
Sierra de Villicum
Matagusanos Valley
12
Ullúm Dam
San Juan City
San Juan River
17CAR
16PN66
16T64
16T63
16PN59
16PN61
Tontal
40
Sierra chica de Zonda
South America
Pacific Ocean
Atlantic Ocean
0 5 10 15 20km

Figure 7. Distribution of the samples analyzed by the U-P method and compared by the K-S test in this work and those analyzed by Arnol et al. (2020, 2022). The filled circles represent the samples with positive values of correlation with the Los Espejos Formation, while the empty ones respond to samples that are not possible to correlate with the Los Espejos Formation.

In this way, it is possible to establish that the Los Espejos Formation share a common source with the Tambolar Formation and from the Talacasto Formation of the Northern region, near the town of San José de Jáchal and Quebrada de Talacasto area.

Formation	Los Espejos	Tambolar	Talacasto					Punta Negra					
Samples	16LE29	17CAR	17T04	16T40	16T45	16T63	16T64	17PN07	16PN33	16PN43	16PN59	16PN61	16PN66
16LE29		0.215	0.459	0.941	0.727	0.001	0.019	0.007	0.014	0.000	0.000	0.000	0.000
17CAR	0.215		0.011	0.898	0.700	0.002	0.001	0.155	0.088	0.000	0.000	0.000	0.000
17T04	0.459	0.011		0.789	0.159	0.000	0.109	0.002	0.001	0.000	0.000	0.000	0.000
16T40	0.941	0.898	0.789		0.846	0.313	0.163	0.327	0.182	0.000	0.000	0.000	0.001
16T45	0.727	0.700	0.159	0.846		0.000	0.003	0.069	0.036	0.000	0.000	0.000	0.000
16T63	0.001	0.002	0.000	0.313	0.000		0.049	0.000	0.001	0.000	0.000	0.000	0.000
16T64	0.019	0.001	0.109	0.163	0.003	0.049		0.000	0.000	0.000	0.000	0.000	0.000
17PN07	0.007	0.155	0.002	0.327	0.069	0.000	0.000		0.027	0.000	0.000	0.002	0.003
16PN33	0.014	0.088	0.001	0.182	0.036	0.001	0.000	0.027		0.000	0.000	0.000	0.000
16PN43	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.788	0.488	0.000
16PN59	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.788		0.694	0.003
16PN61	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.488	0.694		0.015
16PN66	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.003	0.000	0.000	0.003	0.015	

Table 2. Kolmogorov-Smirnov (K-S) test of the studied samples. P-values of samples with correlation grade greater than 0.05 are shown in orange.

4.4 Lu-Hf analysis in detrital zircons

The analysis of the Lu-Hf isotopic ratios of 23 detrital zircon grains reveals the petrogenetic characteristics of the magmas from which they derive. The distribution of the parameters $\varepsilon Hf_{(t)}$ and T_{DM} according to the U-Pb ages are as follows:

Archean: a single zircon of 2520 Ma was analysed. This crystal records an $\varepsilon Hf_{(t)}$ value of 1 and a T_{DM} model age of 2900 Ma (Fig. 8).

Paleoproterozoic: a single zircon of 1800 Ma was analyzed. This crystal records an $\varepsilon Hf_{(t)}$ value of 2 and a T_{DM} model age of 2900 Ma (Fig. 8). As in the previous case, this T_{DM} model age indicates an origin related to an ancient Archean crust.

Mesoproterozoic: 7 zircon grains were analysed. A single Ectasian zircon (1350 Ma) gave $\varepsilon Hf_{(t)}$ and T_{DM} values of 2 and 2300 Ma, respectively. The remaining zircons are Stenian (1130 – 1080 Ma) and gave $\varepsilon Hf_{(t)}$ values of 7-10 as well as T_{DM} model ages of 1500-1200 Ma, so they would have derived from a Mesoproterozoic crust. It should be noted that within this group it can be distinguished a zircon of 1130 Ma with an $\varepsilon Hf_{(t)}$ value of -31 and a T_{DM} model ages of 3600 Ma, indicating an origin related to an ancient Archean crust.

Neoproterozoic: for this interval, 3 grains were analyzed, obtaining $\varepsilon Hf_{(t)}$ and T_{DM} values of -2 and 1600 Ma respectively (Fig. 8).

Cambrian: 8 zircon crystals exhibit $\varepsilon Hf_{(t)}$ values between -5 and 2, whereas the T_{DM} model ages range from 1700 to1200 Ma so they would have derived from Mesoproterozoic and Paleoproterozoic crusts (Fig. 8).

Ordovician: 4 zircon crystals exhibit $\varepsilon Hf_{(t)}$ values between -4 and 0 whereas the T_{DM} model ages ranges from 1600-1400 Ma, so they would have derived from Mesoproterozoic crust (Fig. 8).

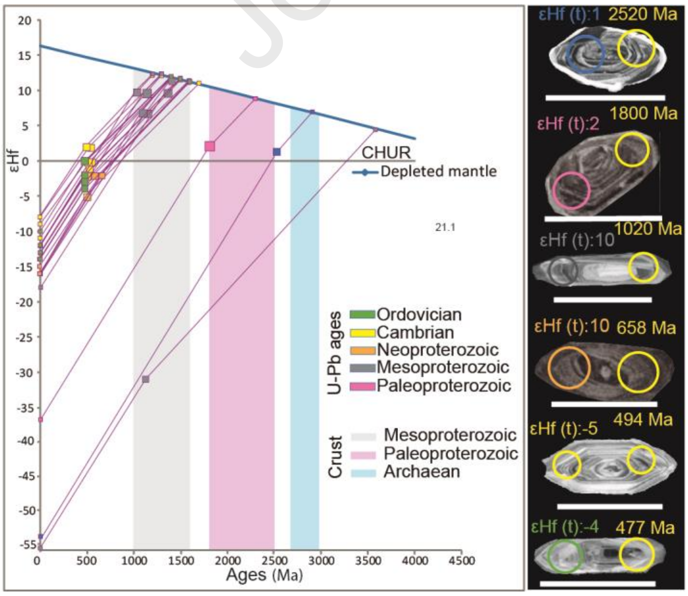


Figure 8. εHf vs. ages diagram for detrital zircons of the Los Espejos Formation. The main T_{DM} model ages are mainly Mesoproterozoic and, in minor proportion, Paleoproterozoic and

Archaean. Examples of selected cathodoluminescence images showing the U-Pb (on the right) and Lu-Hf (on the left) analysis points with their respective results.

5. DISCUSSION

The fact that the petrographically analysed samples of the Los Espejos Formation correspond to quartzites does not necessarily indicate that the involved sediments derived directly from a cratonic area, as indicated by Dickinson´s et al. (1983) ternary diagrams. The strong reworking of the sediments prior to lithification, also evidenced by zircon morphology, resulted in a concentration of chemically mature clastic components with high percentages of quartz and resistant heavy minerals such as zircon, rutile and tourmaline. Due to lithological and faunal similarities, the Los Espejos Formation could be compared with the Tambolar Formation (Heim, 1952) located near the San Juan River (Fiq. 7). According to studies carried out by Benedetto et al. (1992), Astini et al. (1995), and Astini and Maretto (1996), both units would be equivalent and would have had common sedimentary sources. On the other hand, due to the fact that the top unit of the Tucunuco Group (Los Espejos Formation) is of early Lochkovian age towards its upper part in some sectors of the basin (Benedetto et al., 1992), it could be comparable with the Talacasto Formation (basal unit of the Gualilán Group). In this way, based on the comparison of ages of detrital zircon populations from the Silurian and Devonian units, among other characteristics, an attempt was made to establish whether there were no changes in the contribution of sediment sources during this depositional interval. The Los Espejos Formation has predominance of stalky crystals and collision marks, and has similar roundness patterns. The analized detrital zircons of the Tambolar Formation present similar characteristic (Arnol et al., 2022). According to Pupin´s (1980) classification, both Silurian sequences (i.e., Los Espejos and Tambolar formations) would have derived from subsolvus granites. The only observable difference is that the Los Espejos Formation has larger zircons than the Tambolar Formation, although the zircons respect the length-width ratios, so the elongation parameters are similar in both units (Cretacotta, 2022). Regarding the Talacasto Formation (sample 16T45 in Arnol et al., 2020), it presents crystals with well-developed crystalline faces, larger sizes, higher elongation values, and fewer crystals with fractures, which indicate that the sources of detrital zircons could have varied, but that the plutonic igneous origin was maintained.

For the Los Espejos Formation, relative to the Talacasto Formation, a smaller number of zircons were analyzed using Pupin´s (1980) classification because the proportion of zircons with recycling characteristics increases in this Silurian unit. Nevertheless, in both cases, morphotype P is predominant, referring to subsolvus granites. With this information, it could be estimated that recycled zircons dominate in both units, being the rest associated with a plutonic origin. However, compared with the Talacasto Formation, there is less development of crystalline faces in zircons, which could be originated by reworking of sediments previous to lithification/diagenesis. This could be due to the fact that the sediment rocks of the Los Espejos Formation recorded more than one sedimentation cycle or that the contribution areas of the sequence are farther away, which is why the transport of the crystals was increased until their final deposition. This last hypothesis could be applied to the Paleoproterozoic and Archean zircons, since there are no nearby rocks that record these ages, with age records and Hf parameters coinciding with rocks from Río de la Plata Craton, where it is possible to find heterogeneous $\varepsilon Hf_{(t)}$ values. Considering last parameter and the T_{DM} model ages, we can suggest that the oldest zircons from the Los Espejos Formation derived from Tandilia terrane of Argentina (Cingolani et al., 2010; Santos et al., 2017; Angeletti et al., 2021) instead of the Piedra Alta terrane of Uruguay, where the $\varepsilon Hf_{(t)}$ values turn out to be very positive or very negative in the different types of rocks analyzed (Oriolo et al., 2016). For its turn, the first hypothesis is more difficult to verify because it is an old unit. The uplift of the Grenvillian orogen, which have been postulated for the Devonian (Arnol et al., 2020, 2022), could had started in Silurian times. This would leave as a result that the pre-Silurian sedimentary units which have Neoproterozoic-Cambrian and Mesoproterozoic records could have also acted as source areas, indicating that although the distances are reduced from the source rock to the basin, they could have gone through more than one sedimentation cycle.

The considerable contributions from Neoproterozoic sources in the northern region (study area) for the compared samples allow us to infer that the sediment sources, were the same during the Late Silurian and Devonian. The significant difference in the participation of cratonic sources would indicate higher exhumation rates of cratonic areas for the Silurian, which are found in a very reduced or non-existent manner in the upper unit of the Gualilán Group. However, the differences in the populations of registered ages are very significant for the southern region. This is reinforced by the null correlation values between the compared areas, indicating that for this sector of the basin there is evidence of a change in the sediment sources, at least for Paleoproterozoic ages that are present in the Silurian units and are practically absent in the Devonian sequences. This could be linked to what is already suggested by Arnol et al. (2022), who pointed out a greater exhumation of the Mesoproterozoic (Grenvillian) orogen which would have acted as a continuous topographic barrier preventing the entry of sediments located to the east of it.

5.1 Potential rock sources

The U-Pb data from the Los Espejos Formation samples are composed of a clear dominance of Pampean-Brasiliano sources. Basement rocks of early Cambrian age (Fig. 9) are found in the Eastern Pampean Ranges, as for example in Sierra Chica, Sierra Grande, Sierra de Pocho, Sierra de Comechingones, Sierra Norte de Córdoba and Sierra Sur de Santiago del Estero (Gordillo, 1996; Rapela et al., 1998; Sims et al., 1998; Gromet and Simpson, 1999; Candiani et al., 2001; Escayola et al., 2007; Tibaldi et al., 2008; Iannizzotto et al., 2013; Baldo et al., 2014; D'Eramo et al., 2014; Lira et al., 2014; Ramos et al., 2015; Dahlquist et al., 2016; among others). Despite the numerous woks that have provided U-Pb ages of basement rocks from these mountains, works with Lu-Hf data are still scarce. The availability of this isotopic pair would allow greater certainty about the characteristics of magmas from which zircons derived, and would help to clearly identify the rocks that contributed to the basin. The data provided by Dahlquist et al. (2016) for the Guasayán pluton yielded a U-Pb crystallization age of 533 ± 4 Ma and $\varepsilon Hf_{(t)}$ values between -4.76 and -0.12, indicating that rocks with these characteristics could have been the precursor sources of the early Cambrian zircons recorded in the Los Espejos Formation.

In the Eastern Cordillera, many authors provided U-Pb ages for granitois of the Santa Rosa de Tastil Batholith (Fig. 9) (Bachmann et al., 1987; Hongn et al., 2010; Escayola et al., 2011; Hauser et al., 2011; Lucassen et al., 2011; Ortiz et al., 2017). On the other hand, Bachmann et al. (1987) and Escayola et al. (2011), among others, analyzed granitoids of the Cañani Batholith, obtaining early Cambrian ages between 537 and 519 Ma. These rocks are not ruled out as sediment sources, because the $\varepsilon Hf_{(t)}$ values provided by Hauser et al. (2011) and Ortiz et al. (2017) coincide with the $\varepsilon Hf_{(t)}$ values recorded in the Cambrian detrital zircons of the Los Espejos Formation. For its part, in the Puna it is also possible to record these ages, for example in Sierra de Los Cobres or Sierra de Calalaste (Hauser et al., 2008; Zimmermann et al., 2014; among others), but unfortunately there are still no Lu-Hf data for these rocks that allow us to confirm or rule out these rock as sources areas (Fig. 9).

On the other side, Neoproterozoic sources are constrained to the Western Pampean Ranges (e.g., Sierra Pie de Palo), with ages ranging from 850 to 600 Ma and $\varepsilon Hf_{(t)}$ values between -3 and 10 (Baldo et al., 2006; Martin et al., 2020), which coincide with data obtained in this work. Other possible sources for zircons with these ages are found in Sierra de Umango and Sierra de Maz, where granitoids, paragneiss, schists and meta-sedimentary rocks with U-Pb ages between 850 and 700 Ma crop out (Varela et al., 2011; Rapela et al., 2016).

The Mesoproterozoic sources are widespread in the Western Pampean Ranges: in Sierra de Umango (Fig. 9), Varela et al. (2011) provided a TIMS U-Pb zircon upper intercept age (crystallization age) of 1108 ± 4 Ma in an amphibolite of the Tambillito Formation. For the Maz Complex, cropping out in the homonymous range, different authors provided ages between 1330 and 1086 Ma (Casquet et al., 2006; Rapela et al., 2010, among others). On the other hand, in Sierra de Pie de Palo, McDonough et al. (1993), Casquet et al. (2001), Vujovich et al. (2004), Morata et al. (2008) and Rapela et al. (2010), among others, provided different ages obtained for rocks of the Pie de Palo Complex, with values between 1200 and 1000 Ma. However, these ages are not exclusive from this geological province, but it is possible to find them in the Precordillera. To the north of the Precordillera, the Río Bonete Complex is recognized, there a mylonitic granite included in the Jagué shear belt, yielded a U-Pb age of 1118 ± 17 Ma (Martina et al., 2005). Additionally, in basement xenoliths found in the San Juan River area, Abbruzzi et al. (1993), Kay et al. (1996) and Martin et al. (2020), among others, indicated Grenvillian U-Pb crystallization ages between 1188 to 1096 Ma for the analyzed rocks (e.g., mafic xenolith, acid xenolith para-gneiss xenolith), as well as a U-Pb metamorphic age of 1060 Ma for the same zircons (Rapela et al., 2010). Also in the Precordillera, but as granitic clasts immersed in the matrix of the Los Sombreros Formation, Thomas et al. (2012) recorded U-Pb crystallization ages close to 1370 Ma. Extending further south in the San Rafael Block, Thomas et al. (2012) Cingolani et al. (2017) obtained U-Pb crystallization ages around 1204 Ma for the Ponón Trehue Granite.

The Lu-Hf data obtained by Martin et al., (2020) for Mesoproterozoic zircons from different locations within the Western Pampean Ranges and the San Rafael Block indicate that their rocks would be the sediment sources. Mesoproterozoic zircons show juvenile characters, with positive $\varepsilon Hf_{(t)}$ values and mostly Mesoproterozoic T_{DM} model ages. For practically all the Mesoproterozoic zircons of the Los Espejos Formation, the recorded positive values are identical to those found in the Western Pampean Ranges and San Rafael Block.

The Ordovician granitoids are restricted to outcrops of the Famatinian Arc. Rocks related to this magmatic event are mainly found in the Famatina System. However, it is possible to find identical ages, to a lesser degree of representativeness, in other geological provinces such as the Eastern Pampean Ranges or the Puna. Several authors presented U-Pb ages between 493 and 442 Ma for rock related to the Famatinian orogenic cycle (Dahlquist, 1999; Dahlquist et al., 2008, 2013; Pankhurst and Rapela, 1998; Pankhurst et al., 1998, 2000, 2008; Baldo et al., 2001, 2005; Varela et al., 2008, 2011; Casquet et al., 2012; Bellos et al., 2015, 2020; among others). Dahlquist et al. (2013) provided $\varepsilon Hf_{(t)}$ values between -14.7 and 3.3 for different granitoids of the Eastern Pampean Ranges and the Famatina System. Recently, Martin et al. (2020) reported $\varepsilon Hf_{(t)}$ values between -5 and 0 for Famatinian granitoids from La Rioja Province. These results are identical to those found in Ordovician ages detrital zircons present in the Los Espejos Formation, so it can be deduced that the Famatinian granitoids were the source area for these zircons.

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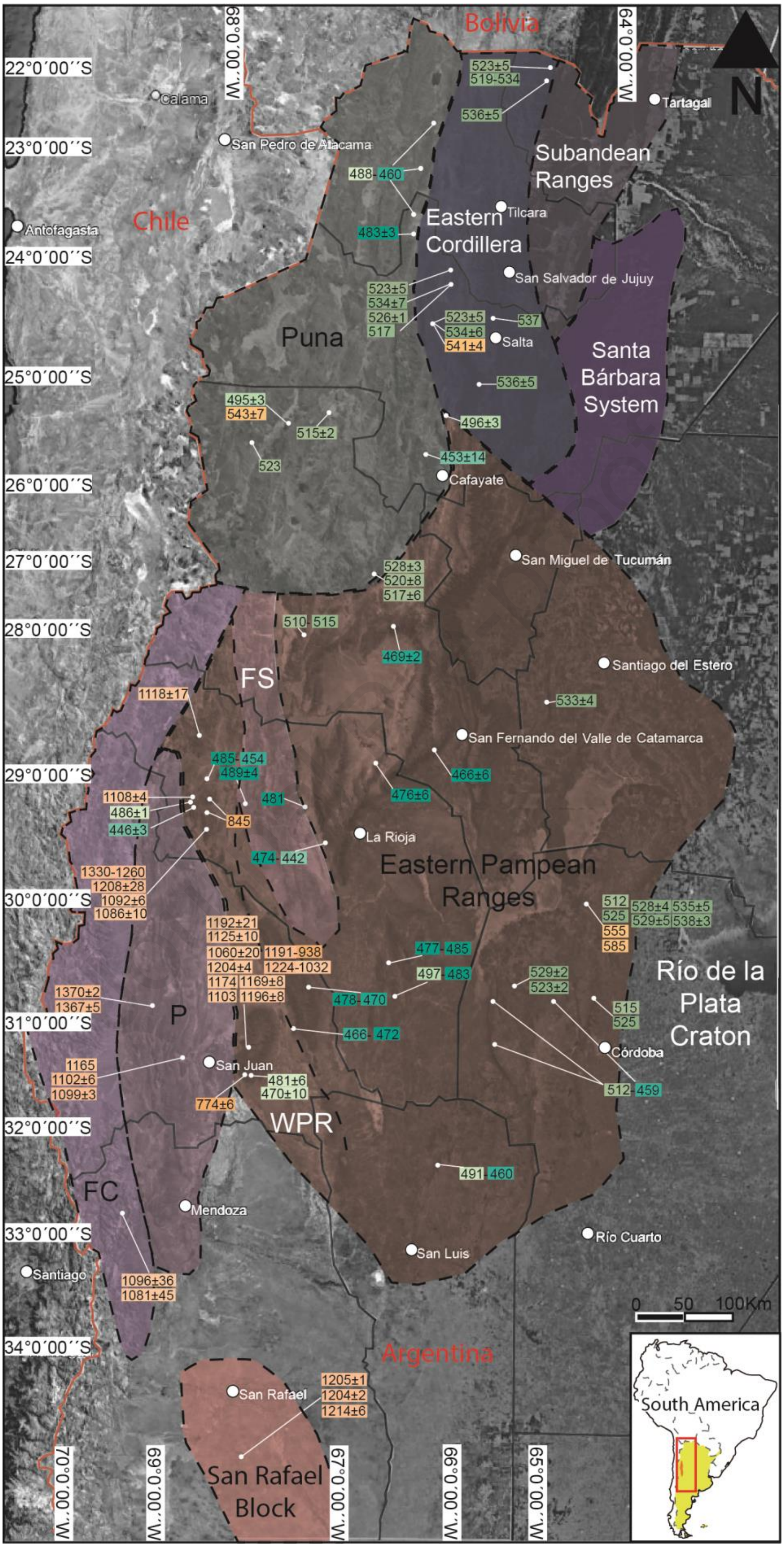
Bolivia
Chile
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Puna
Eastern Cordillera
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Santa Bárbara System
Eastern Pampean Ranges
Río de la Plata Craton
San Rafael Block
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Calama
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Antofagasta
Tartagal
Tilcara
San Salvador de Jujuy
Salta
Cafayate
San Miguel de Tucumán
Santiago del Estero
San Fernando del Valle de Catamarca
La Rioja
San Juan
Córdoba
Mendoza
San Luis
Río Cuarto
Santiago
San Rafael

Figure 9. Time–space plot of Proterozoic and early Paleozoic (Cambrian-Ordovician) plutonic and metamorphic rocks on the western Gondwana margin at 22°–35°S, displaying the main regions discussed in the text as possible sediment sources. The figure shows plutonic and metamorphic outcrops, including U–Pb zircon data. The colors of the boxes are consistent with the color scale adopted by the IUGS. The works considered for this figure are cited in Section 5.1. Abbreviations: FS: Famatina System P: Precordillera, FC: Frontal Cordillera, WPR: Western Pampean Ranges.

FINAL REMARKS

- The petrographic analysis of the Los Espejos Formation shows that this unit is mostly composed of quartz-bearing rocks classified as quartzites. The unit also contains iron rich mantles. The morphology of detrital zircons indicates mainly recycled sources. Recycled zircons from relatively nearby source rocks could be linked to more than one sedimentation cycle. In addition to this evidence, the low participation of ancient sources leads us to conclude that, for this case, the diagrams of Dickinson et al. (1983) do not reflect to the sedimentary history of the rock analyzed, since they would not derive from a cratonic area, but from a recycled orogen that suffered repeated sedimentation cycles.
- The Los Espejos Formation has a clear predominance of Neoproterozoic to early Cambrian sources. As a secondary mode, there are Mesoprototerozoic sources, mainly Stenian. In similar percentages, the Famatinian sources are recorded with scarce contribution of ancient sources.
- The maximum sedimentation age for sample 16LE29 corresponds to the Tremadocian (478.5 ± 4.4 Ma), indicating that the youngest sources that contributed sediments to this region of the basin correspond to rocks of the Famatinian Orogen.

- The Lu-Hf data indicate that the main areas of sediment contribution were the Western Pampean Ranges and the Famatina System, whose zircons derived mainly from a Mesoproterozoic crust.
- The Los Espejos Formation shares sediment sources with the Tambolar Formation, in the San Juan River area and with the Talacasto Formation in the north of the basin. The difference between the Silurian samples and the Talacasto Formation in the San Juan River area would be linked to paleogeographic changes within the basin and along its edges, which influenced the amounts of zircons grains of different ages that arrived and were recorded for the different areas.

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Sample	Latitud	Longitud	Methodology
16LE12	30°17'49.69"S	68°46'21.49"W	Petrography
16LE13	30°17'49.26"S	68°46'18.76"W	Petrography
16LE22	30°15'30.84"S	68°56'14.79"W	Petrography
16LE25	30°15'35.42"S	68°56'9.32"W	Petrography
16LE26	30°13'11.96"S	68°55'15.77"W	Petrography
16LE29	30°12'35.25"S	68°53'7.95"W	Petrography, Zr morphology, U-Pb and Lu-Hf

Sample	Latitud	Longitud	Methodology
16LE12	30°17'49.69"S	68°46'21.49"W	Petrography
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16LE26	30°13'11.96"S	68°55'15.77"W	Petrography
16LE29	30°12'35.25"S	68°53'7.95"W	Petrography, Zr morphology, U-Pb and Lu-Hf

Formation	Los Espejos	Tambolar	Talacasto					Punta Negra					
Samples	16LE29	17CAR	17T04	16T40	16T45	16T63	16T64	17PN07	16PN33	16PN43	16PN59	16PN61	16PN66
16LE29		0.215	0.459	0.941	0.727	0.001	0.019	0.007	0.014	0.000	0.000	0.000	0.000
17CAR	0.215		0.011	0.898	0.700	0.002	0.001	0.155	0.088	0.000	0.000	0.000	0.000
17T04	0.459	0.011		0.789	0.159	0.000	0.109	0.002	0.001	0.000	0.000	0.000	0.000
16T40	0.941	0.898	0.789		0.846	0.313	0.163	0.327	0.182	0.000	0.000	0.000	0.001
16T45	0.727	0.700	0.159	0.846		0.000	0.003	0.069	0.036	0.000	0.000	0.000	0.000
16T63	0.001	0.002	0.000	0.313	0.000		0.049	0.000	0.001	0.000	0.000	0.000	0.000
16T64	0.019	0.001	0.109	0.163	0.003	0.049		0.000	0.000	0.000	0.000	0.000	0.000
17PN07	0.007	0.155	0.002	0.327	0.069	0.000	0.000		0.027	0.000	0.000	0.002	0.003
16PN33	0.014	0.088	0.001	0.182	0.036	0.001	0.000	0.027		0.000	0.000	0.000	0.000
16PN43	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		0.788	0.488	0.000
16PN59	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.788		0.694	0.003
16PN61	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.488	0.694		0.015
16PN66	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.003	0.000	0.000	0.003	0.015	

- The Los Espejos Fm evidences multiple cycles of erosion-transport-sedimentation.
- The Pampean-Brasiliano orogen represents the main source of sediments.
- The provenance proxies indicate a connection between the Jáchal and San Juan Rivers depocenters.
- The main sources of sediments are the Western and Eastern Pampean Ranges.

Declaration of interests

None