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# The Pacific Gondwana margin in the late Neoproterozoic–early Paleozoic: Detrital zircon U–Pb ages from metasediments in northwest Argentina reveal their maximum age, provenance and tectonic setting

C.J. Adams [a],*, H. Miller [b], F.G. Aceñolaza [c], A.J. Toselli [c], W.L. Griffin [d]

[a] GNS Science Private Bag 1930, Dunedin, New Zealand
[b] Department für Geo- und Umweltwissenschaften, Sektion Geologie, Luisenstrasse 37, D-80333, Munich, Germany
[c] Facultad de Ciencias, Universidad de Tucumán, Miguel Lillo 205, 4000 San Miguel de Tucumán, Argentina
[d] ARC Key Centre for Geochemical Evolution and Metallogeny of Continents, Department of Earth and Planetary Sciences, Macquarie University, North Ryde, NSW 2109, Australia

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## ABSTRACT

U–Pb detrital zircon ages are reported from Puncoviscana Formation (late Neoproterozoic–Early Cambrian) and Mesón Group (Late Cambrian) greywackes of northwest Argentina, to constrain provenance and depositional environment.

The new data are combined with previously-published detrital zircon ages, to show that Puncoviscana Formation age patterns contain two broad groups: late Mesoproterozoic–early Neoproterozoic (1150–850 Ma) and late Neoproterozoic–Early Cambrian (650–520 Ma); with their relative proportions varying inversely with youngest component age. The 1150–850 Ma age components are dominant in greywackes with oldest late Neoproterozoic components >600 Ma. The former diminish considerably when late Neoproteozoic components become dominant and younger, to 520 Ma. A northernmost greywacke sample from Purmamarca, Jujuy, is distinctive: whilst its zircon age pattern partly resembles other Puncoviscana Formation samples, it contains no Cambrian–late Neoproterozoic ages, the youngest ages being early Neoproterozoic. This may reflect an early, Neoproterozoic, passive-margin depocentre for the Formation, or an older (early Neoproterozoic) succession within it, which may predate the Brasiliano orogeny in Brazil. The youngest age components, c. 520 Ma, in a greywacke from Rancagua (Cachi, Salta province), dominate an almost unimodal pattern suggestive of contemporary volcanic sources at a late Early Cambrian depocentre. Detrital zircon age patterns of the Mesón Group (Lizoite Formation) have major Cambrian–latest Neoproterozoic components resembling those of the Puncoviscana Formation, but its Mesoproterozoic component is diminished, and there are no significant age components of this age. Small youngest components at c. 500 Ma suggest a maximum Late Cambrian stratigraphic age. The Puncoviscana Formation detrital zircon patterns suggest a provenance in a continental hinterland having a stabilised, extensive late Mesoproterozoic orogen (with minor Paleoproterozoic and Archean precursors), and a more variable late Neoproterozoic orogen containing an evolving sequence of less extensive subcomponents. A direct relationship with the Brazilian Shield is suggested; with sediment supplies originating within active-margin orogens of the interior and collisional orogens at the suture between African and South American cratons, but ultimate deposition in passive-margin environments of western Gondwanaland.

## 1. Introduction

In late Neoproterozoic–early Paleozoic time, extensive sedimentary basins and fold belts bordered a youthful Gondwanaland continent along its proto-Pacific margin, from southern South America through Antarctica to Australia (Aceñolaza and Miller, 1982; Söllner et al., 2000b; Cawood, 2005; Veevers, 2005; Vaughan and Pankhurst, 2008). In South America, across the northwest Argentine provinces of Tucumán, Salta and Jujuy, this margin is represented by major successions of the Puncoviscana Formation and its metamorphic equivalents, comprising in total, a sedimentary basin at least 1000 km N–S, and 250 km E–W (Fig. 1). In late Neoproterozoic–Early Cambrian times this formed, in its most likely interpretation, southwest of the Brazilian craton, exposed around or underlying the Phanerozoic sediments and volcanics of the Paraná Basin (Cordani et al., 2000), along the Western Gondwanaland margin (Aceñolaza and Miller, 1982; Aceñolaza et al., 2005; Pankhurst and Rapela, 1998; Cawood, 2005; Hauser et al., 2010). However, alternative scenarios have also been proposed: as development in a context of Laurentia–Gondwana collision (e.g. Dalziel et al., 1994; Thomas and Astini, 2003), as intracontinental basins (Omarini et al., 1999), or as a foreland basin setting to a rising orogen (Keppie and

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* Corresponding author. Tel.: +64 3 4799671.
*E-mail address:* argon@gns.cri.nz (C.J. Adams).

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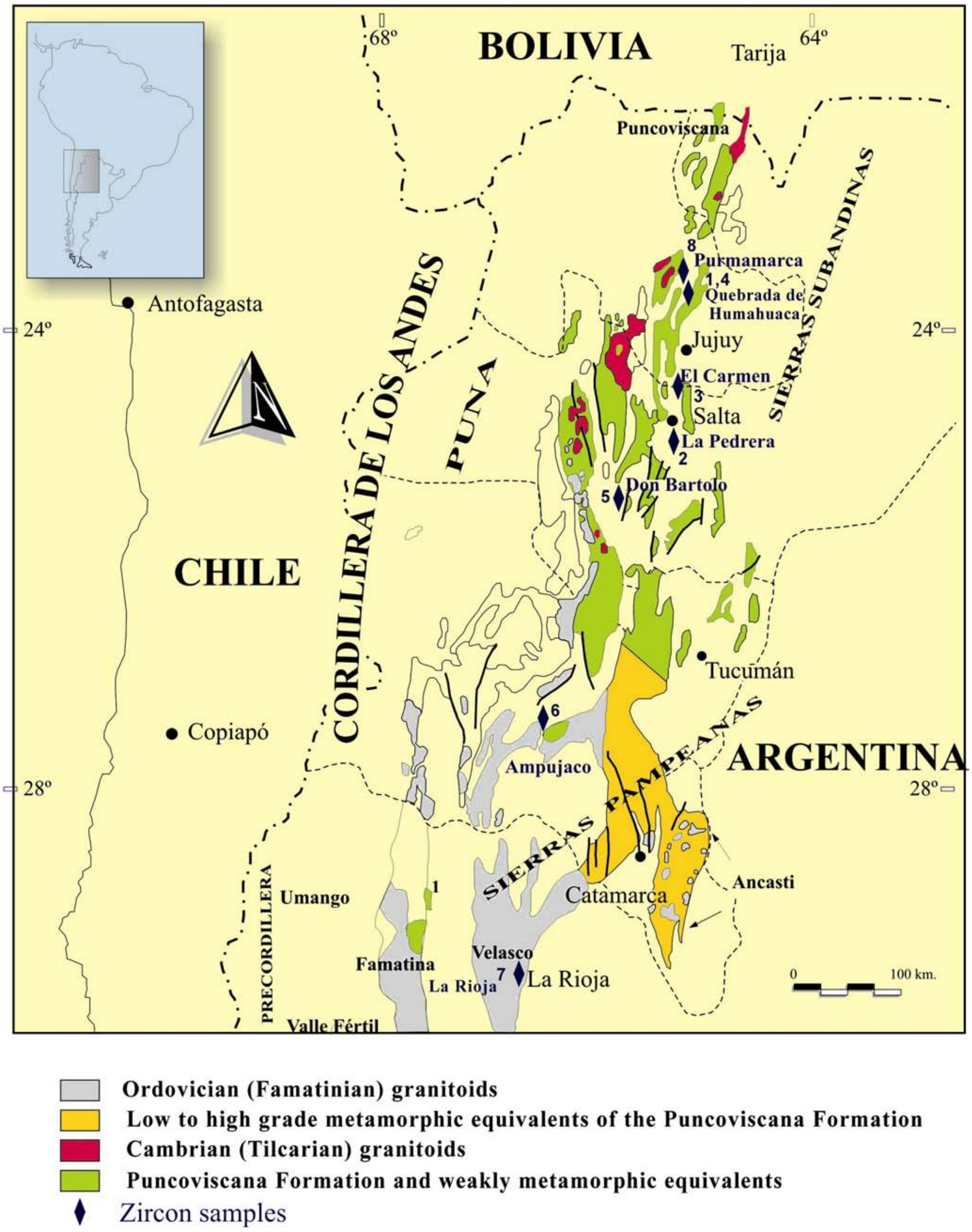

**Fig. 1.** Outcrop area of the Puncoviscana Formation and metamorphic equivalents, in northwest Argentina, showing sample localities for detrital zircon age studies. Extensive plutons are also shown. Modified from Ježek and Miller (1987).

Bahlburg, 1999; Zimmermann, 2005). A comprehensive review of these scenarios is given by Finney (2007), and the most likely is a passive margin to Gondwanaland. The so-called Pampean Cycle ended in the Middle Cambrian with the Tilcarian orogeny. This was followed by the Late Cambrian, Mesón Group, a molasse-type post-orogenic unit, as the first step of an Ordovician widespread volcano-sedimentary series (Fig. 2).

In this work, a comparison is attempted of the late Neoproterozoic/early Paleozoic sedimentary processes at the western border of Gondwanaland with the tectonic events at the site of Gondwana-building amalgamation of African and South American cratons, and with orogenic events in the interior of Precambrian South America.

### 1.1. Puncoviscana Formation

The Puncoviscana Formation (Turner, 1960) comprises monotonous tracts of multiply deformed, low-grade metasediments (lowest greenschist facies) at least 3000 m thick. Continuous stratigraphic successions are rare and formal subdivision is not possible. Fossil (trace and soft-body) occurrences are sparse, but several species of the genus *Oldhamia* are characteristic of the Early Cambrian, whilst several others are only post-Proterozoic. Large outcrops of higher-grade metamorphic equivalents of the Puncoviscana Formation occur to the south, in Catamarca (Aceñolaza and Miller, 1982). Sedimentological features, e.g., flute casts, wave ripples, pebble orientation (Ježek, 1990; Ježek et al., 1985), indicate a range of environments, ranging from wave-base shallow-water mainly in the east, to mid-fan turbidites mainly in the west, respectively named '*Oldhamia*-belt' and '*Nereites*-belt', on the basis of rare, but significant, trace- and soft-body fossil occurrences (Aceñolaza et al., 1988; Aceñolaza and Aceñolaza, 2005). Greywacke (dominant)–siltstone–mudstone graded-bed successions (Figs. 2, 3) are widespread, but limestones and intercalated volcanic rocks are very rare. Geochemical and petrological features of the sediments suggest a recycled-orogen provenance (Ježek et al.,

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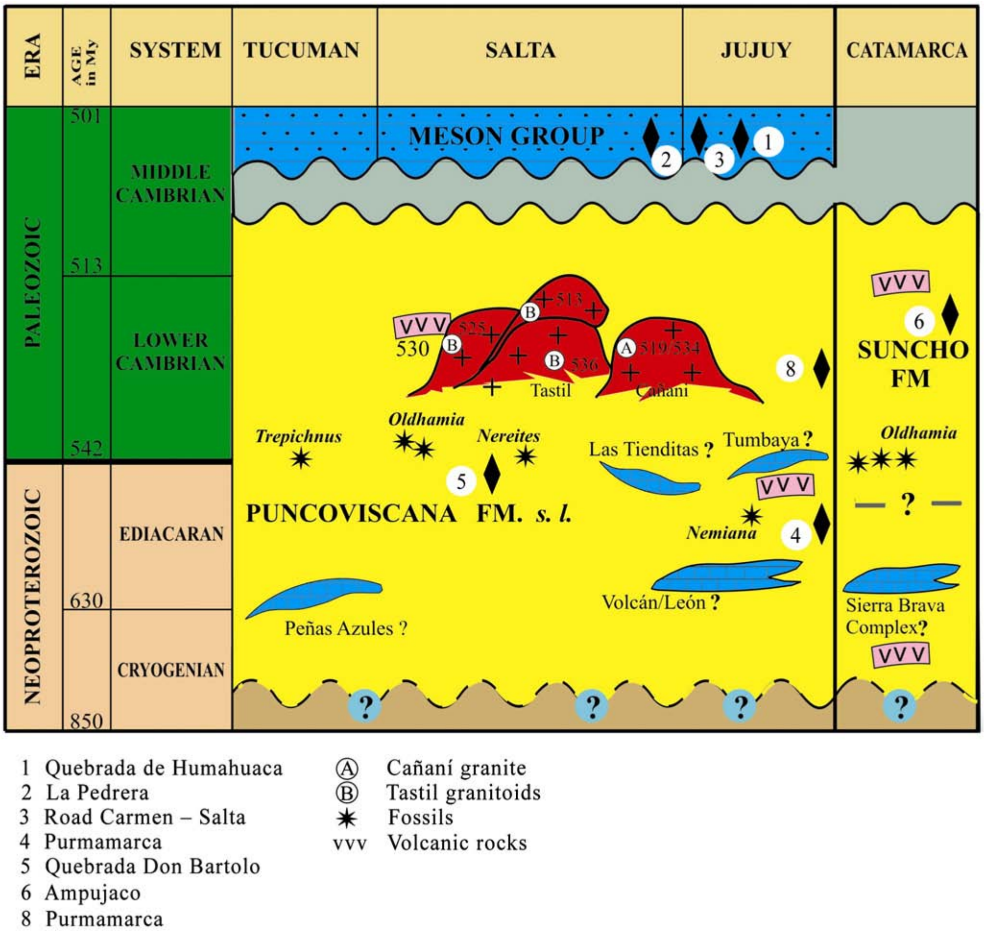

**Fig. 2.** Lithostratigraphical overview of the Late Neoproterozoic and Early Cambrian in northwest Argentina with sample locations (except (*7*), stratigraphic position uncertain—see Fig. 1).

1985; Ježek and Miller, 1987; Ježek, 1990; Pankhurst and Rapela, 1998; Do Campo and Guevara, 2005; Zimmermann, 2005). Omarini (1983) and Omarini et al. (1999) considered the Puncoviscana Formation to be mostly late Proterozoic in age, with only a minor Early Cambrian part but, on faunal evidence, Durand and Aceñolaza (1990) and Aceñolaza and Aceñolaza (2005) assigned it mostly to the Early Cambrian, and only minor parts to the Neoproterozoic. This latter assignment is supported by Early Cambrian U–Pb ages of euhedral (volcanicrystic) detrital zircons in greywackes near Cachi (Lork et al., 1990). This initial geochronological work has been enlarged with new U–Pb (single crystal) detrital zircon and Rb–Sr metamorphic age studies (Adams et al., 2005, 2008, and this study) of the Puncoviscana Formation, and similar work on possible correlative rocks in central and western Argentina (Schwartz and Gromet, 2004; Finney et al., 2005; Escayola et al., 2007; Rapela et al., 2007).

In northwest Argentina, the Puncoviscana Formation was strongly folded and weakly metamorphosed, and intruded by granitoids during the Tilcarian Orogeny in mid-Cambrian times. This orogenic event is known also from metamorphic rocks of provinces to the south, Tucumán, Santiago del Estero, Catamarca and La Rioja, and in central Argentina from the Sierras de Córdoba and San Luis. These phyllites, micaschists and gneisses have been compared with the Puncoviscana Formation by Aceñolaza and Miller (1982), Prozzi, 1990; von Gosen and Prozzi, 1998; Söllner et al. (2000b) and Pankhurst and Rapela (1998), and more recently confirmed by Steenken et al. (2008), in contrast to Steenken et al. (2004). Most authors regard these metasedimentary rocks as equivalents of the Puncoviscana Formation deposited in the same sedimentary basin.

### *1.2. Mesón Group*

In northwest Argentina, in Jujuy and Salta provinces, siliciclastic sedimentary rocks of the Mesón Group rest with pronounced angular unconformity upon the Puncoviscana Formation. These comprise mostly sandstone, partly conglomerate, siltstone and mudstone, and are divided into 3 formations: Lizoite, Campanario, and Chalhualmayoc. Thickness varies from a few tens of metres at the basin margin, to several hundreds of metres, and exceptionally to 2000 m at the border with Bolivia (Sánchez and Salfity, 1999). Trace fossils, e.g. *Skolithos*, are frequent, but body fossils are rare and poorly preserved. The Mesón Group is regarded as the basal unit for the sedimentation of the Famatinian (Ordovician–Devonian) orogenic cycle in northwest Argentina. The siliciclastic rocks of the Mesón Group (Figs. 4, 5) were deposited in shallow, near-coastal and tide-dominated environments in the form of sand bars (Sánchez and Salfity, 1999; Aceñolaza, 2003, 2005).

Generally, the age of the Mesón Group has been considered Cambrian. On paleontological evidence, Sánchez and Salfity (1999) and Aceñolaza (2003, 2005) restricted the age range from Middle to Late Cambrian. But the few badly preserved body fossils are not distinctive enough for an exact biostratigraphical age determination. The presence of late Early Cambrian zircons in part of the underlying Puncoviscana Formation (Adams et al., 2008), and the Early to mid-Cambrian zircon ages of the Santa Rosa de Tastil and Cañaní granitoids intruding the Puncoviscana Formation (514 ± 4, 519 ± 3, 536 ± 7 Ma: Bachmann et al., 1987; 536 ± 3, 525 ± 3 Ma: Matteini et al., 2008; 513 ± 4 Ma: Adams, unpubl. data.), further constrain the age of the Mesón Group to early Late Cambrian or younger. As a lithological unit, the Mesón Group

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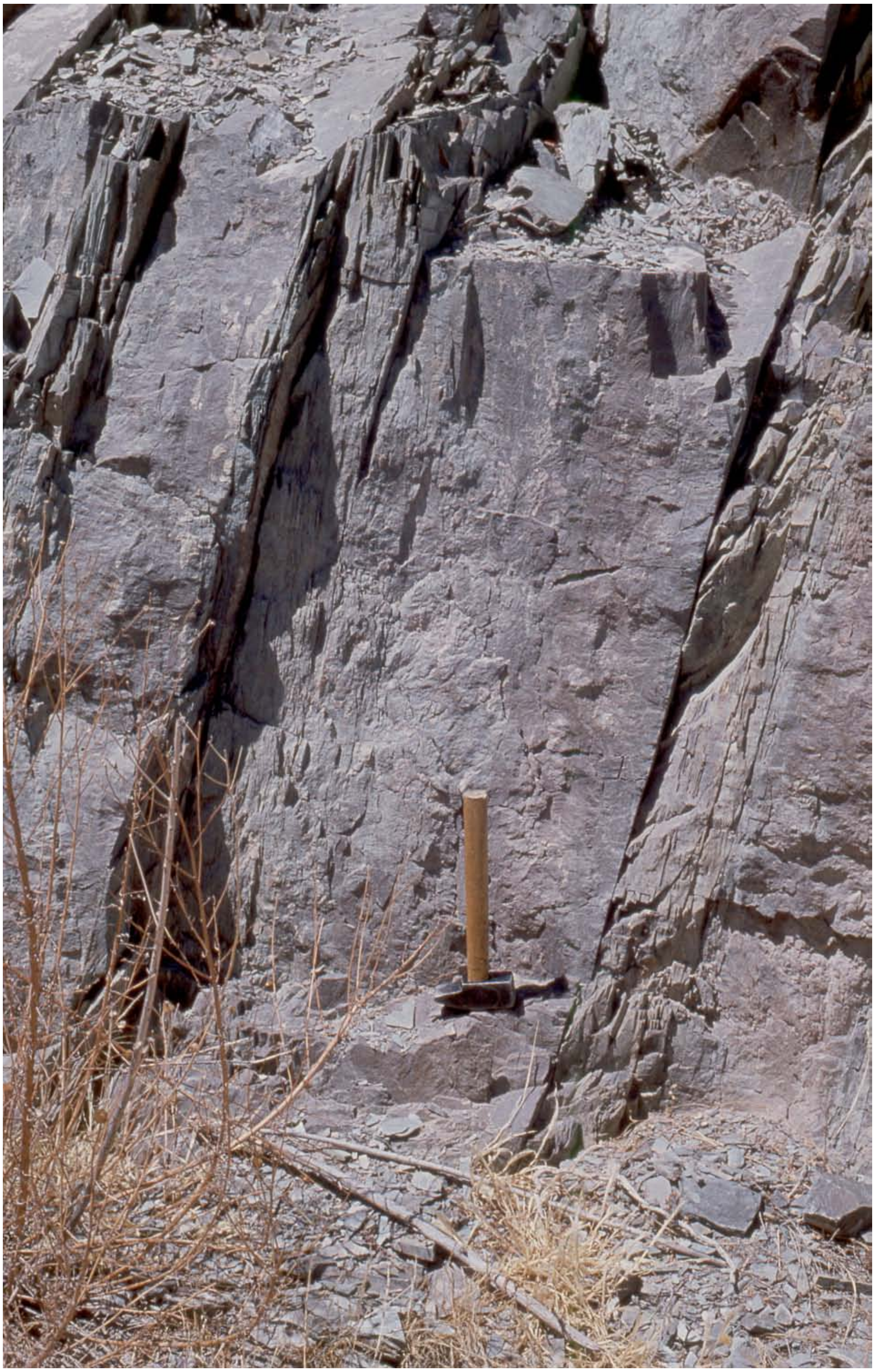

**Fig. 3.** Greywacke horizon in Puncoviscana Formation turbidites at junction of Hwy 9 from Jujuy and Hwy 52 to Purmamarca and Susques. Locality (*8*) of Fig. 6.

terminates before the Ordovician. Its top is defined by the Iruyican uncomformity (Astini et al., 2008). The overlying basal parts of the Santa Rosita Formation were dated as very late Cambrian (Furongian Stage 10 that begins at 492 Ma) by Zeballo and Albanesi (2008) and Esteban and Tortello (2008).

### *1.3. Objectives*

A main objective of this new study was to confirm more fully the stratigraphic age range and provenance of the Puncoviscana Formation, as initially described by Adams et al. (2008), by sampling over the full outcrop area of the Formation, and including areas of presumed higher-grade metamorphic equivalents in La Rioja and Catamarca Provinces.

A further objective was to sample the basal parts of the Mesón Group (and the underlying Puncoviscana Formation) in order to investigate the nature of the geotectonic transition between them and to note any provenance changes by local reworking at the continent margin, and/or from more distant sources within the Brazilian Shield. This then allows an interpretative model for development of the

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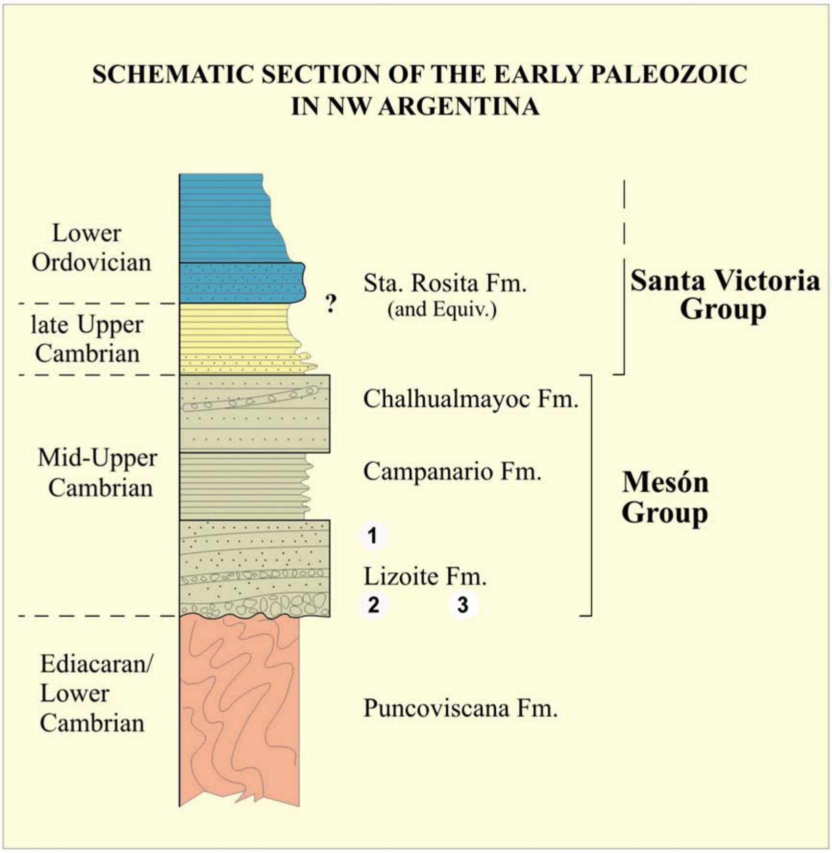

**Fig. 4.** Lithological section of the Cambrian in northwest Argentina. Numbers represent position of samples for Fig. 7.

Western Gondwanaland margin after initial consolidation of its central parts, and commencement of convergent environments at its continent/ocean transition.

## 2. Technical details

Eight samples were collected from the Puncoviscana Formation and Mesón Group (Figs. 1, 2), in particular at trace- and soft-bodied fossil localities (Durand and Aceñolaza, 1990). Coarser greywacke/ sandstone lithologies were collected from massive (dm- to m-scale) horizons. Note that samples (*1*, Mesón) and (*4*, Puncoviscana) were collected from the same locality, whilst sample (*7*) is from turbiditic rocks of Puncoviscana type in the Quebrada La Rioja, east of the city of La Rioja, but mapped locally as La Cébila Formation, and regarded as a possible equivalent of the Mesón Group.

**Fig. 5.** Typical outcrop of Mesón Group sedimentary rocks, at the boundary between Lizoite (right) and Campanario formations at Quebrada de Humahuacoa. Outcrop of sample locality (*1*).

Representative zircon samples were prepared minimising contamination, by reducing 500 g samples at the outcrop to a medium gravel, then in the laboratory crushing briefly (few seconds) in a tungsten carbide swingmill, and reducing to a 250 micron size through a single sieve. Mud-size particles were removed by washing in water, and zircon was separated in a sodium polytungstate heavy liquid with specific gravity 2.98.

Detrital zircon U–Pb ICPMS analyses followed methods developed at GEMOC laboratory, Macquarie University, Sydney (Jackson et al., 2004). Technical details of zircon preparation, analytical techniques, system calibration, data processing and age calculation are given in Adams et al. (2007). Full U–Pb isotopic ratio and age data of the present, and previously-published (Adams et al., 2008), work are given in a Supplementary Data Table (XXXX).

The zircon ages are shown in probability curves and histograms in Fig. 6 (Puncoviscana Formation) and Fig. 7 (Mesón Group), where ages $<1000$ Ma are $^{206}Pb/^{238}U$ data, and $>1000$ Ma are $^{207}Pb/^{206}Pb$ data. All age data presented here have concordant $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ages at 95% confidence limits. Ages of some zircon component peaks regarded as significant i.e. with at least 4, and commonly 8–25, grains with ages within experimental error (at 95% confidence limits), *and* comprising at least 4% of total, are shown in bold italic type. Where large, for example $n>10$, the zircon age groups were checked for overlapping age components by deconvolution, and the stated component ages and their errors are then derived from a Gaussian fit. For zircon smaller groups, but still with $^{206}Pb/^{238}U$ ages overlapping at 95% confidence limits, the ages and errors are those for a simple weighted mean. Following these acceptance criteria, significant component age peak data are then summarised in Table 1, where also there are included previously-published data of Puncoviscana Formation samples, similarly calculated and presented by Adams et al. (2008). The component peak age data of Table 1 are further summarised graphically in Fig. 8, and include data (sample numbers with an 'A' suffix) previously published by Adams et al. (2008). In this diagram the detrital zircon component ages (and their errors) are plotted as boxes on the horizontal axis, and stacked (in the absence of independent accurate stratigraphic age evidence) on the vertical axis, primarily in order of youngest zircon age component (i.e. maximum stratigraphic age). In some cases, Rb–Sr metamorphic age data constrain their position, too. The height of each box reflects the age component proportion (as %) of the total. This type of diagram has the benefit of efficiently summarising zircon age data from many rather similar probability curves, taking into account the age precision of the apparent component age peaks, and their importance (as % of total) within the total dataset. In doing so, it also avoids the over-zealous interpretation of single individual ages, often isolated and intriguing, but without completely trustworthy independent means to validate them. The rather conservative criteria set for the significance of any age component (see above) at least minimises this risk, and those that dominate a dataset, with ages having low standard errors (i.e. the 'skyscaper' boxes in Fig. 8), are particularly important and require critical attention. It is possible that the less dominant age components, with larger standard errors (i.e. 'woolshed' boxes in Fig. 8), although still significant, are in fact an amalgamation of closely connected subcomponents (e.g. volcanic lava sequence) beyond the statistical means to discriminate them. The diagram further provides a clear view of the essentially polymodality of the age patterns and any long-term change in this, and the persistence (or loss) of particular components with time. The larger-scale grouping of the age components (late Mesoproterozoic–early Neoproterozoic and late Neoproterozoic–Cambrian), especially with respect to the stratigraphic age limit, is nicely seen to reflect the balance between uplift and erosion at source, and burial rate at depocentre.

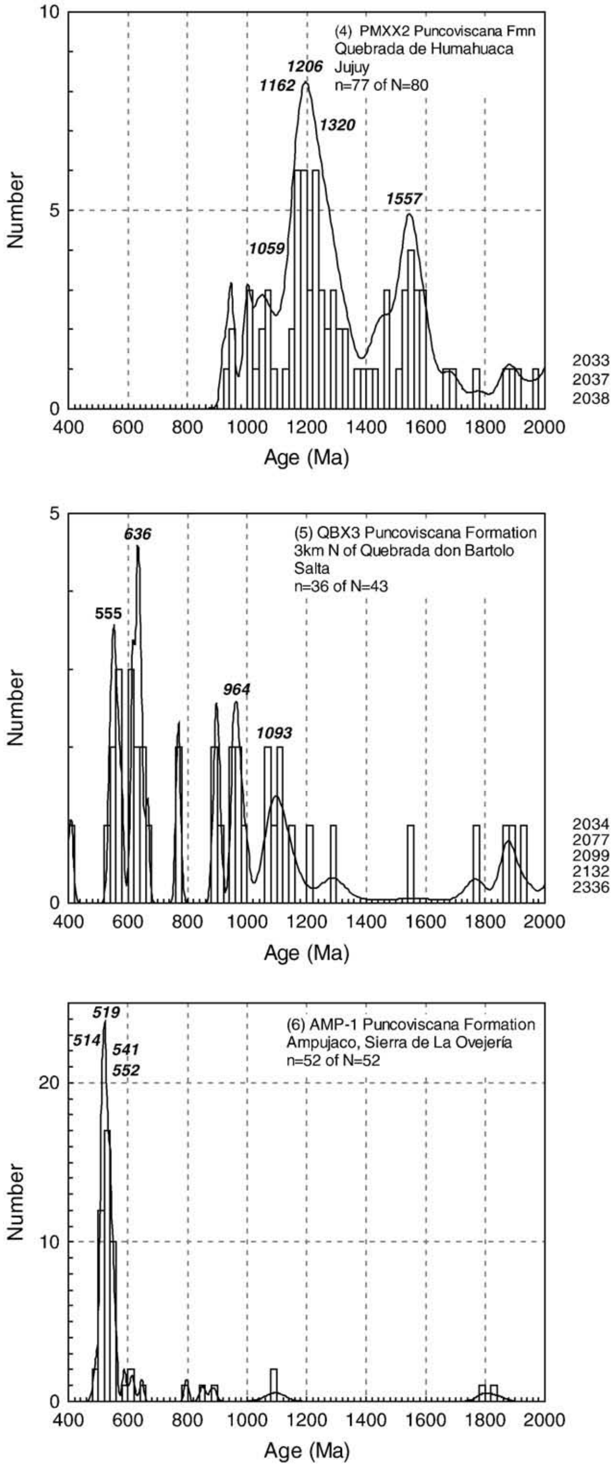

**Fig. 6.** Combined probability density and histogram diagram for detrital zircon ages from the Puncoviscana Formation of northwest Argentina. Ages <1000 Ma are $^{206}$Pb/$^{238}$U analyses, ages >1000 Ma are $^{207}$Pb/$^{206}$Pb analyses. Ages > 000 Ma are stacked at the right margin. The ages of some significant age components are shown in bold italics.

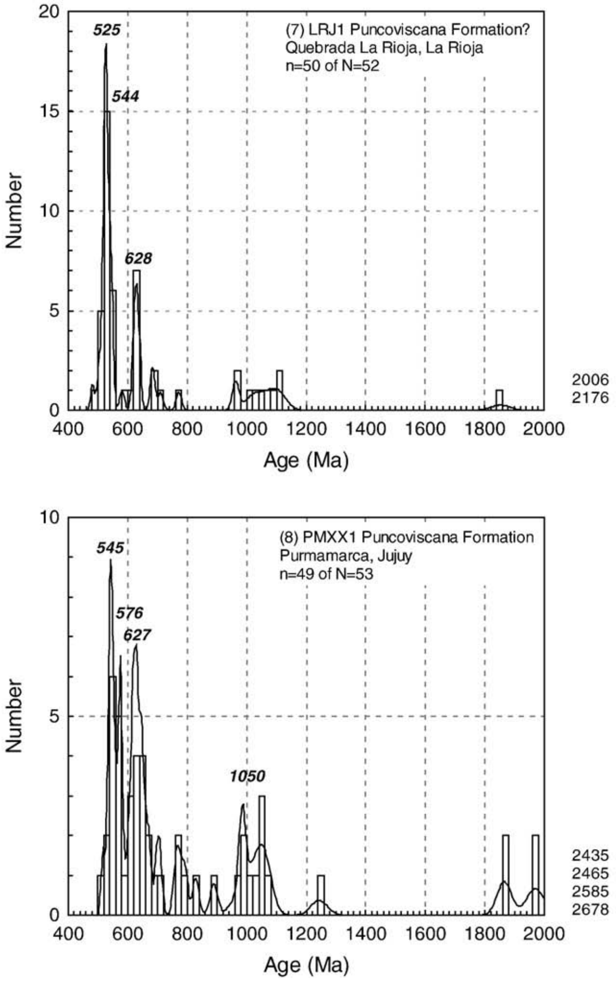

**Fig. 6** (*continued*).

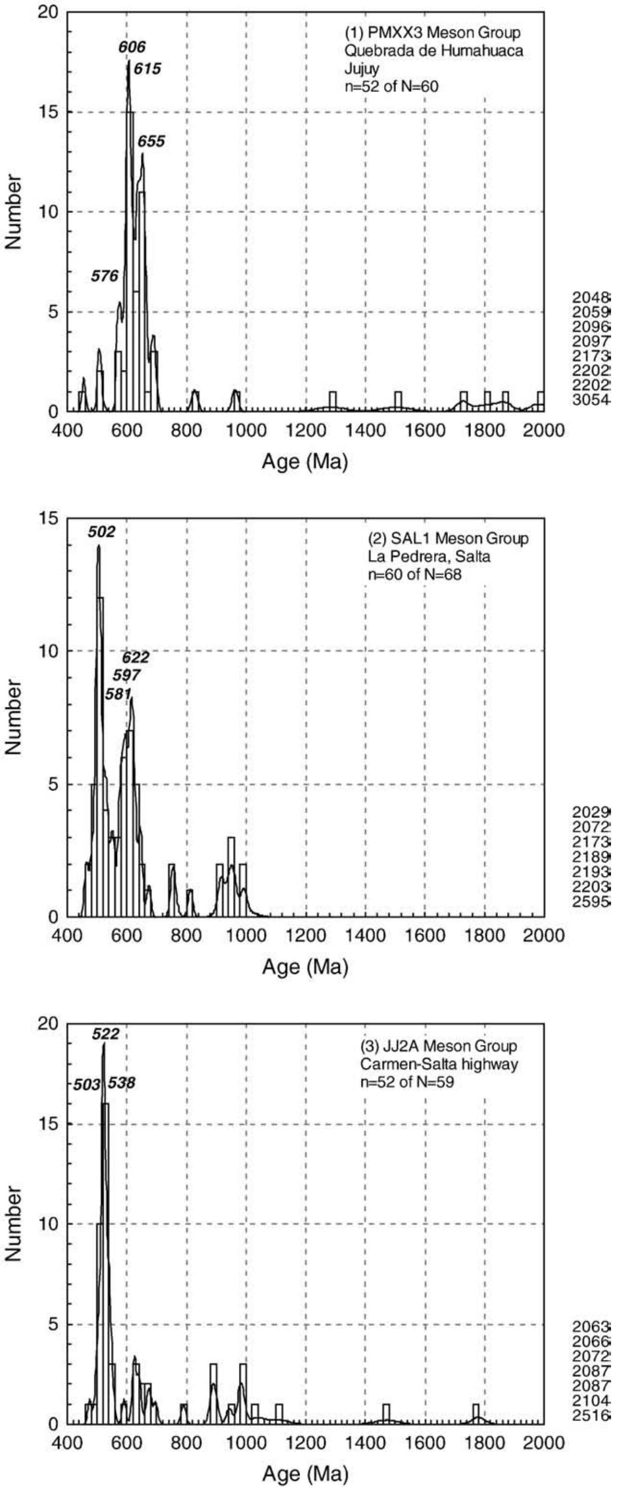

**Fig. 7.** Combined probability density and histogram diagram for detrital zircon ages from the Mesón Group of northwest Argentina. Ages <1000 Ma are $^{206}Pb/^{238}U$ analyses, ages >1000 Ma are $^{207}Pb/^{206}Pb$ analyses. Ages >2000 Ma are stacked at the right margin. The ages of some significant age components are shown in bold italics, and one less so, in italics.

**Table 1**
Meson group and Puncoviscana Formation, northwest Argentina: summary of detrital zircon U–Pb age components.

| Locality no./ zircon component | Detrital zircon age component (Ma) ± 2e | % of total zircon pop. | Zircon set total, *N* |
|---|---|---|---|
| *Meson group* | | | |
| (1) PMXX-3, Quebrada de Humahuaca, road outcrop in Lizoite Formation, Hwy 9, nr. Tilcarara;23°49′16″S 65°28′28″W | | | |
| a | 576 ± 6 | 8 | 60 |
| b | 606 ± 4 | 18 | |
| c | 615 ± 14 | 8 | |
| d | 655 ± 5 | 12 | |
| (2) SAL-1, La Pedrera, road outcrop above basal unconformity, Salta-La Quesera, Salta;23°49′16″ 65°28′28″W | | | |
| a | 502 ± 4 | 16 | 68 |
| b | 581 ± 8 | 6 | |
| c | 597 ± 7 | 10 | |
| d | 622 ± 6 | 7 | |
| (3) JJ-2A quartzite, road outcrop, Camino Carmen-Salta, 24°27′29.4″S65°17′43.4″W | | | |
| a | 503 ± 5 | 6 | 60 |
| b | 522 ± 11 | 31 | |
| d | 538 ± 6 | 7 | |
| e | 2077 ± 21 | 8 | |
| *Puncoviscana Formation* | | | |
| (4) PMXX-2, Quebrada de Humahuaca, road outcrop, Hwy 9, nr. Purmamarca, Jujuy;23°44′61″S 65°28′46″W | | | |
| a | 1059 ± 32 | 8 | 80 |
| b | 1162 ± 27 | 8 | |
| c | 1206 ± 27 | 19 | |
| d | 1320 ± 33 | 16 | |
| e | 1557 ± 16 | 16 | |
| (5) QBX-1, Quebrada don Bartolo, road outcrop, Hwy 68, nr. Chorrillos, Jujuy;25°47′21″S 65°41′06″W | | | |
| a | 555 ± 7 | 9 | 43 |
| b | 636 ± 7 | 9 | |
| c | 964 ± 10 | 9 | |
| d | 1093 ± 28 | 12 | |
| (6) AMP-1, Ampujaco, river outcrop, pipeline access road, 5 km east of Ampujaco village, Salta;27°27′08″S 66°40′04″W | | | |
| a | 514 ± 8 | 15 | 52 |
| b | 519 ± 13 | 25 | |
| c | 541 ± 5 | 16 | |
| d | 552 ± 8 | 10 | |
| (7) LRJ-1-1, road outcrop, Quebrada La Rioja, La Rioja, Salta; 29°24′16″S 66°56′15″W | | | |
| a | 525 ± 3 | 33 | 52 |
| b | 544 ± 6 | 12 | |
| c | 628 ± 6 | 10 | |
| (8) PMXX-1, Purmamarca, road outcrop 1 km W of Hwy 9, Jujuy; 23°44′38″S 65°28′15″W | | | |
| a | 545 ± 5 | 9 | 53 |
| b | 576 ± 6 | 8 | |
| c | 627 ± 7 | 8 | |
| d | 1050 ± 24 | 9 | |
| *Puncoviscana Formation (previously-published data, Adams et al., 2008)* | | | |
| (1A) QT-4 Quebrada del Toro, road outcrop, Hwy51, nr. Chorrillos; 65°55′W24°40′S | | | |
| a | 636 ± 7 | 6 | 83 |
| b | 668 ± 13 | 7 | |
| c | 891 ± 10 | 10 | |
| d | 920 ± 8 | 7 | |
| e | 943 ± 11 | 5 | |
| f | 1021 ± 17 | 7 | |
| g | 1208 ± 25 | 5 | |
| h | 1867 ± 21 | 5 | |
| (2A) SJX-1, road outcrop Loma Bola Cerro San Javier, 26°50′32.5″S65°22′56.2″W | | | |
| a | 612 ± 13 | 10 | 67 |
| b | 628 ± 6 | 6 | |
| c | 904 ± 9 | 6 | |
| d | 1019 ± 18 | 6 | |
| e | 1052 ± 19 | 26 | |

(*continued on next page*)

## 3. Results

The zircon age patterns for the Puncoviscana Formation (Fig. 6) and Mesón Group (Fig. 7) have similar, dominant (>33%), late

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**Table 1** (*continued*)

| Locality no./ zircon component | Detrital zircon age component (Ma) ± 2e | % of total zircon pop. | Zircon set total, *N* |
|---|---|---|---|
| (3A) SNX-1, metagreywacke, road outcrop, Sierra Nogalito, 26°26′01.8″S65°03′13.6″W | | | |
| a | 596 ± 6 | 10 | 69 |
| b | 624 ± 5 | 9 | |
| c | 1014 ± 10 | 13 | |
| d | 1056 ± 10 | 19 | |
| e | 1112 ± 27 | 10 | |
| (4A) RCX-1, greywacke, road outcrop, Rio Choromoru, Cumbres Calchiques, 26°23′04.6″S65°27′53.3″W | | | |
| a | 551 ± 5 | 6 | 79 |
| b | 583 ± 6 | 5 | |
| c | 612 ± 5 | 6 | |
| d | 626 ± 4 | 8 | |
| e | 650 ± 6 | 5 | |
| f | 1026 ± 16 | 12 | |
| h | 1893 ± 20 | 6 | |
| (5A) JJ-2 greywacke, road outcrop, Camino Carmen-Salta, 24°27′29.4″S65°17′43.4″W | | | |
| a | 530 ± 4 | 40 | 73 |
| b | 555 ± 5 | 7 | |
| c | 618 ± 5 | 7 | |
| d | 2120 ± 24 | 5 | |
| (6A) CAC-3, greywacke, road outcrop, Rancagua, 25°10′37.8″S66°11′00.9″W | | | |
| a | 522 ± 4 | 16 | 74 |
| b | 534 ± 4 | 18 | |
| c | 656 ± 7 | 5 | |
| d | 1006 ± 30 | 5 | |
| e | 1065 ± 27 | 7 | |

Notes.
e = standard error.

Neoproterozoic–Cambrian, zircon groups (with locality (*4*)[1] an important exception), but they are different in the absence in the latter of any significant Mesoproterozoic age components, that are quite characteristic of the former. On the other hand, the Mesón Group has a small zircon age group, c. 500 Ma (Late Cambrian), which is absent in the Puncoviscana Formation, and thus sets a younger depositional age limit for the Formation. The Puncoviscana Formation samples, whilst having features in common with previously-published age data (Table 1, and Adams et al. (2008)), now show the evolving late Neoproterozoic–Cambrian detrital zircon age pattern which links this formation with the Mesón Group.

## 3.1. Puncoviscana Formation

Detrital zircon U–Pb age patterns for five greywackes (Figs. 2, 6) include a northernmost locality, just east and southeast of Purmamarca, Jujuy (*4*); an isolated central outcrop near Quebrada don Bartolo, Río de las Conchas, Salta (*5*) from which youngest Rb–Sr metamorphic ages are 504 ± 15 Ma (Adams et al., 2008); a more southern outcrop of the Suncho Formation (Puncoviscana Formation equivalent) at Ampujaco, Sierra de La Ovejería, Catamarca (*6*) and a southernmost outcrop at the Quebrada La Rioja, west of the city of La Rioja (Figs. 2, 6) .

The zircon age patterns follow a trend, also observed by Adams et al. (2008), in the change in proportion of the late Mesoproterozoic to late Neoproterozoic–Early Cambrian age groups with decreasing age of the youngest significant age component. The Quebrada don Bartolo greywacke (*5*) has the most typical Puncoviscana pattern. Although this dataset, $n = 43$, is smaller than ideal, and the component peaks cannot be determined accurately, it does show the two major age groups in similar proportions. No fossils are known from this locality (Quebrada don Bartolo, Río de las Conchas area), but nearby, in the Lerma Valley, the Puncoviscana Formation contains *Nereites saltensis*. The chronological significance of the latter is not yet finally settled, but in the Sierra de Mojotoro, it accompanies the ichnospecies *Treptichnus* characteristic of the Ediacaran/Early Cambrian boundary.

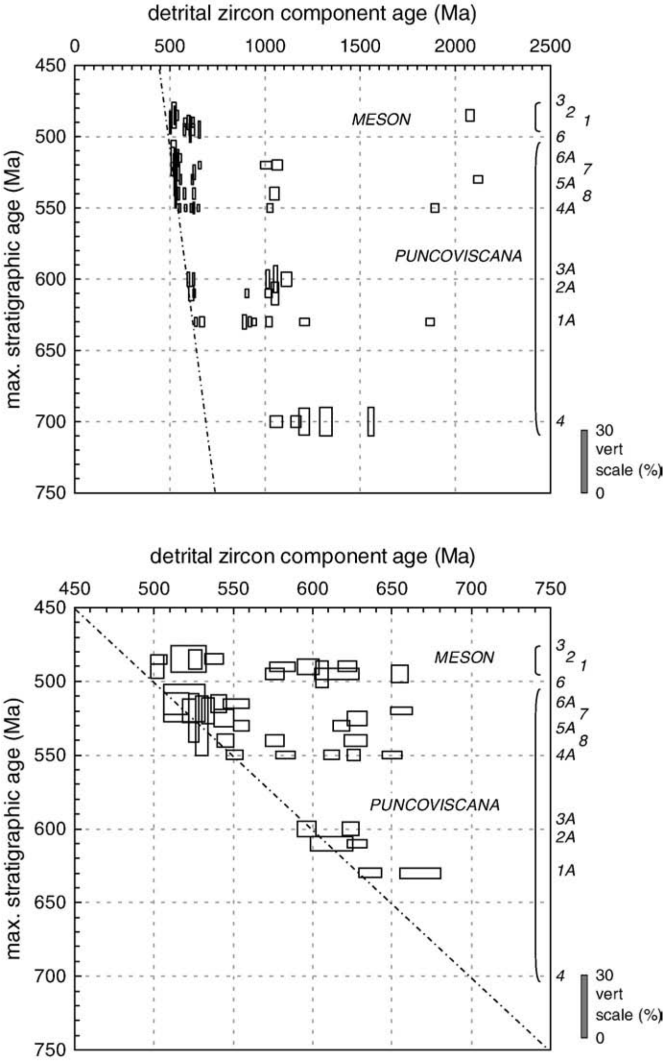

**Fig. 8.** Summary of significant detrital zircon U–Pb age components in Mesón Group and Puncoviscana Formation samples from northwest Argentina. The zircon component age data are shown on the horizontal axis as boxes whose width represents the component age error, and the height reflects the proportion of that component as a percentage of the total (see scale bar at right side). The sample locality numbers are shown in italics at the right side. Less precise component ages from the smaller dataset from locality (5) are omitted. In the absence of independent stratigraphic age control, the sample sets are stacked on the vertical axis in ascending order of maximum stratigraphic age, as constrained by their youngest zircon age components, but with the exception of 'old' sample (4), which is *arbitrarily* placed at a maximum stratigraphic age position, 700 Ma (see text). The dot-dash line is the stratigraphic age limit—detrital zircon ages must fall to the right of this. An enlargement of the late Neoproterozoic–Cambrian section is shown as an inset below.

The Purmamarca (*4*) and Ampujaco (*6*) samples (Fig. 6) represent extremes dominated respectively by the older or younger age group of zircons.

In comparison with other Puncoviscana Formation samples (*5*, *6*, *1A*–*6A*, Table 1, Figs. 6, 8), the Quebrada de Humahuaca "Purmamarca" sample (*4*) is most distinctive. It has the largest proportion of Mesoproterozoic zircons, and its youngest individual zircon ages are quite older than in every other sample, c. 920 Ma. The late Neoproterozoic–Cambrian group, so important (often > 30%) in all other Puncoviscana samples (Figs. 6, 8), is absent. However, the usual minor (< 20%), Paleoproterozoic–Archean age component is present (Adams et al., 2008). In the area near sample (4), discus-like moulds have been found which are identified as *Nemiana*

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[1] Italics indicate a sample locality number.

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*simplex* and "*Vendella larini*", the impressions of medusoid animals of Ediacarian age (Fedonkin et al., 2007; Leonov, 2007). This, in conjunction with the lack of typical Phanerozoic trace fossils, suggests that this sampling site (*4*) is within the oldest parts of the Puncoviscana Formation. Considering the detrital zircon geochronology alone, the depositional age of this sample could be as old as early to mid-Neoproterozoic. However, it differs from its next-oldest, counterpart at Quebrada del Toro, (*1A*), in not having the latter's distinctive early Neoproterozoic (c. 900–950 Ma) age component (Figs. 6, 8). A further Puncoviscana sample of very similar greywacke, was collected at locality (*8*), 4 km to the north to further check the extent of the "oldest" Puncoviscana Formation. However, this sample (*8*) has a more normal zircon age pattern (Fig. 6), with a broad age group at 627–545 (major) Ma and 1100–1000 Ma (minor). The change in relative proportions of these two major age groups from locality (4) to locality (5) to locality (8) may indicate an evolutionary trend. The apparently "oldest" sample may therefore be considerably younger than 900 Ma, but either predates the major influx of Late Neoproterozoic zircons which were not being supplied before c. 700 Ma, or was in some part of the depocentre where these zircons were somehow excluded. Detrital zircon age patterns hitherto obtained from Puncoviscana Formation and its metamorphic equivalents (Adams et al., 2005, 2008; Schwartz and Gromet, 2004; Finney et al., 2005; Escayola et al., 2007; Rapela et al., 2007) all show c. 600–650 Ma ages characteristic of the widespread Brasiliano Orogeny of south central and southeast Brazil. Thus, the lack of zircons younger than 900 Ma in the apparently oldest Purmamarca sample (*4*) suggests it may immediately predate the Brasiliano Orogeny.

The Ampujaco sample from locality (*6*), where the Early Cambrian trace fossil *Oldhamia* is present, is dominated (75%) by a 510–560 Ma age group (Fig. 6), within which the youngest zircon age component, 518 ± 8 Ma, imposes the youngest maximum stratigraphic age of all Puncoviscana Formation-like samples (Fig. 8). The large age error reflects the imprecision involved in the deconvolution of minor age components in the presence of overlapping major ones. The Mesoproterozoic component (<4%) has almost disappeared and there are no significant age components. Its closest counterpart is the sample (*5A*) from Cachi (Adams et al., 2008, Table 1), which comes from a succession with clear volcaniclastic features (Lork et al., 1990), and in which euhedral volcanic zircon grains, c. 523 Ma, are dominant (Adams et al., 2008). It is thus likely that the age of the youngest zircon component is here synchronous with the depositional age, in this case late Early Cambrian–early Middle Cambrian. This is confirmed by the presence of *Oldhamia radiata*, a trace fossil, whose occurrence is known worldwide from the Early Cambrian. The sample from Quebrada La Rioja (*7*) also resembles the youngest sample (*5A*) from the more northern region. Its lithostratigraphic position is not clear. It may represent the southernmost part of the La Cébila Formation which forms a large part of the eastern slope of the Sierra de Velasco, or it may be an analogue of the Puncoviscana Formation. In either case, the data show that at this locality there is an equivalent of the youngest parts of the sedimentary pile pre-dating the mid-Cambrian Tilcarian orogeny.

The new and previously-published data (Adams et al., 2008) are summarised in Fig. 8, where it can be seen that the proportion of the late Neoproterozoic–Cambrian age group increases steadily as its youngest age component becomes younger, and there is a commensurate decrease in the proportion and polymodality of the Mesoproterozoic age group. The 'older' samples (*4*, *1A–3A*) are particularly polymodal, and have several mid-Proterozoic age components, c. 950–900, 1150–1000, 1250–1200 Ma, of which only the 1150–1000 Ma group persists in the 'younger' samples (*4A*) The reverse is true within the late Neoproterozoic–Cambrian group, where the polymodality increases slightly in the 'younger' samples. After they first appear, age components in the ranges 650–600, 560–550 and 540–520 Ma are all persistent.

There is no consistent geographic pattern to the above variation; 'older' types, i.e. with Mesoproterozoic zircons dominant, are widespread, at Purmamarca (*3*), Quebrada del Toro (*1A*), Cerro San Javier (*2A*), and Sierra Nogalito (*3A*); whilst the 'younger' types, i.e. with late Neoproterozoic–Cambrian zircons dominant, occur at Río Choromoro (*4A*), Carmen (*5A*), Cachi (*6A*) and Ampujaco (*6*). (Note that samples with 'A' suffix are from previously-published data of Adams et al., 2008). Where there is the independent fossil age control (admittedly imprecise), and a minimum age constraint imposed by metamorphic ages (*4A*, *6A*), the youngest zircon age components are always close to the depositional age, and as concluded above, probably originate from contemporary volcanic sources. Within the late Neoproterozoic–Cambrian group, its gradual decrease in age of the group as a whole from 'older' to 'younger' types (as defined by their maximum stratigraphic age) suggests that the youngest zircon age component may (but not necessarily), reflect the depositional age. If this is accepted, then over a depositional interval 700 to 510 Ma, the increasing predominance of contemporary zircon populations would signal a fundamental change from a passive-margin setting in the late Neoproterozoic (as exemplified by samples (*4*, *1A*)), to more active-margin setting in the Early–Middle Cambrian (as exemplified by samples (*6*, *6A*)). This transition would have culminated with the widespread Middle Cambrian deformation and plutonism of the Tilcarian Orogeny, which closed the Pampean cycle.

### 3.2. Mesón Group

Sample (*1*) was collected from the uppermost part of the Lizoite Formation in the Humahuaca Valley, whilst samples (*2*) and (*3*) come from horizons close to the basal Mesón Group, unconformable upon the Puncoviscana Formation south of Salta. As only *Skolithos* trace fossils are found here, their exact lithostratigraphic position and correlation within the classical three-fold Mesón Group in the Humahuaca Valley is uncertain. Mesón Group-like sandstones are found at localities far to the south in the Sierra del Campo northeast of Tucumán (Aceñolaza, 2003; Aceñolaza and Nieva, 2003; Mángano and Buatois, 2003).

Mesón Group detrital zircon age patterns (Fig. 7) recapitulate some trends that are seen in Puncoviscana Formation datasets (above), and which culminate in the 'youngest' sample from Ampujaco (*6*). These datasets have large (>60%), and polymodal, late Neoproterozoic–Cambrian groups, and small proportions of Mesoproterozoic (<7%) and older (<20%) components (Figs. 7, 8). With the exception of 560–550 Ma ages, most of the several late Neoproterozoic–Cambrian components seen in the 'younger' Puncoviscana samples are inherited by Mesón Group samples. However, there are two important distinguishing features: (1) the presence of small components at c. 500 Ma, not seen in the Puncoviscana Formation, that set an early Late Cambrian maximum depositional age for the Mesón Group and (2) in the Precambrian part of the Mesón Group datasets, there are relatively more Paleoproterozoic, 2200–2000 Ma, and relatively fewer Mesoproterozoic, 1100–1000 Ma, individual ages than in the Puncoviscana Formation.

## 4. Discussion

A detailed discussion of the provenance and tectonic setting of Puncoviscana Formation sedimentation is given in Adams et al. (2008), and with new data presented here, this is briefly re-stated and extended to provide new constraints. The Mesón Group data also provide an essential post-Pampean Orogeny perspective to the evolution of the Cambrian–Ordovician Gondwanaland margin.

With the exception of sample (*6*), the constant feature of all U–Pb detrital zircon age datasets of the Puncoviscana Formation is the persistence of zircons derived from a Late Mesoproterozoic source (Fig. 8). The most persistent components are 1090–1000 Ma, and but less persistent groups at 950–900 Ma and c. 1200 Ma are important. Since Puncoviscana Formation deposition was widespread (500 × 200 km at least, more than 1000 × 400 km including the metamorphic equivalents to the south and southwest; see above) and encompassed all late Neoproterozoic–Early Cambrian time, perhaps

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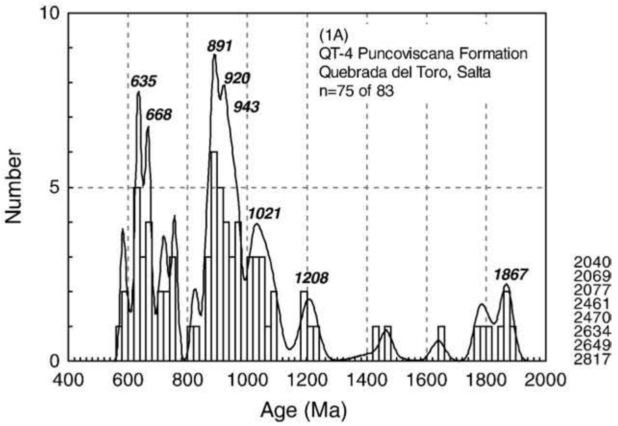

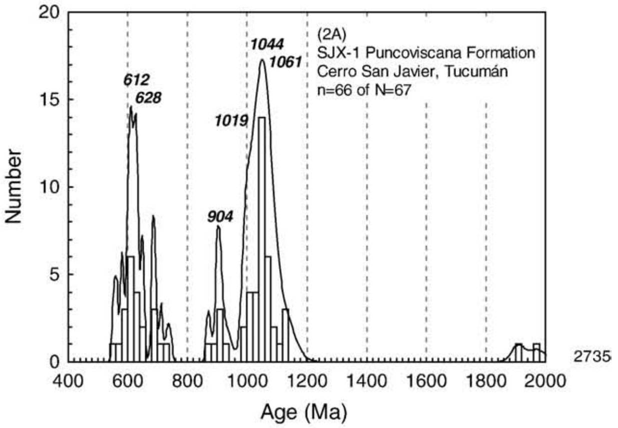

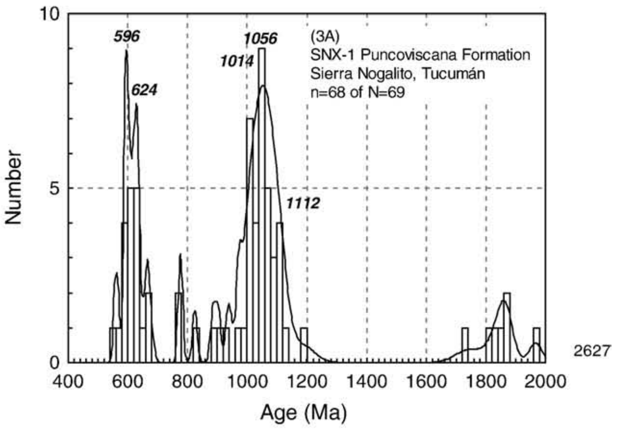

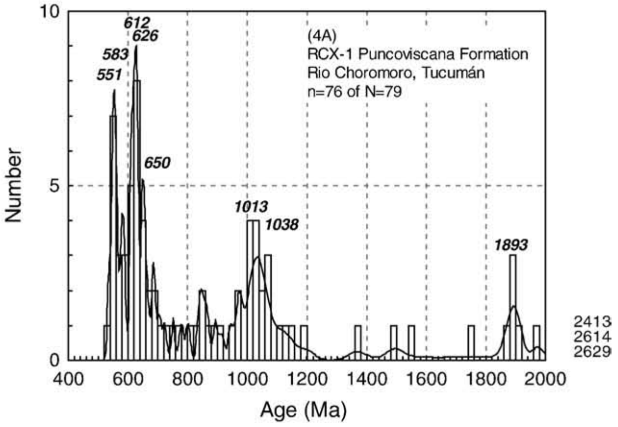

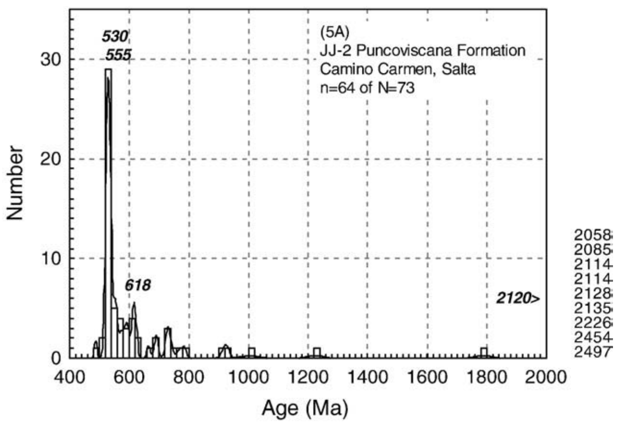

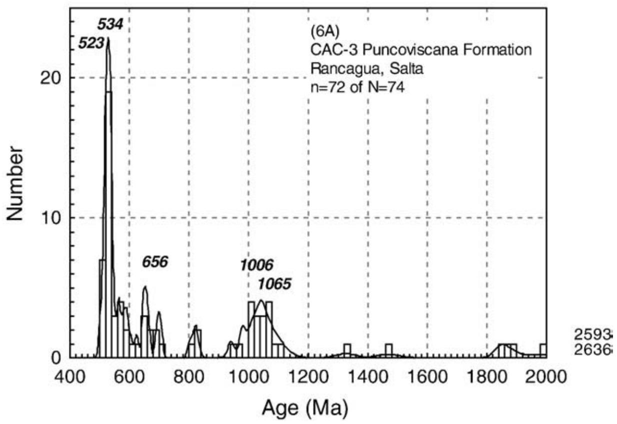

**Fig. 9.** Precambrian tectonic provinces of the Brazilian Shield as provenance areas for Mesón Group and Puncoviscana Formation sediments of northwest Argentina. Modified from Adams et al. (2008) after Cordani et al. (2000). Subsurface extension of the Río de la Plata craton after Rapela et al. (2007).

750–510 Ma, then the persistent zircon sources must be equally extensive and voluminous complexes of plutonic and metamorphic rocks, rather than limited, superficial volcanic centres. In this situation, a Precambrian craton is the most likely source, and additionally, would provide supplies of older Paleoproterozoic and Archean zircons. With a Puncoviscana depocentre operating (perhaps intermittently) over a 150–200 million year timespan, the Mesoproterozoic orogen supplying such voluminous sediments would undergo substantial erosion, and by the Middle Cambrian could have been greatly diminished. Thus, in this scenario, we suggest that Puncoviscana Formation deposition commenced in an essentially passive-margin environment.

However, the relative diminishment of the Mesoproterozoic sediment sources with time, at the expense of increasing Late Neoproterozoic and Early Cambrian inputs, is clearly connected to the gradual development of late Neoproterozoic (<700 Ma) igneous complexes that provided zircons. As argued above, these would be created in active-margin and/or compressional orogens, in which fore- and back-arc depocentres and/or burial-induced magmatism produced great sources for erosion of zircon-bearing rocks. If such orogens evolved continuously over 100 million years, then erosion of the subjacent plutonic equivalents would also be expected, and zircon supplies from these would continue over millions of years. This would explain the persistence of the late Neoproterozoic–Cambrian zircon components, which are seen to track the stratigraphic age limit (Fig. 8) as a broader scale grouping of age components in a 100 million year bandwidth, c. 620–520 Ma, in the Puncoviscana Formation and Mesón Group datasets.

To match detrital zircon components ages to possible provenances in the adjacent Brazilian Shield (Fig. 9), we rely here on the regional

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reviews of Basei et al. (2000), Cordani et al. (2000) and Brito Neves et al. (2000), and recent studies presented at the VI South American Symposium on Isotope Geology hold in 2008 in Bariloche, Argentina.

Firstly we can recognise plutonic and metamorphic complexes in the Brazilian Shield of Late Mesoproterozoic to Early Neoproterozoic age (1200 to 1000 Ma) in the Sunsás Orogen at the southwest margin of the Brazilian craton, i.e. possibly close to the Puncoviscana deposition site. Present outcrops are relatively small, but Santos et al. (2008a) suppose a former extension of up to 6000 km from northeast Argentina and Paraguay into eastern Venezuela. Ages of Sunsás type also occur elsewhere in the Brazilian Shield (e.g. Campanha et al., 2008; Sato et al., 2003). Whether the Western Sierras Pampeanas (Sierra de Maz and others) are autochthonous or parautochthonous to the margin of Gondwana (Casquet t et al., 2006), they can be considered as prolongation of the Sunsás orogen to the south, and may have contributed to any zircon detritus of Grenvillian age.

Secondly, Paleoproterozoic and Archean detrital zircon components could originate farther into the craton interior, respectively in the Ventuari-Tapajós Orogen and Central Amazonia complexes.

Thirdly, the frequent Late Neoproterozoic components (650–550 Ma) most probably originate in the classical Brasiliano Orogen of southeast and south central Brazil. Late Proterozoic magmatism and metamorphic overprints are widespread (e.g. Saalmann et al., 2006: 879–560 Ma, Philipp and Machado, 2005: 630–590 Ma and 570–550 Ma, Pimentel et al., 2006: 800 (±?) and 759 ± 65 Ma, Leite et al., 2007: 615–600 Ma). Increasing LA–ICP-MS zircon dating studies are dramatically improving the Brazilian orogenic history in many parts of southeast and south central Brazil (e.g. Schutesky Della Giustina et al., 2008; Junges et al., 2008; Cordani et al., 2003; Da Silva Schmitt et al., 2007; Laux et al., 2005; Santos et al., 2008b; Matteini et al., 2010). Volcanism from the adjacent southern Paraguay Belt dated at 543 Ma (Babinski et al., 2008) may also be responsible for zircons of such age in the Puncoviscana Formation. Similarly from the Sierra Norte de Córdoba (southeast of the Puncoviscana Fm. area), Miró et al. (2005) and Schwartz et al. (2008) described a magmatic arc with zircon ages of respectively 554 to 532 Ma and 555 to 525 Ma. An age of 584 + 22/−14 Ma has there been determined for ignimbrites by Llambías et al. (2003).

In addition, these Late Proterozoic and Early Cambrian mobile zones could provide also many of the older zircon age components (e.g. Söllner et al., 2000a; Pimentel et al., 2006; Leite et al., 2007; Campanha et al., 2008). The youngest zircons found in samples *5A*, and *6A* (Puncoviscana Formation), and sample *6* (Suncho Formation) with age peaks from 530 to 514 Ma, may be associated with nearby volcanic activity known in parts of the Puncoviscana Formation sedimentary succession in the Cachi Valley. Similarly some of the older, c. 535–525 Ma, granitoids within the Early–Middle Cambrian, Tastil Batholith of northwest Argentina (Matteini et al., 2008), may have been rapidly exhumed to provide zircons for the youngest Puncoviscana Formation and the Mesón Group (see below).

For the Mesón Group, the important youngest zircon component at 500 Ma (Table 1: *2*, *3*) may be closely associated with volcanic rocks nearby in the Puna (El Niño Muerto metadacites: 495 ± 4 Ma, and Río Blanco basalts: 501 ± 9 Ma; Hauser et al., 2008). These data jointly with the biostratigraphical Late Furongian age (492–488 Ma) of the base of the overlying Santa Rosita Fm. allow the definition of a very exact upper age limit for the Mesón Group at the base of the Furongian Series of the Late Cambrian.

In northwestern-most Argentina, close to our samples of Puncoviscana Formation and Mesón Group, Upper Cambrian to Lower Ordovician rocks have detrital zircon age patterns similar to those of this work (Di Cunzolo and Pimentel, 2008). A provenance from the Brazilian Shield is also supposed by these authors, and hence a Gondwana origin for the sediments. Di Cunzolo and Pimentel (2008) suggest a provenance for 2200–2000 Ma zircons in these rocks within the Río de la Plata Craton, and clearly this might also be true for zircons of this age in the Mesón Group. However, it remains unexplained why, prior to this, the Río de la Plata craton did not also supply similar zircons to the Puncoviscana depocentre (cf. Rapela et al., 2007).

## 5. Conclusions

The detrital zircon patterns of the Puncoviscana Formation and Mesón Group suggest two main sediment sources: (1) in a continental, cratonic hinterland having a stabilised, extensive late Mesoproterozoic–early Neoproterozoic orogen, 1200 to 900 Ma old (with minor Paleoproterozoic and Archean precursors, >1800 Ma), which became relatively diminished with time at the expense of inputs from (2) late Neoproterozoic–Early Cambrian orogens, c. 700–550 Ma, containing an evolving sequence of contemporary volcanic/plutonic components. Thus, the importance of Grenvillian and Pan-African zircon ages as noted by Rino et al. (2008) in recent river-mouth sands all over the Earth is well recorded even in sediments of the Proterozoic/Cambrian transition in western and southern South America.

A direct sediment provenance from the Brazilian Shield is suggested, within which Mesoproterozoic (Sunsás) and Late Neoproterozoic (Brasiliano) Orogens contributed the major sediment supply. Paleoproterozoic sources have never produced an important input to the sediments. They are placed within various Proterozoic sectors of the Brazilian craton, partially as old nuclei of the later orogens. By the end of the Proterozoic, sources from the Late Mesoproterozoic–Early Neoproterozoic became closed off from the Puncoviscana Formation depocentre. Before, this input of zircons with ages at c. 1200–1000 Ma was persistent, and their decline, as a percentage of total, may simply reflect the overwhelming dominance of Early Cambrian inputs (Table 1, Nrs. 6, 5A, 6A). However, this also may be due only to the gradual development of a Late Neoproterozoic sediment cover on at least part of the Sunsás Orogen (e.g. Gaucher et al., 2003; Trompette et al., 1998; Babinski et al., 2008), which may have closed the erosional processes at the Sunsás orogen.

The youngest U–Pb detrital zircon age components in Puncoviscana Formation greywackes, some of which originate from contemporary volcanic sources, indicate a maximum depositional age in the late Early Cambrian, and this age range might extend down into the Late Neoproterozoic, and in one case to mid-Neoproterozoic. It cannot be decided conclusively whether those samples with older maximum ages are in fact older, or if the age differences are purely an artefact of different provenance areas or of river course variation. The youngest U–Pb detrital zircon ages in post-Pampean Mesón Group, indicate a depositional age at or younger than early Late Cambrian.

The predominance of Late Neoproterozoic zircons in nearly all samples implies an extensive and complex provenance area of this age, which we believe can be most simply traced to the Brasiliano Orogen of southeast and south central Brazil. The birth of Gondwana, with the joining of the African and South American cratons, also influenced the formation of orogens within the latter. As a proto-Atlantic Ocean closed, the rising Brasiliano Orogen imposed a major river system that then transported its eroded mountain debris to a proto-Pacific Ocean. By Middle Cambrian time, the original, Late Neoproterozoic passive margin there was transformed into an active margin that culminated with the speeding up of sediment accumulation, magmatism, and deformation of the Tilcarian Orogeny. This history is confirmed by the development of magmatic arc scenarios in the Sierras de Córdoba (Schwartz et al., 2008).

Thus, sedimentation at the proto-Pacific border of the recently formed Gondwanaland, is not only the result of the accumulation of sediments at the passive margin of West Gondwana, but it is also triggered by the orogenic events at the site of collision of African and South American cratons.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gr.2010.05.002.

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