



Combined U–Pb and Lu–Hf isotope study from the Las Lozas volcanics, northwestern Argentina: Evidence of juvenile Cryogenian-derived, lower Pennsylvanian volcanism in western Gondwana



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ABSTRACT

Las Lozas volcanic succession, cropping out in the southwestern Puna, Catamarca province, Argentina, consists of an intracontinental volcanic sequence of Carboniferous age. The lavic members are predominantly rhyolites, and subordinated andesites and basalts. The volcanoclastic layers consist of monomictic and polymictic breccias with structures denoting processes of lava fragmentation. They constitute a bimodal suite, ranging from basalts to high silica rhyolites. A new U–Pb SHRIMP age of 320 ± 2 Ma for a rhyolite allows extending the Mississippian magmatism of the region to the lower Pennsylvanian. Hf data point to juvenile sources of Cryogenian age with no evidence of older reworked crustal contamination.

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1. Introduction

In the last decades voluminous volcanic deposits of Ordovician age have been described in northwestern Argentina (e.g. Coira, 1975, 1979; Cisterna et al., 2010; Cisterna and Coira, 2013), and they were related to an active subduction zone along the western margin of Gondwana (e.g. Coira et al., 1982; Ramos, 1988; Conti et al., 1996; Cisterna et al., 2010). In the northern portion of the Famatina System and southern Puna the Ordovician volcanic successions are usually covered by thick Late Paleozoic siliciclastic units (e.g. Turner, 1967). However recent studies carried out in this area indicate that rhyolitic rocks, previously mapped as Ordovician and included within the Famatina magmatic arc (Turner, 1967; Mpodozis et al., 1997; Rubiolo et al., 2001; Coira et al., 2005), have a Carboniferous age, pointing out to a previously unknown

volcanic event in the region (e.g. Martina et al., 2011). The available Mississippian ages (348–342 Ma) obtained by the latter authors in the Carboniferous volcanic units outcropping at Cazadero Grande (Catamarca) and Cerro Pabellones (La Rioja) allowed to regard these units to be associated to crustal extension in a retro-arc environment, there also being related to coeval A-type granites (340–353 Ma) exposed to the east, in the Sierras Pampeanas (Grosse et al., 2009; Dahlquist et al., 2006, 2013). The latter authors have reported isotope data of zircons from Lower Carboniferous granites that indicate its derivation from recycling of juvenile crustal material, in accordance with regional studies presented by Willner and Gerdes. (2008).

This study focuses on the volcanic-volcanoclastic section that crops out along the Las Lozas valley ($27^{\circ} 10' 38.1'' - 27^{\circ} 10' 15.9''$ S and $68^{\circ} 07' 16.3'' - 68^{\circ} 07' 11.9''$ W), to the northwest of the Famatina System, and south of the Puna region (NW Argentina) (Fig. 1). These rocks have been originally interpreted as part of the Ordovician Las Planchadas Formation (Turner, 1967; Maissonave, 1979; Rubiolo et al., 2001) but new U–Pb SHRIMP and Hf isotope data presented herein allow to extend the Early Carboniferous volcanism to the lower Pennsylvanian in the northwestern border

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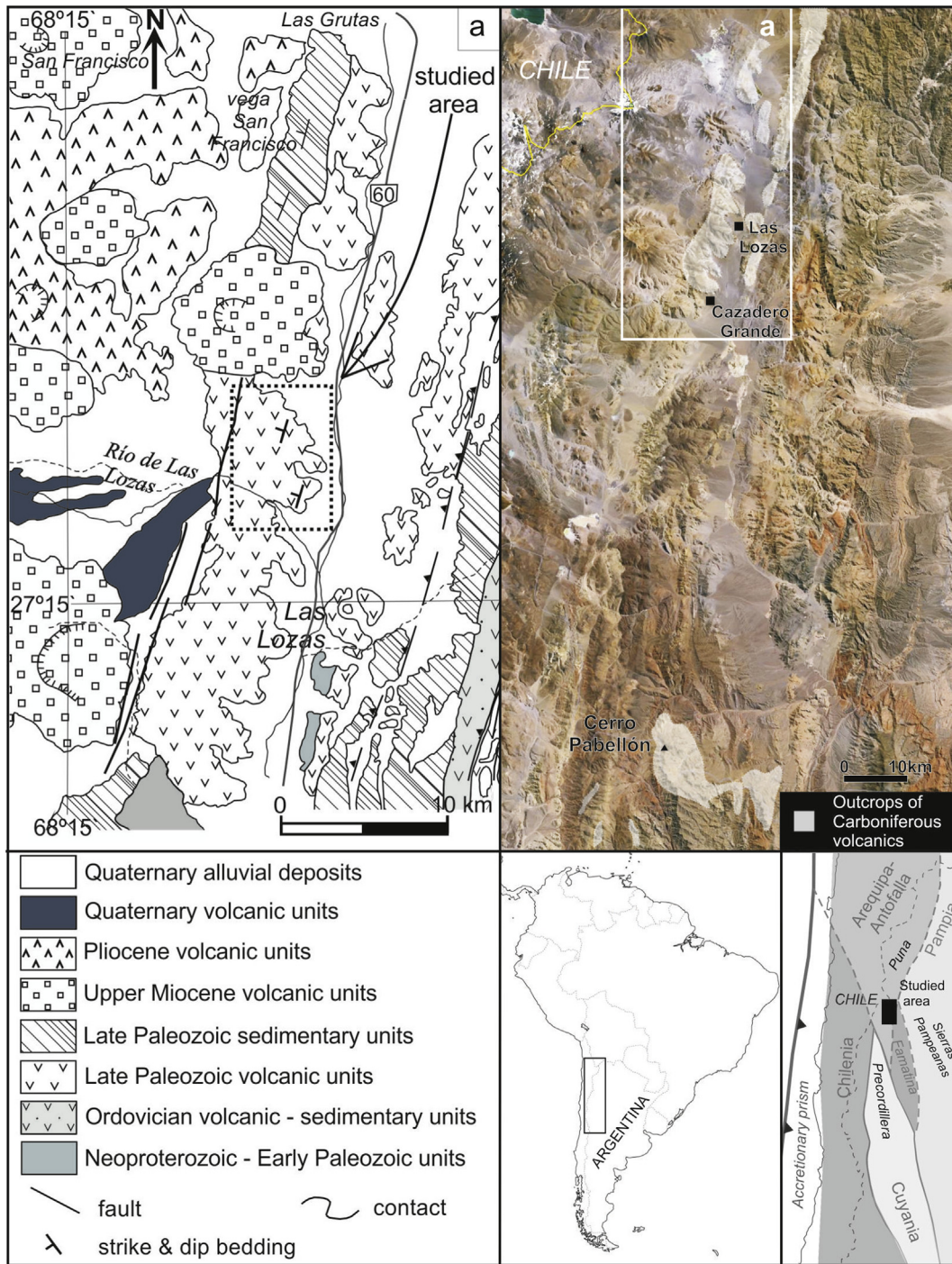


Fig. 1. Regional extension of the Carboniferous volcanic outcrops. Tectonic setting after Ramos et al. (2010). a) Geological map of the Chaschuil Valley region.

of the Famatina belt and the southern Puna region, as well as to analyze the tectonic setting and magma sources of this magmatic activity.

2. Geologic setting

The volcanic succession identified along the Las Lozas valley (Cisterna et al., 2013) unconformably covers metamorphic basement units, and underlies a sedimentary succession attributed to

the Upper Paleozoic. The studied section, nearly 550 m thick, is characterized by the abundance of the rhyolitic lavic members and their fragmented equivalents, with subordinated intercalation of andesites and basalts (Fig. 2a). These rocks are not affected by metamorphism and are slightly altered. Quartz, calcite and/or hematite veins less than 3 cm thick that crosscut the unit are common.

The lavic lithofacies consist of layers up to 15 m thick of predominantly rhyolitic composition (comprising autoclastic facies) of

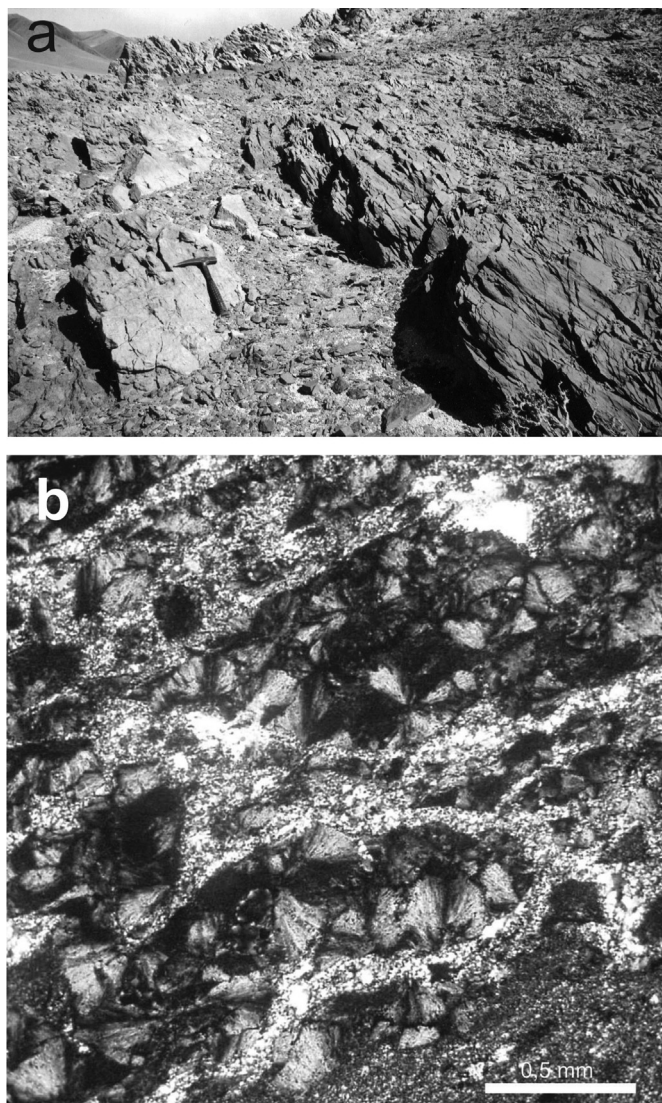


Fig. 2. a) Outcropping of afanitic light gray rhyolitic lava with flow pattern highlighted by parting-plane lineation with moderate inclination angle. b) Rhyolite groundmass with irregular bands showing textural variations from fine grained microgranular intergrowth of quartz and alkali feldspar to bands ranging from glassy to radial aggregates of chalcedony. Crossed nicols, enlargement $\times 10$.

reddish, brown to black colour, one black andesitic flow (mostly consisting of autobreccias) and 2–15 m thick greenish to greenish black, usually massive and porphyritic to fine-grained basalts.

The volcanoclastic lithofacies are represented by layers up to 60 m thick, almost entirely composed of lava clasts. According to the grain size, shape and nature of the clasts, they are classified as monomictic rhyolitic breccias, rhyolitic vitrophyric breccias and polymictic breccias, the latter being predominant. A detailed petrographic description of the unit is to be presented in a separate paper.

The dated sample corresponds to a rhyolitic lava that has well-developed flow banding structures and shows porphyritic texture with euhedral crystals of K-feldspar (10–15%) up 2 cm oriented along the flow direction, euhedral or subrounded quartz crystals (0.5–5 mm), minor plagioclase predominantly 2–5 mm long and scarce biotite (<1%). The groundmass consists of a fine grained microcrystalline quartz-feldspar mosaic that contains abundant, randomly oriented, feldspar laths; fine granophyric and spherulitic

textures are also present (Fig. 2b). Flow bands are common and are defined by differences in quartz abundance or in the size of feldspar crystals, as well as by groundmass texture variations.

Previously reported chemical data (Cisterna et al., 2013) indicate that the studied succession belong to an alkaline bimodal series. Basaltic members have E-MORB as well as intraplate signature; both basaltic and the acid members show moderate enrichment in LREE with respect HREE. The trace element of the series plot in the within plate field of the tectonic discriminant diagrams.

3. U–Pb SHRIMP geochronology

3.1. Methodology

U–Pb analysis of zircon was carried out at the Curtin University, Perth. The 60–250 mesh fractions were treated with heavy liquids (to remove light minerals) and magnetic separator (to concentrate the less magnetic minerals such as zircon). Zircon was handpicked and organized in an epoxy mount, which was polished and carbon-coated for SEM (Scanning Electron Microscope) study. Back-scattered images (BSE) were taken using a JEOL6400 SEM at the Centre for Microscopy and Microanalyses at University of Western Australia. Images of zircon are critical for identifying internal features such as core and rims and to help avoiding areas with high common lead content (inclusions, fractures, and metamict areas). Epoxy mount (UWA 11–31) was gold-coated for SHRIMP analyses. Sensitive High Mass Resolution Ion MicroProbe (SHRIMP II) U–Pb analyses were performed at Curtin University, under a Consortium between that university, the Western Australia University, and the Geological Survey of Western Australia. Data was collected in two sessions using an analytical spot size of about 20–25 μm . Hf-isotope analyses reported here were carried out in situ using a New Wave Research LUV213 laser ablation microprobe, attached to a Nu Plasma multicollector ICPMS at GEMOC Key Centre, Macquarie University, Sydney. Most analyses are carried out with a beam diameter of about 40 μm , a 10 Hz repetition rate, and energies of 0.6–1.3 mJ/pulse. The ^{176}Lu decay constant used to calculate initial $^{176}\text{Hf}/^{177}\text{Hf}$, ϵ_{Hf} values, and model age is 1.983×10^{-11} (Bizzarro et al., 2003). Sample preparation, analytical methods, procedures and data processing follow those described by Santos et al. (2000). Only relevant information is herein given.

3.2. U–Pb geochronology

Dating young zircons (Phanerozoic) faces the problems of low counts of ^{207}Pb and the difficulty to detect deviations from slightly older cores and from subtle amounts of Pb loss. To minimize the first problem the time of counting ^{207}Pb was increased from 10 s to 20 s, and grains and areas of grains poor in U (<100 ppm) were avoided. Additionally we have used the TuffZirc algorithm (Ludwig and Mundil, 2002), which is largely insensitive to both Pb loss and inheritance to plot the $^{206}\text{Pb}/^{238}\text{U}$ ages corrected using the ^{207}Pb counts. Most of the data group in the Concordia plot, with one analysis deviating from the Concordia line.

Rocks of the Las Lozas volcanic succession are relatively rich in zircon. All grains are 75–300 μm prisms terminated in pyramids (aspect ratio 2:1 to 2.5:1). The zircon grains are simple and back-scattered electron images show no evidence of older inherited cores or of younger metamorphic rims or zones. They have characteristics of magmatic grains such as the zoning and the Th/U ratios averaging 0.96 (Table 1). BSE images of dated zircons are provided in Fig. 3. Six analyses group at the $^{206}\text{Pb}/^{238}\text{U}$ age of 319.5 ± 2.2 Ma (MSWD = 0.85; 2σ) (Fig. 4). The age obtained is considered the age of crystallization of the volcanic succession.

Table 1
U–Pb–Th SHRIMP data on zircon of the Las Lozas volcanic succession.

| Spot | Ratios | | | | | Ages | | | Disc. | | | | |
|--|--------|-----|------|-------------------|-----------------------------|------------------|-------------------|-------------------|-------|----------------|-------------------|-------------------|-------------------|
| | U | Th | Th | ²⁰⁶ Pb | ^{4f²⁰⁶} | ²³⁸ U | ²⁰⁷ Pb | ²⁰⁷ Pb | | Error | ²⁰⁸ Pb | ²⁰⁶ Pb | ²⁰⁶ Pb |
| | ppm | ppm | U | ppm | % | ²³⁸ U | ²⁰⁶ Pb | ²³⁵ U | | Correl | ²³² Th | ²³⁸ U | ²⁰⁷ Pb |
| CG1, rhyolitic lava (27° 10' 31.5" S, 68° 07' 36.1" W) | | | | | | | | | | | | | |
| f.4-1-2 | 136 | 131 | 0.99 | 6.1 | 1.40 | 19.5995 ± 2.09 | 0.05477 ± 14.23 | 0.3853 ± 14.39 | 0.146 | 0.0126 ± 11.53 | 320.8 ± 6.6 | 403 ± 319 | 20 |
| f.4-2-5 | 191 | 333 | 1.81 | 7.8 | 0.87 | 21.2464 ± 2.34 | 0.05559 ± 10.87 | 0.3608 ± 11.12 | 0.211 | 0.0112 ± 4.80 | 296.5 ± 6.8 | 436 ± 242 | 32 |
| f.4-3-1 | 120 | 68 | 0.59 | 5.1 | 0.00 | 20.1878 ± 1.78 | 0.05285 ± 3.57 | 0.3610 ± 3.99 | 0.446 | 0.0158 ± 3.25 | 311.7 ± 5.4 | 323 ± 81 | 3 |
| f.5-1 | 177 | 94 | 0.55 | 7.8 | 0.52 | 19.5065 ± 2.09 | 0.05274 ± 7.69 | 0.3728 ± 7.97 | 0.262 | 0.0150 ± 6.64 | 322.3 ± 6.6 | 318 ± 175 | -2 |
| f.6-1 | 453 | 392 | 0.89 | 19.8 | 0.07 | 19.6634 ± 1.48 | 0.05335 ± 2.05 | 0.3741 ± 2.53 | 0.585 | 0.0158 ± 1.96 | 319.8 ± 4.6 | 344 ± 46 | 7 |
| f.7-1 | 369 | 504 | 1.41 | 16.1 | 0.00 | 19.7059 ± 1.51 | 0.05303 ± 2.09 | 0.3710 ± 2.57 | 0.585 | 0.0159 ± 2.12 | 319.1 ± 4.7 | 330 ± 47 | 3 |
| f.7-2 | 123 | 64 | 0.54 | 5.5 | 0.70 | 19.3917 ± 1.72 | 0.05197 ± 7.44 | 0.3695 ± 7.63 | 0.225 | 0.0167 ± 6.31 | 324.1 ± 5.4 | 284 ± 170 | -14 |

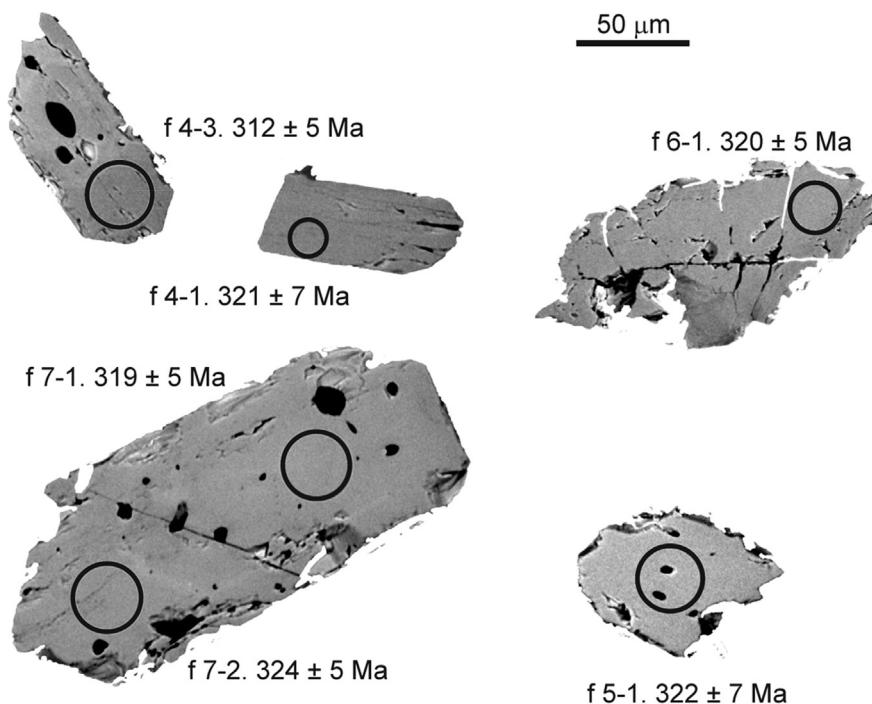


Fig. 3. BSE images of dated zircons from the Las Lozas volcanic succession.

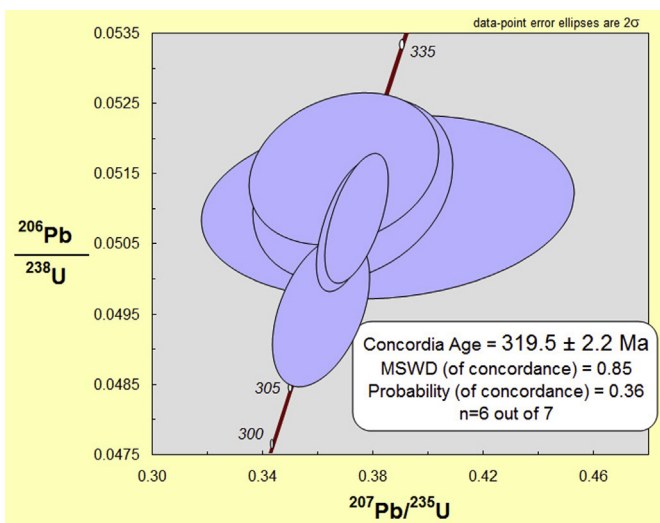


Fig. 4. Concordia diagram for magmatic zircon samples from the Las Lozas volcanic succession.

3.3. Lu–Hf isotopes

While the zircon U–Pb age for igneous rocks represents the timing of magma crystallization, Hf isotopes allow distinguishing juvenile, essentially mantle-derived crust of a given age, having positive $\epsilon_{\text{Hf}(t)}$ from contemporary crust derived from re-melting of older crust, characterized by negative $\epsilon_{\text{Hf}(t)}$. Juvenile magmas are defined as those generated from the depleted mantle or by re-melting of material recently extracted from it (Belousova et al., 2010).

When considering Hf data some point need to be addressed: firstly, ¹⁷⁶Lu decay constant, taking into account that there are three main models (Blichert-Toft, 1997; Scherer et al., 2001; Bizzarro et al., 2003); secondly, the choice of the model age T_{DM} or $T_{\text{DM}(c)}$; and thirdly the initial ¹⁷⁶Lu/¹⁷⁷Lu ratio, i.e. for sources of more acidic composition the value 0.015 is used whereas for more mafic magmas the value is closer to 0.018, what makes model ages older. Hf isotopes of the analyzed zircons have model ages ranging between 1020 and 1240 Ma (for mafic sources and a crustal depleted mantle) and between 670 and 860 Ma for a non crustal depleted mantle source of relatively acid composition.

The single-stage Hf model age (T_{DM}) value was preferred since zircons have positive $\epsilon_{Hf(t)}$, representing a proxy for the maximum age of magma extraction from the depleted mantle. Hf model age (T_{DM}) based on a depleted mantle source, was calculated using ($^{176}\text{Hf}/^{177}\text{Hf}$)_i = 0.279718 at 4.56 Ga and $^{176}\text{Lu}/^{177}\text{Hf}$ = 0.0384, and producing a present-day value of $^{176}\text{Hf}/^{177}\text{Hf}$ = 0.28325 (Griffin et al., 2000, 2004). The $T_{DM(c)}$ age in zircon was calculated from the initial Hf isotopic composition of the zircon, using an average crustal Lu/Hf ratio close to that of a granitic composition (0.015; Griffin et al., 2004). The initial Hf composition of zircon represents the $^{176}\text{Hf}/^{177}\text{Hf}$ value calculated at the time the zircon crystallized, using the U–Pb age previously obtained in the same spot of the same crystal. Such model ages indicate the crustal residence time for the rocks that hosted the zircon.

Five zircons of the unit already dated by U–Pb were selected for Hf analyses. The grains were selected according to the degree of concordance and lower common lead content. All $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are similar and the data produced positive $\epsilon_{Hf(t)}$ (from +1.64 to +6.57). The average Lu–Hf model age of the zircon, assuming a depleted mantle origin as previously indicated (T_{DM} in Table 2), is about 770 Ma.

4. Discussion

The 320 Ma age obtained for the Las Lozas volcanic succession confirms its adscription to the Carboniferous volcanic episode identified by Martina et al. (2011), though extending the magmatic activity to the Lower Pennsylvanian. Martina and Astini (2009) have obtained a dominant peak at 336 Ma for detrital zircons from a volcano-sedimentary succession near Jagüé (27° S) and Gulbranson et al. (2010) dated a volcanic flow at 336 ± 0.06 Ma in the same section. Willner et al. (2008) obtained ages between 331 ± 4.0 Ma and 298 ± 11 Ma for granitic and rhyolitic pebbles from a retrowedge basin exposed further south (31° S). All these data confirm a continuum in the magmatic activity during the Carboniferous in an extensional tectonic setting, as indicated by previous work (Martina et al., 2011; Cisterna et al., 2013) associated to the orogenic collapse that followed the docking of the Chilenia terrane, and at least until the reinitiation of subduction evidenced in Argentina by I-type granitoids younger than 320 Ma in the Frontal Cordillera, as well as calc-alkaline volcanics with arc signature from Punta del Agua formation, in northern Precordillera (Fauqué and Caminos, 2006).

Hf data from Las Lozas volcanic succession, with positive $\epsilon_{Hf(t)}$ values and T_{DM} ages of ca. 770 Ma, indicate that the source of the magma had a predominant juvenile component of Cryogenian age or sedimentary material derived from crust of that age, beneath the Puna region. The existence of juvenile crust of this age is coincident with the youngest (MC1: 0.8 to 1.2 Ga) of the three episodes of juvenile crust formation identified by Willner et al. (2008) through the study of detrital zircons from late Paleozoic accretionary systems between (present day) 29° and 36° S at the western margin of Gondwana.

The 670 to 860 Ma T_{DM} zircon Hf ages for the Las Lozas volcanic succession as well as similar data reported by Munizaga et al. (2008) and Poma et al. (2014), with positive $\epsilon_{Hf(t)}$ and T_{DM} Hf ranging between 604 and 748 Ma and between 650 and 790 Ma, respectively, support a model that considers the existence of juvenile, essentially mantle-derived Cryogenian crust in the region, associated with the older Mesoproterozoic basement crust, already defined in Southern Puna. Early Ediacarian to Cryogenian T_{DM} Hf ages (620 and 760 Ma), with $\epsilon_{Hf(t)}$ (+2.5 to +5.0), have also been reported by Zappettini and Santos (2011) for a 153 ± 2 Ma diorite intrusion in Eastern Puna. Furthermore, the occurrence of an active enriched mantle in the range of 700–800 Ma (late Rodinia breakup) has been described in Sierras Pampeanas by Rapela et al. (2010). The lack of xenocrystic cores or inherited zircons in Las Lozas volcanic succession would indicate high magmatic temperatures as well as absence of reworked crust as magma source. This precludes the obtained T_{DM} Hf ages to be interpreted as a mix of such a crust and mantle material at the time of magma generation. The presence of a distinct basement of late Mesoproterozoic age below the Chilenia terrane has been proposed by Willner and Gerdes. (2008) and is consistent with a crust of similar age obtained for the Precordillera basement (Nd model ages from xenoliths; Kay et al., 1996).

Significantly, the positive $\epsilon_{Hf(t)}$ obtained herein in Las Lozas rhyolite differs from the negative $\epsilon_{Nd(t)}$ values reported by Martina et al. (2011) who interpreted the Mississippian (348–342 Ma) rhyolites as originated by crustal melting pointing to a strongly enriched source reservoir with local primitive mantle contribution. Also the Mesoproterozoic T_{DM} Nd model ages coincident with the age of an inherited zircon reported by the latter authors differ from our data. Considering the age difference between the Mississippian and lower Pennsylvanian units (28 Ma), this would indicate a change in the magma source, consistent with a more pronounced extensional tectonic regime for the younger Las Lozas volcanic succession, pointing to a more primitive source without evidence of crustal input.

5. Conclusions

New U–Pb SHRIMP zircon data allow to extend the Carboniferous retro-arc extensional volcanism of Southern Puna, previously constrained to the Mississippian, to the Lower Pennsylvanian. The available geochemical data (Cisterna et al., 2013), pointing to a setting with intraplate affinities, are consistent with the Hf isotope geochemistry; this indicates a juvenile source of Cryogenian age without evidence of older reworked crust input, suggesting a change in the magma source when compared to that of the Mississippian magmatism described by Martina et al. (2011) in the same region. Also it would confirm the presence of juvenile Cryogenian crust within the Chilenia-Antofalla basement. This Cryogenian juvenile crust may have been originated during the breakup of the Rodinia supercontinent or as an accretionary arc to the west of the

Table 2
Hf Isotopic data of dated zircons from the Las Lozas volcanic succession.

| Analysis N° | $^{238}\text{Pb}/^{206}\text{Pb}$ age (Ma) | 1 σ (Ma) | $^{176}\text{Hf}/^{177}\text{Hf}$ | 1 σ | $^{176}\text{Lu}/^{177}\text{Hf}$ | $^{176}\text{Hf}/^{177}\text{Hf}$ initial | Epsilon Hf | 1 σ | T_{DM} (Ga) | T_{DM} crustal |
|-------------|--|-----------------|-----------------------------------|------------|-----------------------------------|---|------------|------------|---------------|------------------|
| 1131F-04.3 | 312 | 5 | 0.282624 | 0.000051 | 0.001869 | 0.282612 | 1.64 | 1.79 | 0.86 | 1.17 |
| 1131F-05.1 | 322 | 7 | 0.282661 | 0.000028 | 0.001210 | 0.282653 | 3.33 | 0.98 | 0.79 | 1.07 |
| 1131F-06.1 | 320 | 5 | 0.282751 | 0.000035 | 0.003601 | 0.282728 | 5.92 | 1.23 | 0.72 | 0.92 |
| 1131F-07.1 | 319 | 5 | 0.282754 | 0.000029 | 0.001100 | 0.282747 | 6.57 | 1.02 | 0.67 | 0.88 |
| 1131F-07.2 | 324 | 5 | 0.282638 | 0.000024 | 0.001204 | 0.282630 | 2.56 | 0.84 | 0.82 | 1.12 |

The 'crustal' model ages ($T_{DM}(C)$) assume that the zircon's parental magma was produced from a volume of average continental crust ($^{176}\text{Lu}/^{177}\text{Hf}$ = 0.015; Griffin et al., 2004), that was originally derived from the depleted mantle. ^{176}Lu decay is $1.983 \times 10^{-11} \text{ yr}^{-1}$ (Bizzarro et al., 2003).

Mesoproterozoic crust that underlies the Pampean Ranges (Pampia terrane).

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