# Low-Grade Metamorphic Conditions and Isotopic Age Constraints of the La Horqueta Pre-Carboniferous Sequence, Argentinian San Rafael Block

**Hugo Tickyj, Carlos A. Cingolani, Ricardo Varela and Farid Chemale Jr.**

**Abstract** The San Rafael block is a pre-Andean geological entity situated in central-western Mendoza Province, Argentina. It is part of the Cuyania composite terrane. In this terrane it is important to consider the units exposed at the 'pre-Carboniferous' outcrops because they record geological events before the accretion to Gondwana. One of which is the siliciclastic La Horqueta Formation of an uncertain Lower-Middle Paleozoic sedimentary age. It is characterized by asymmetric, open to similar folds, with southeast vergence. KI values obtained from the La Horqueta Formation in its type area vary from 0.24 to 0.33 $\Delta°2\theta$, indicating very low-grade (high anchizonal) to low-grade (epizonal) metamorphic conditions, that increase slightly from south to north. The white mica b-parameter measured (9.016 ± 0.007 Å) suggest an intermediate pressure regime. Whole rock Rb-Sr isochronic ages were obtained on metapelites from the key outcrops in the La Horqueta area (379 ± 15 Ma, MSWD: 1.4) and in the Los Gateados area (371 ± 62 Ma, MSWD: 3.7), indicating that metamorphism and deformation occurred during the Devonian Chanic Orogenic phase, probably related to Chilenia

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terrane collision. U-Pb LA-MC-ICPMS detrital zircon ages patterns suggest that the La Horqueta Formation received a dominant sedimentary input from Mesoproterozoic sources, minor contributions from cratonic environments of Paleoproterozoic and Neoarchean ages, and finally a younger input from Pampean and Famatinian orogenic belts. U-Pb detrital zircon ages indicate a maximum sedimentation age close to the Silurian-Devonian limit for the La Horqueta Formation.

**Keywords** Metamorphism · Tectonic vergence · Rb-Sr age · Detrital zircons · Silurian-Devonian

## 1 Introduction

The geological evolution of the proto-Andean Gondwana margin in southern South America during the Paleozoic has been related in several studies to the accretion of allochthonous or displaced terranes (Ramos et al. 1986; Dalla Salda et al. 1992; Astini et al. 1996; Aceñolaza et al. 2002). One of the better studied areas is the Cuyania terrane that was accreted to the active margin of South America contemporaneously with the development of a major orogenic episode—the Famatinian cycle—(Aceñolaza and Toselli 1973; Pankhurst and Rapela 1998). During Upper Devonian-Lower Carboniferous times, the Chilenia terrane was accreted (Ramos 1988; Ramos et al. 1998) along the western side of Cuyania terrane and coetaneous with the Chanic tectonic phase.

The San Rafael Block, located in western Argentina, constitutes, with the Las Matras Block, the southern part of the Cuyania terrane (Fig. 1). It is mainly composed of 'pre-Carboniferous units' (Mesoproterozoic to Devonian), Upper Paleozoic sedimentary and volcaniclastic rocks, superimposed by Gondwanic (Permian-Triassic) magmatism and a widespread Cenozoic volcanism (Dessanti 1956; Polanski 1964; González Díaz 1972; Cuerda and Cingolani 1998; Cingolani et al. 2001).

The 'pre-Carboniferous units' (Fig. 2) include a Mesoproterozoic igneous-metamorphic basement (Cerro La Ventana Formation), Ordovician mafic rocks (El Nihuil complex), Ordovician fossiliferous carbonates and siliciclastic sedimentary rocks of the Ponón Trehué and Pavón Formations, marine metasedimentary rocks known as the Río Seco de los Castaños Formation (Upper Silurian-Lower Devonian) and the La Horqueta Formation which is the subject of this study.

The aim of this paper is to constrain the age and the P-T conditions of the low-grade metamorphic event and the concomitant deformational episode that affected the La Horqueta Formation using white mica b-parameter and Kübler index values, Rb-Sr whole rock isotopic data, and a U-Pb geochronological provenance

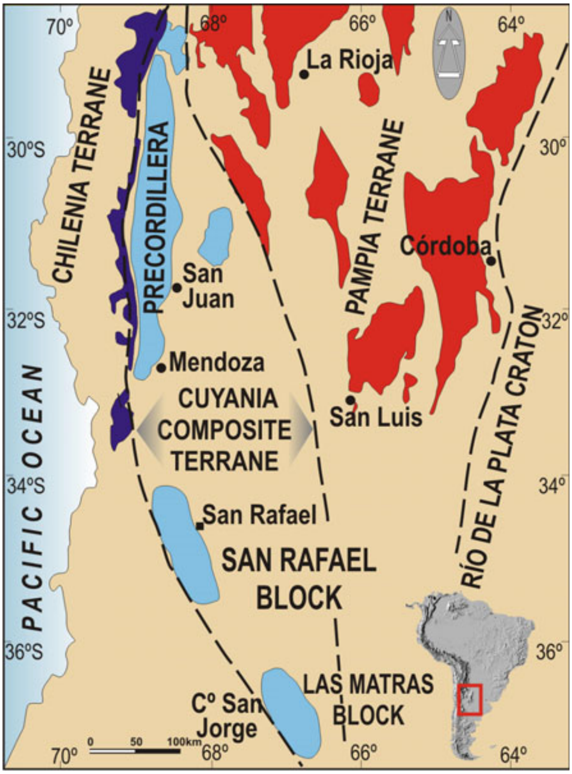


**Fig. 1** Different terranes from central-western Argentina and location of the study area in the San Rafael Block, as a southern part of the Cuyania composite terrane (Ramos et al. 1998; Manassero et al. 2009)

study of detrital zircons. The obtained results are discussed in the context of the geological evolution of the SW Gondwana margin.

## 2 Geological Setting

This sedimentary unit was originally mapped and described by Dessanti (1945, 1956) who called it 'Serie de la Horqueta'. Later, it was renamed as La Horqueta Group (Dessanti and Caminos 1967), and then considered as a Formation by several authors (e.g. González Díaz 1981; Criado Roqué and Ibañez 1979). It is a sandy-dominated meta-sedimentary sequence deposited in a marine environment. The base of the sequence is not exposed. The metamorphic conditions were estimated to range from very low grade in the southernmost outcrops (González Díaz 1972; Criado Roque and Ibáñez 1979; Tickyj and Cingolani 2000) to amphibolite facies in the northern area (Polanski 1964). The sequence was affected by deformational events that developed folding with cleavage. In the area crossed by the Diamante River, Dessanti (1956) described a tight folding with similar, recumbent to asymmetric folds. The northernmost outcrops show folded rocks characterized by

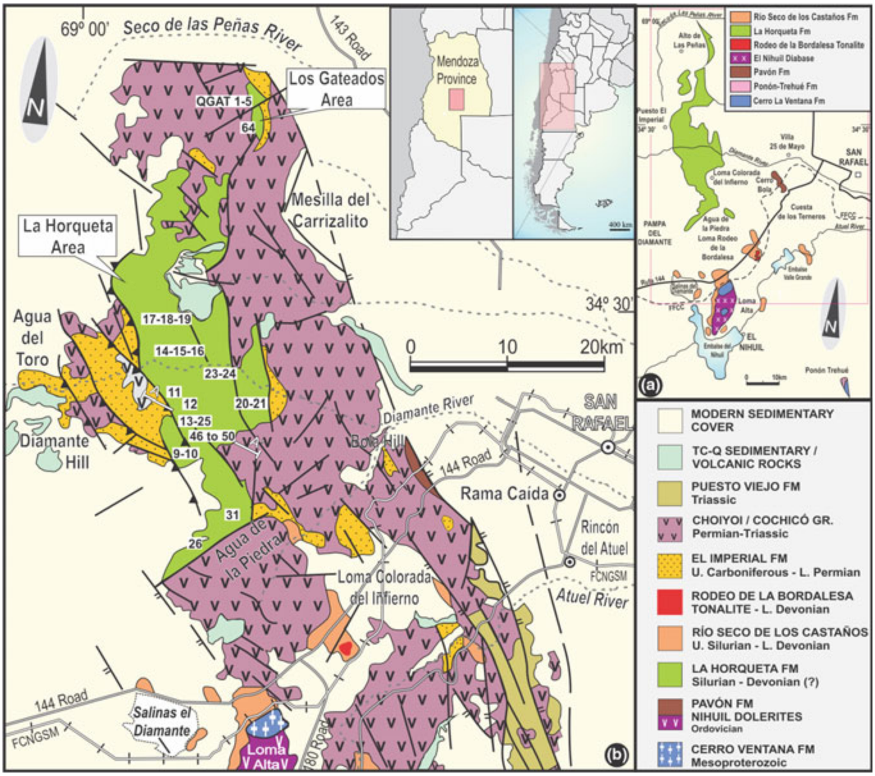


**Fig. 2** **a** Sketch map of the 'pre-Carboniferous' units in the San Rafael Block (modified from González Díaz 1981). **b** Outcrop distributions of the main geological units within the study area (Dessanti 1956). Numbers correspond to sample locations from the La Horqueta Formation. A–A′: Structural section shown on Fig. 5

tight to isoclinal gently plunging, upright folds with N-S trending axial planes and rare recumbent folds (Polanski 1964). The La Horqueta Formation was affected by a tectonic phase that put the metasedimentary sequence in contact with the Carboniferous continental to shallow marine (glacial) deposits of the El Imperial Formation. Some faults could have been reactivated during the Cenozoic Andean Orogeny (Moreno Peral and Salvarredi 1984; Cortés and Kleiman 1999; Japas and Kleiman 2004).

It is important to note that the "La Horqueta" unit initially comprised all 'pre-Carboniferous' sedimentary rocks of the San Rafael Block, exposed between the Los Gateados area and the Lomitas Negras and Agua del Blanco localities. Due to the lack of diagnostic fossils, an uncertain Precambrian to Devonian age was assigned (Dessanti 1956; Polanski 1964). At a later date, a fossil record including a Devonian coral similar to *Pleurodyctium* in Agua del Blanco exposures (Di Persia 1972), microfossils (acritarchs) of the Upper Silurian age in outcrops near the 144 road and ichnofossils like *Nereites-Mermia facies* in several outcrops (Rubinstein 1997; Poiré et al. 2002) were mentioned. More recently Morel et al. (2006) found herbaceous *Lycophytes* in the Atuel River section. These data support an Upper Silurian-Lower Devonian sedimentation age for part of the rocks included originally in the "La Horqueta" unit, now assigned to the Río Seco de los Castaños Formation. According to Manassero et al. (2009) this formation was deposited in a marine platform-deltaic system, the dominant sedimentary processes were wave and storm action, whereas source areas were located mainly to the east. However, K-Ar geochronological data of two magmatic complexes (originally described as intrusive bodies) yielded Lower Paleozoic ages and suggested that the "La Horqueta" unit could be Lower Paleozoic in age (González Díaz 1981). U-Pb age on zircons of $401 \pm 4$ Ma was obtained for the intrusive Rodeo de la Bordalesa Tonalite (Cingolani et al. 2003a), which is in according with mentioned fossil record, at least for a part of the unit now called Río Seco de los Castaños Formation.

At this point it is important to mention some stratigraphic changes (a) González Díaz (1981) splitted up the La Horqueta unit in the sense of Dessanti (1956) into two units: the La Horqueta and Río Seco de los Castaños formations. The latter lacks the regional metamorphic overprint as well as the mafic rock mentioned by Dessanti (1956) in the La Horqueta Formation. Furthermore, the Río Seco de los Castaños Formation preserved some diagnostic fossils as we mentioned before (acritarchs, lycophytes, coral). This suggestion was followed by Cuerda and Cingolani (1998), Cingolani et al. (2005) and Manassero et al. (2009) who also included in the Río Seco de los Castaños Formation the outcrops placed near road 144 (Fig. 2a) where Rubinstein (1997) found Upper Silurian microfossils (acritarchs), and Rodeo de la Bordalesa section with the intrusive tonalite; and (b) the Caradocian graptolite-rich sedimentary rocks located on the eastern slope of the Cerro Bola and originally comprising the "La Horqueta" unit, are now know as the siliciclastic Pavón Formation (Holmberg 1948 *emend*; Cuerda and Cingolani 1998).

Summarizing, we agree with the suggestions of Cuerda and Cingolani (1998) and Cingolani et al. (2003b) that the La Horqueta Formation (sensu stricto) should be restricted to the outcrops located on a strip reaching from the Seco de las Peñas River in the North to the Agua de la Piedra creek in the South. Where the best section is exposed—at the Diamante river area (Fig. 2)—these outcrops are 12 km wide. The La Horqueta Formation is bounded by reverse faults that bring this unit in contact with the Carboniferous El Imperial sedimentary sequence (Dessanti 1956; Giudici 1971) but in some outcrops like at Punta del Agua area, the Carboniferous rocks overlay the La Horqueta Formation separated by an angular unconformity (Fig. 3). The La Horqueta folded metasedimentary sequence is intruded by the Permian granitic stocks like Agua de la Chilena (Cingolani et al. 2005). All these rocks are overlain by Permian-Triassic volcano-sedimentary sequences related to the Choiyoi Gondwanian magmatism (Llambías 1999; Rocha Campos et al. 2011) (Fig. 2b).

Previous geochronological data of the metamorphic event that affected the "La Horqueta Formation" are K-Ar whole rock ages of $320 \pm 20$, $390 \pm 15$ and $395 \pm 15$ Ma (Toubes and Spikermann 1976, 1979; Linares and González 1990).

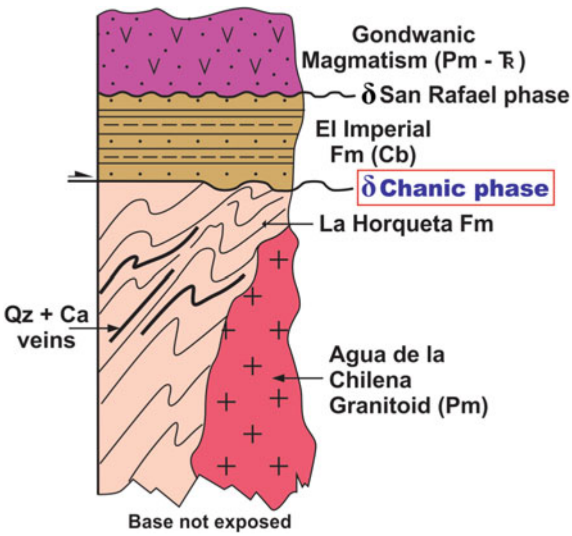


**Fig. 3** Schematic main stratigraphical relationships of the La Horqueta Formation in the San Rafael Block

## 3 Results on key sections of the La Horqueta Formation

Two separate and very well exposed areas—as previously stated—were selected to perform metamorphic and isotopic studies: La Horqueta type section and Los Gateados area (Fig. 2).

**Sedimentological and petrographical aspects**: At the La Horqueta type area the sequence consists of alternate beds of metawackes, metasiltstones, metapelites, and rare metaconglomerates, deposited in a marine environment (Fig. 4a, b). The metasandstones are the commonest rock type. They show tabular layers of variable thickness—between 0.1 and 6 m—which usually preserve sedimentary structures such as graded bedding, lamination and cross-bedding. The meta-sandstones show metaclastic textures with a matrix recrystallized into chlorite, illite, quartz, albite and minor smectite. The original texture has been modified to variable degrees. Thick layers usually present rough foliation with recrystallized matrix (Fig. 4c, d), while other layers show penetrative foliation with ductile deformed clasts and pseudo-matrix development (Fig. 4e, f). In less deformed metawackes, clasts are mainly composed of quartz (mono and polycrystals), and sedimentary and metasedimentary, with scarce volcanic and limestone lithoclasts, and minor feldspars. The presence of carbonaceous material (0.5–2%) and authigenic pyrite is common.

Fine grained sediments are less abundant and they have been mostly metamorphosed to phyllites. They are mainly composed of well oriented crystals of illite and chlorite (up to 10μ wide) with a minor proportion of quartz and feldspar. Abundant thin veins of quartz and calcite cut the phyllites. The meta-conglomerates are scarce and usually appear at the base of graded sandy layers.

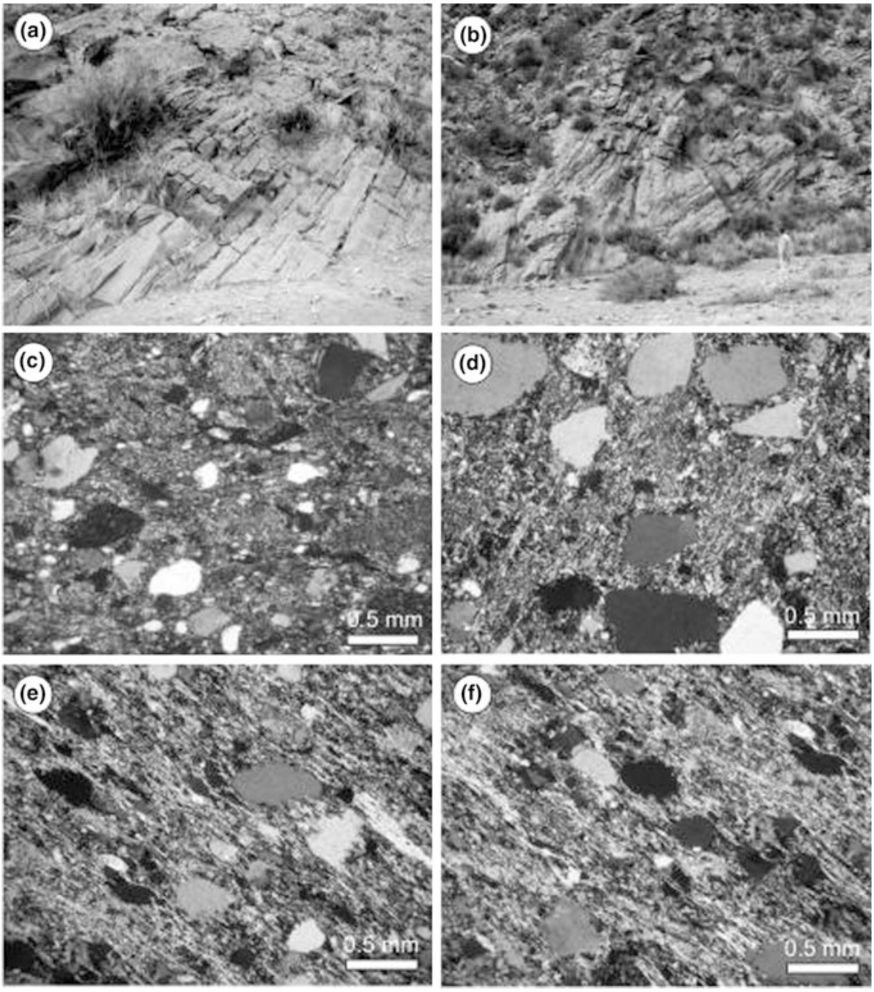


**Fig. 4** **a** General view of the La Horqueta unit outcrop at the La Horqueta type section. **b** Similar folding, east vergence **c** and **d** Photomicrographs of metawackes showing a slight modification of the clastic texture. **e** and **f** strong foliated metasandstones (crossed nicols)

At the Los Gateados river area, the unit consists of intercalated layers of muscovite-biotite schists and quartzitic schists. They have granolepidoblastic textures with a typical mineral association of chlorite + muscovite + quartz ± biotite, with accessory tourmaline, zircon and opaque minerals. Its structure is characterized by a continuous penetrative foliation, with a NNE trend and dips of 35–40° to the East.

**Structural characteristics**: A structural profile was described between the Puesto La Horqueta and Loma Colorada del Infierno at the La Horqueta River area (Fig. 5). In this section the La Horqueta Formation is in tectonic contact by a

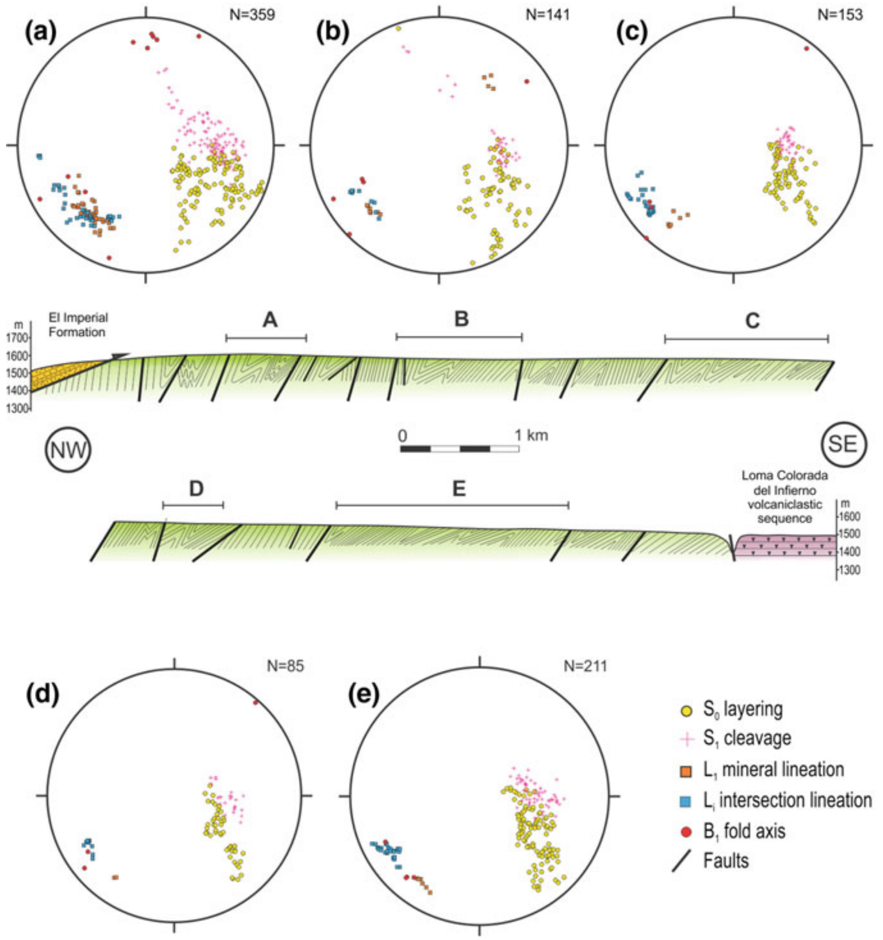


**Fig. 5** Geological cross-section through the La Horqueta Formation. For location see A–A′ profile in Fig. 2. Structural data plotted in lower hemisphere equal area stereonets

reverse faulting with the mainly Carboniferous El Imperial Formation at the Northwestern tip of the profile. In the SE outcrops the La Horqueta Formation is covered by the Loma Colorada del Infierno sub-volcanic rocks (Dessanti 1956; Giudici 1971; Rubinstein et al. 2013). The whole sequence is characterized by asymmetric, open to similar folds, with straight limbs and rounded hinges. These folds have axial planes striking to the NE and dipping to the NW, and axes plunging a few degrees to the NE or SW (Figs. 4b and 5). The fold vergence of the whole unit is towards SE. The main mesoscopic structure is a secondary foliation $S_1$, usually defined by aligned illite and chlorite. It has a consistent orientation with a north strike and moderate dip to the west. The $S_1$ foliation is continuous in metapelites, whereas it is anastomosed and spaced in metasandstones. Two types of lineations have been recognized linked to the folding. On $S_1$-planes a first mineral lineation is indicated by aligned illite + chlorite and tails of quartz on clasts, whereas another lineation is determined by the intersection of bedding planes and cleavage surfaces (Fig. 5).

Several faults have been recognized, some of them are in the limbs of large folds, suggesting that they could be reverse faults related to the asymmetric folding. However, they may have been reactivated, or even generated, by post-Carboniferous tectonic events.

These folds have axial planes striking to the NE and dipping to the NW, and axes plunging a few degrees to the NE or SW (Figs. 4b and 5). The fold vergence of the whole unit is towards SE.

**Metamorphic conditions (clay minerals)**: Thirty two samples of fine to medium grain (shale to fine sandstone) were collected from several outcrops covering a wide area (Tickyj and Cingolani 2000) (Fig. 2). Clay minerals assemblages and Kübler index (Kübler 1968; Guggenheim et al. 2002) were determined in all of them. Thirteen samples from the La Horqueta type section were selected to determine the white mica b-parameter.

**Methodology**: Whole rock samples were crushed using an agate-mill and sieved repeatedly#30 sieves to avoid over grinding. Organic matter and carbonates were eliminated using acid treatment. Twenty grams of each sample were dispersed with an ultrasound equipment during 25 min and the <2 µm fractions were separated by centrifugation. Clay mineral identification and Kübler index measurements were performed in the Centro de Investigaciones Geológicas (La Plata, Argentina). The <2 µm fractions were sedimented onto glass slides from which X-ray diffractions patterns were obtained using a Philips PW 2233/20 X-ray diffractometer, CuKα radiation, Ni filter, γ 1.54 Å and 36 kV/18 mA. Samples were scanned over the range $2\theta = 2$–$32°$ at $2°\ 2\theta$/min, time constant = 1 s, and using divergent slits of 1° and receiving slits of 0.2 mm. Samples for qualitative and semi-quantitative clay mineral identification were first air dried and then treated with ethylene glycol and heated to 550 °C during 2 h (Brindley 1980; Moore and Reynolds 1989).

The obtained Kübler index values ($KI_{CIG}$) from the width of the (001) white mica peak at half height on air-dried samples, expressed in terms of $\Delta°2\theta$. $KI_{CIG}$, were converted to standards values, using the international parameters after Warr and Rice (1994). The equation used was: $KI = 1.0999\ KI_{CIG} - 0.1548$, $R^2 = 0.9755$.

Values used to delimitate diagenetic, low anchizonal, high anchizonal and epizonal conditions were $KI > 0.52\ \Delta°2\theta$, KI: $0.52-0.42\ \Delta°2\theta$, KI: $0.42$–$0.32\ \Delta°2\theta$ and $KI < 0.32\ \Delta°2\theta$, respectively (Warr and Ferreiro Mählmann 2015). Kl values in the La Horqueta Formation vary from 0.24 to 0.33 $\Delta°2\theta$. Almost all samples belong to the epizone, except for a sample from the central area (HOR 12) that underwent high anchizonal metamorphic conditions.

Measurements of the white mica b-parameter were performed at the Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC, La Plata, Argentina). Randomly-oriented <2 µm powdered samples were analyzed in the range 59–

64° 2θ, using routine parameters indicated in Padan et al. (1982). The results were statistically analyzed by mean values and the relative standard deviation and are presented as cumulative frequency curves.

**Results**: The clay mineral assemblages are fairly homogeneous in the 32 analyzed samples. They mainly consist of illite (56–86%) and chlorite (14–44%). A few samples have small quantities of smectite and kaolinite (Table 1). The presense of smectite in high anchizone-epizone could be by retrograde phase.

Illite was identified by a strong reflection at 10 Å and weak reflections at 5 and 3.33 Å, which were modified neither in ethylene-glycol nor in heated samples. The presence of chlorite was determined by reflections at 14.2 and 7.1 Å and 3.5 Å on untreated samples; when the samples were heated the first reflection increase its intensity while the second almost disappear.

In two rocks from the Puesto Imperial area significant proportion of smectite, were identified, because the XRD trace of the ethylene-glycol treated samples show reflections at 16.6–16.8 Å (Figs. 2 and 6b, c; Table 1). Other samples show weak reflections in the range 17–18 Å, which probably represent small quantities of smectite. Kaolinite was identified for its reflection at 3.58 Å, close to the (004) peak of chlorite (Moore and Reynolds 1989).

KI values in the La Horqueta Formation vary from 0.24 to 0.33 Δº2θ. Almost all samples belong to the epizone, except for a sample from the central area (HOR 12) that underwent high anchizonal metamorphic conditions.

The whole data set shows a slight increase of metamorphic grade from south to north, as mentioned by Polanski (1964) in its regional study.

Natural K-white micas are a solid solution between the ideal muscovite and celadonite end-members (Guidotti 1984). The content of celadonite is controlled by the Tschermak substitution $[(Mg, Fe^{2+})^{VI}Si^{IV} = Al^{VI}Al^{IV}]$, which is particularly sensitive to pressure at low-grade metamorphic conditions (Guidotti et al. 1989). The increase of celadonite content in white micas has been widely used to estimate geobaric conditions in low- and very low-grade metamorphic terranes (Padan et al. 1982).

The b-parameter values obtained for the La Horqueta Formation range from 9.004 to 9.029 Å, with an average of 9.016 Å (σ: 0.007 Å), indicating a low-intermediate pressure regime as they plot between the curves corresponding to the New Hampshire and the Ryoke terranes in the cumulative frequency plot (Fig. 7) proposed by Sassi and Scolari (1974).

**Rb-Sr whole-rock data**: To constrain the age of the main deformational event of the La Horqueta Formation we applied the whole rock Rb-Sr method (Tickyj et al. 2001). The determinations of Rb and Sr contents were performed by XRF whereas the isotopic composition on natural Sr was analyzed by mass spectrometry. Sample preparation, chemical attack and extraction of natural Sr using cation exchange resin, were carried out at the clean laboratory of the Centro de Investigaciones Geológicas (CIG, University of La Plata, Argentina). Mass spectrometry (TIMS) measurements were developed at the Laboratorio de Geología Isotópica, Porto Alegre, Brazil. The results were plotted on isochronic diagrams, using the Isoplot software after Ludwig (1998).

**Table 1** Mineral composition of <2 μ fraction and KI (Kübler index) values of the La Horqueta Formation (location of samples in Fig. 2)

| Sample | Location | | Illite-Mus. (%) | Chlorite (%) | Smectite (%) | Kaolinite (%) | KI |
|---|---|---|---|---|---|---|---|
| Hor 9 | La Horqueta area | 34° 38′ 16.53″S<br>68° 53′ 11.11″W | 67 | 27 | 2 | 4 | 0.28 |
| Hor 10 | La Horqueta area | 34° 38′ 16.53″S<br>68° 53′ 11.11″W | 63 | 37 | – | – | 0.27 |
| Hor 11 | La Horqueta area | 34° 33′ 57.64″S<br>68° 54′ 05.05″W | 75 | 25 | – | – | 0.28 |
| Hor 12 | La Horqueta area | 34° 35′ 27.18″S<br>68° 53′ 29.63″W | 71 | 29 | – | – | 0.33 |
| Hor 13 | La Horqueta area | 34° 36′ 46.12″S<br>68° 50′ 41.23″W | 74 | 22 | – | 3 | 0.31 |
| Hor 14 | EI Baqueano | 34° 33′ 02.56″S<br>68° 51′ 04.83″W | 84 | 16 | – | – | 0.25 |
| Hor 15 | Puesto EI Chacay | 34° 33′ 02.56″S<br>68° 51′ 04.83″W | 76 | 24 | – | – | 0.3 |
| Hor 16 | EI Baqueano | 34° 33′ 02.56″S<br>68° 51′ 04.83″W | 76 | 20 | 3 | 1 | 0.24 |
| Hor 17 | Puesto Imperial | 34° 30′ 04.40″S<br>68° 55′ 07.01″W | 72 | 19 | 9 | – | 0.28 |
| Hor 18 | Puesto Imperial | 34° 30′ 04.40″S<br>68° 55′ 07.01″W | 64 | 19 | 15 | 2 | 0.3 |
| Hor 19 | Puesto Imperial | 34° 30′ 04.40″S<br>68° 55′ 07.01″W | 58 | 42 | – | – | 0.28 |
| Hor 20 | Los Reyunos | 34° 34′ 25.96″S<br>68° 46′ 40.08″W | 60 | 40 | – | – | 0.28 |

(continued)

**Table 1** (continued)

| Sample | Location | | Illite-Mus. (%) | Chlorite (%) | Smectite (%) | Kaolinite (%) | KI |
|---|---|---|---|---|---|---|---|
| Hor 21 | Los Reyunos | 34° 34′ 25.96″S<br>68° 46′ 40.08″W | 56 | 44 | – | – | 0.28 |
| Hor 23 | La Picaza | 34° 33′ 53.22″S<br>68° 49′ 35.48″W | 81 | 19 | – | – | 0.28 |
| Hor 24 | La Picaza | 34° 33′ 53.22″S<br>68° 49′ 35.48″W | 81 | 17 | 1 | – | 0.27 |
| Hor 25 | La Horqueta area | 34° 38′ 02.00″S<br>68° 50′ 49.31″W | 86 | 14 | – | – | 0.29 |
| Hor 26 | Agua de la Piedra | 34° 44′ 31.69″S<br>68° 49′ 34.90″W | 68 | 32 | – | – | 0.26 |
| Hor 31 | Agua de la Piedra | 34° 43′ 04.69″S<br>68° 46′ 53.81″W | 70 | 25 | 5 | – | 0.26 |
| Hor 46 | La Horqueta area | 34° 35′ 52.09″S<br>68° 52′ 28.63″W | 69 | 31 | – | – | 0.25 |
| Hor 47 | La Horqueta area | 34° 36′ 10.59″S<br>68° 51′ 54.36″W | 62 | 38 | – | – | 0.25 |
| Hor 48 | La Horqueta area | 34° 36′ 24.78″S<br>68° 51′ 26.53″W | 78 | 22 | – | – | 0.25 |
| Hor 49 | La Horqueta area | 34° 37′ 33.36″S<br>68° 49′ 50.92″W | 67 | 33 | – | – | 0.27 |
| Hor 50 | La Horqueta area | 34° 38′ 08.78″S<br>68° 48′ 49.57″W | 84 | 16 | – | – | 0.24 |

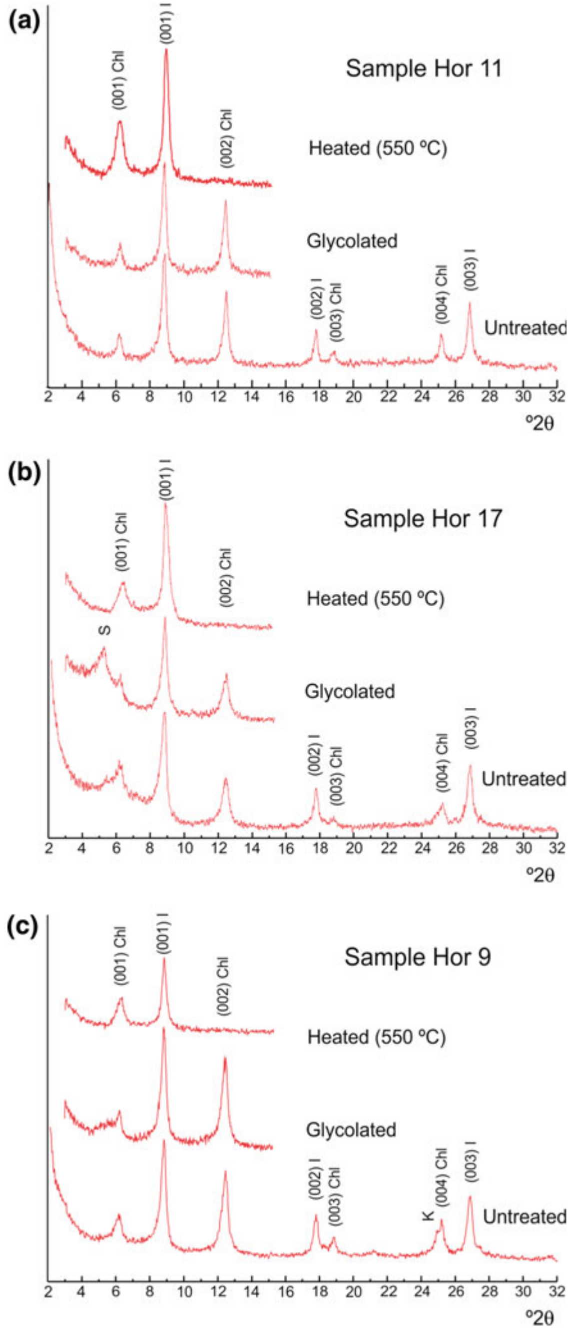


**Fig. 6** Powder X-ray diffraction patterns of oriented mounts of the <2 µm fraction of representative samples of La Horqueta Formation

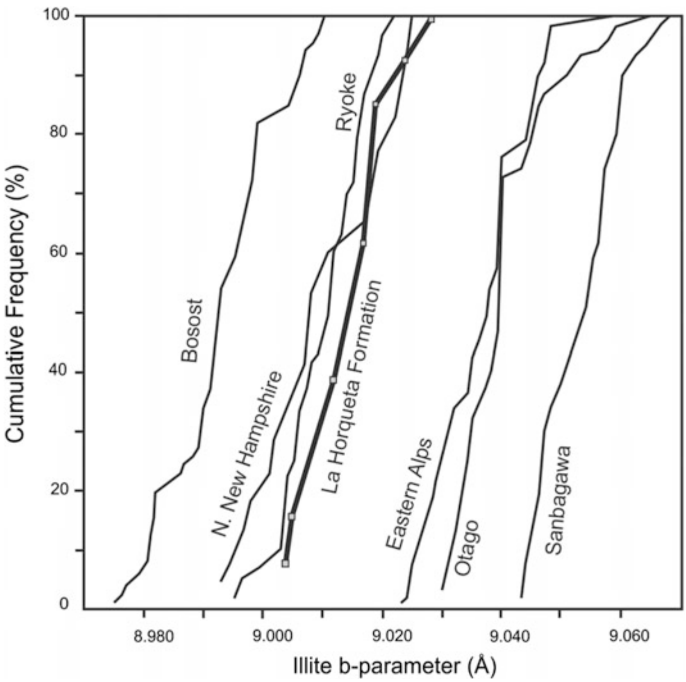


**Fig. 7** Cumulative frequency-white mica b parameter plots for samples of the La Horqueta Formation (this study) and from other regional metamorphic terrains (Sassi and Scolari 1974)

**Results**: Six samples of micaschists from the Los Gateados section were analyzed. The Rb contents vary between 57 and 151 ppm, while the Sr contents vary from 50 to 83 ppm (Table 2). The age obtained from the isochron calculated with using Isoplot/Ex Model 1 (Ludwig 1998) is 371 ± 62 Ma, initial $^{87}Sr/^{86}Sr$ 0.7165 ± 0.0034 and MSWD: 3.7 (Fig. 8a). Furthermore, seven samples of metapelites from the La Horqueta type section were analyzed. The Rb contents vary between 116 and 290 ppm, whereas the Sr contents from 29 to 57 ppm (Table 2). The Rb-Sr isochron calculated with Isoplot/Ex Model 1 (Ludwig 1998) yielded an age of 379 ± 15 Ma, with IR: 0.7151 ± 0.0026, and MSWD: 1.4 (Fig. 8b) (Tickyj et al. 2001).

The Rb-Sr data pointed out that the low-grade metamorphism and folding events of the La Horqueta Formation are Late Devonian.

These data agree with previous K-Ar ages reported by Linares and González (1979). Similar data were obtained on low-grade metamorphic units from the western and south-western sections of the Precordillera (Cucchi 1971; Buggisch et al. 1994; Gerbi et al. 2002). This geochronological data let infer a Devonian age for the synmetamorphic Ductile deformation in the western side of the Cuyania terrane, probably connected with the accretion of the Chileniaterrane (Ramos 1988). This hypothesis is also supported by $^{40}Ar/^{39}Ar$ plateau data on white micas

**Table 2** Rb-Sr analytical data

| Lab. Number | Field sample | Rb | Sr | $^{87}Rb/^{86}Sr$ | Error | $^{87}Sr/^{86}Sr$ | Error |
|---|---|---|---|---|---|---|---|
| La Horqueta formation | | | | | | | |
| CIG 1205 | QGAT 1 | 74.2 | 82.6 | 2.6063 | 0.0521 | 0.730473 | 0.000037 |
| CIG 1206 | QGAT 2 | 83.4 | 62.3 | 3.8869 | 0.0777 | 0.738029 | 0.000059 |
| CIG 1207 | QGAT 3 | 85.3 | 56.9 | 4.3530 | 0.0871 | 0.738759 | 0.000051 |
| CIG 1208 | QGAT 4 | 70.3 | 61.2 | 3.3341 | 0.0667 | 0.734435 | 0.000066 |
| CIG 1209 | QGAT 5 | 57.4 | 50.5 | 3.2987 | 0.0660 | 0.733119 | 0.000029 |
| CIG 1210 | HOR 64 | 151.5 | 73.7 | 5.9745 | 0.1195 | 0.748189 | 0.000120 |
| CIG 1232 | HOR 11 | 258.7 | 53.6 | 14.0907 | 0.2818 | 0.794198 | 0.000008 |
| CIG 1233 | HOR 12 | 247.2 | 35.3 | 20.5050 | 0.4101 | 0.824753 | 0.000009 |
| CIG 1234 | HOR 24 | 289.7 | 28.7 | 29.6940 | 0.5939 | 0.872864 | 0.000010 |
| CIG 1235 | HOR 25 | 253.6 | 57.5 | 12.8633 | 0.2573 | 0.784016 | 0.000008 |
| CIG 1236 | HOR 46 | 205.8 | 40.2 | 14.9486 | 0.2990 | 0.796088 | 0.000007 |
| CIG 1237 | HOR 47 | 116.2 | 38.5 | 8.7833 | 0.1757 | 0. 761234 | 0.000008 |
| CIG 1238 | HOR 50 | 142.9 | 53.0 | 7.8438 | 0.1569 | 0.757868 | 0.000010 |

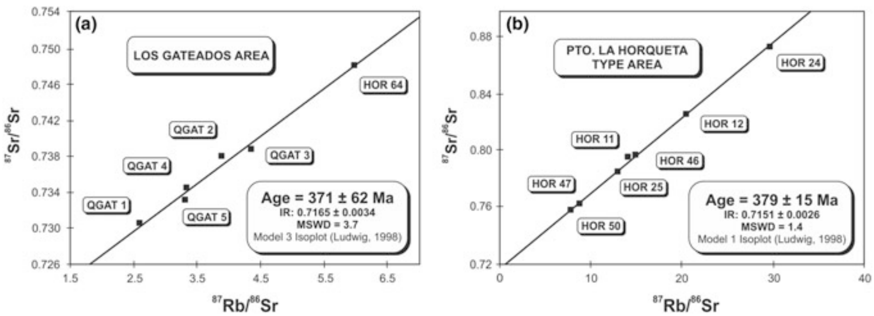


**Fig. 8** Rb-Sr isochronic plot of samples from Los Gateados region (**a**) and from Puesto La Horqueta type region (**b**) (after Tickyj et al. 2001)

(384 ± 0.5 and 378 ± 0.5 Ma) from low-grade metamorphic rocks from Bonilla and Portillo areas obtained by Davis et al. (1999).

**U-Pb geochronology**: U-Pb dating on detrital zircons of six metasandstone was performed in order to estimate maximum age of deposition and to accomplish a geochronological provenance study of the La Horqueta unit. In situ U–Pb zircon dating was carried out at the Isotope Geology Laboratory of the Federal University of Rio Grande do Sul, Porto Alegre, Brazil, by means of the LA-MC-ICPMS technique (Jackson et al. 2004); preliminary results were presented by Cingolani et al. (2008). In this technique all zircon grains and a sample of the GJ-1 (GEMOC ARC Nat. Key Center) standard zircon were mounted in 2.5 cm-diameter circular epoxy and polished until the zircons were revealed. Back-scattered electron images of zircons were obtained using a Jeol JSM 5800 electron microscope in order to analyze the internal morphology of grains and select the spot areas to be dated with a New Wave UP213 laser ablation microprobe coupled to a Neptune MC-ICPMS, with collector configuration for simultaneous measurements of Th, U, Pb and Hg isotopes. The isotope ratios and inter-element fractionation data were evaluated in comparison with the GJ-1 standard at every set of 4–10 zircon spots, and used to estimate the necessary corrections and internal instrumental fractionation. The laser spot size was 25 μm. For each standard and spot run, a blank sample was also run and its values subtracted from all individual cycle measurements. The $^{204}$Pb value was corrected for $^{204}$Hg, assuming the $^{202}$Hg/$^{204}$Hg ratio to be 4.355. The necessary correction for common $^{204}$Pb, after Hg correction based on the simultaneously measured $^{202}$Hg was insignificant in most cases and the Pb isotopic composition assumed to follow the isotopic evolution proposed by Stacey and Kramers (1975), which is required to attribute an initial estimated age. After the blank and common Pb corrections, the ratios and their absolute errors (1σ) of $^{206}$Pb*/$^{238}$U, $^{232}$Th/$^{238}$U and $^{206}$Pb*/$^{207}$Pb* were calculated in an Excel spreadsheet. Usually zircon-rims were dated and in some cases also grain-cores, for comparison.

**Results**: As we depicted in Fig. 9 the detrital zircon population of samples **Hor 21**(*n* = 61), **Hor 46** (*n* = 60) and **Hor 10** (*n* = 60) show patterns dominated by grains of Mesoproterozoic ages, minor peaks corresponding to Neoproterozoic-Lower Paleozoic age and few subordinate peaks in the Paleoproterozoic-Neoarchean.

As it is shown in Fig. 9 the sample **Hor 21** notably record 85% of zircons derived from Mesoproterozoic sources, most of them from Upper Mesoproterozoic ("Grenvillian-age" or M3) in a polymodal detrital zircon-age pattern. The 9% correspond to the Neoproterozoic (Pampean-Brasiliano cycle), 6% of zircon grains were derived from cratonic domains (Paleoproterozoic ages). The sample **Hor 46** could be described as bimodal that shows (Fig. 9) more than 80% of zircons of Mesoproterozoic sources, with 55% that correspond from the"Grenvillian-age" or M3; 11% are from the Pampean-Brasiliano cycle, 9% from cratonic sources and only 3% derived from the Famatinian belt. The sample **Hor 10** also presents main peaks (unimodal age pattern) in the Mesoproterozoic (72%) with 62% from the M3 or "Grenvillian-age". Zircons of the Pampean-Brasiliano cycle are present with 18% and about 10% derived from cratonic sources (Paleoproterozoic).

The samples **Hor 15** (*n* = 59) and **Hor 81** (*n* = 56) record a pattern with main peaks in the Neoproterozoic-Lower Paleozoic as well as in the Mesoproterozoic, with minor peaks from Paleoproterozoic to Neoarchean ages (Fig. 10). The detrital zircon age pattern for sample **Hor 15** shows two major groups corresponding to Mesoproterozoic (62% of the grains, with 42% of M3), and Pampean (27% of zircons), with minor contribution from cratonic sources (11%), where 3% were Neoarchean. For the sample **Hor 81** the zircon population is dominated by a strong peak corresponding to Pampean-Brasiliano ages (40%), then 37% from Mesoproterozoic ages (25% of M3), 13% from Paleoproterozoic ages (major percentage of cratonic sources without Neoarchean ages), whereas zircons from the Famatinian cycle represent a 10% of the analyzed grains.

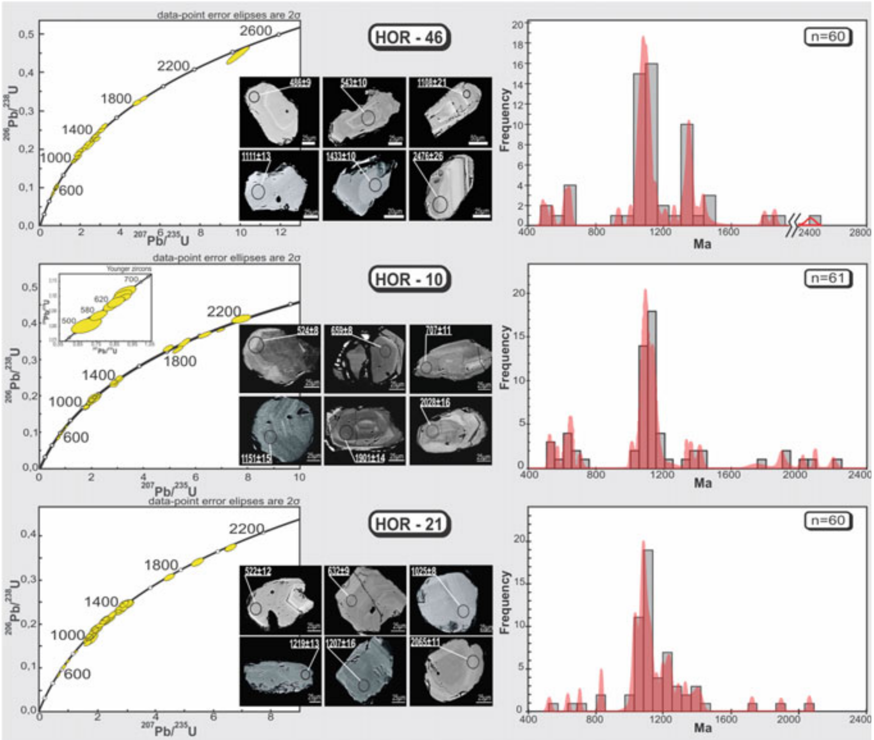


**Fig. 9** U-Pb (LA-ICP-MS) concordia diagrams, frequency histograms and some of the electronic microscope (SEM) images of the studied zircon grains from samples Hor 46, Hor 10 and Hor 21. The location of the spots and obtained ages by LA-ICP-MS are in Ma. See Tables 3, 4 and 5 (supplementary material)

The sample **Hor 27** ($n$ = 64) show a quite different pattern from other studied samples (Fig. 10). In this sample the detrital zircon age pattern is dominated by 54% of Famatinian zircon grains (23% Silurian and 31% Early Devonian in age), then a 35% derived from a source of Mesoproterozoic age (while 26% from M3), and subordinate contributions from Pampean-Brasiliano sources (8%) and cratonic areas (4%, with 2% from Neoarchean).

Constrains on provenance of the main detrital zircon sources could be as follows, from older to younger age components (Fig. 11):

(1) Archean to Paleoproterozoic: The source rocks of the obtained clusters (4–13%) are probably derived from the erosion of the basement of the Río de la Plata craton located toward the East. (2) Mesoproterozoic: Prominent clusters at M3 or "Grenvillian-age" 1.0–1.2 Ga were registered in all samples (26–62%), the most probable source of zircons of this age is the juvenile basement of Laurentian affinity of Precordillera-Cuyania, outcropping at the Pie de Palo, Umango ranges, Cerro La Ventana Formation at the San Rafael and Las Matras blocks (Sato et al. 2000;

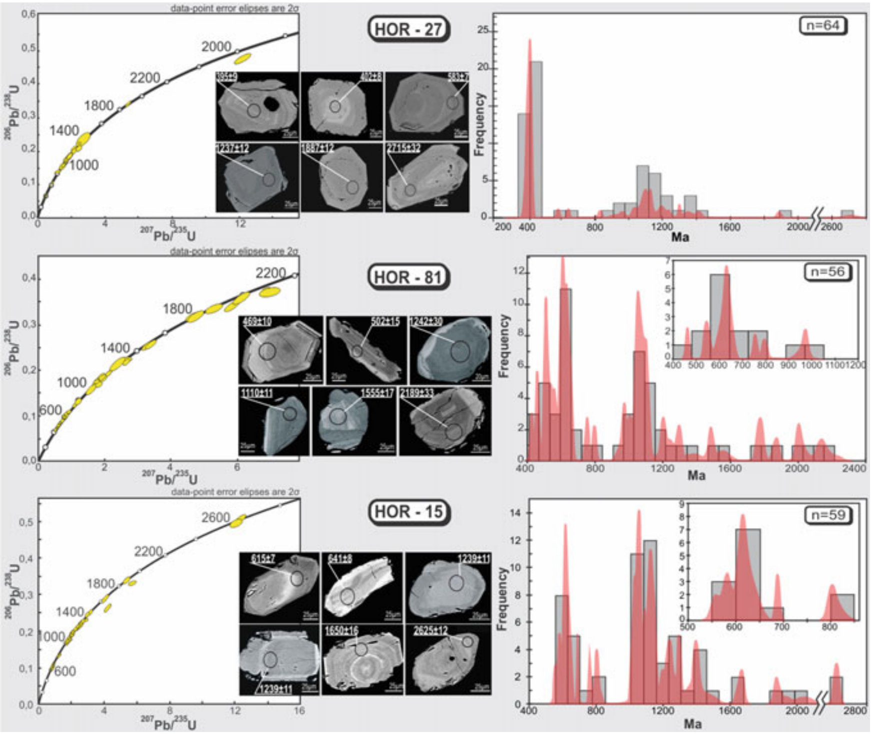


**Fig. 10** U-Pb (LA-ICP-MS) concordia diagrams, frequency histograms and some of the electronic microscope (SEM) images of the studied zircon grains from samples Hor 15, Hor 81 and Hor 27. The location of the spots and obtained ages by LA-ICP-MS are Ma. See Tables 6, 7 and 8 (supplementary material)

Varela et al. 2011 and references). (3) Neoproterozoic-Lower Paleozoic: Clusters of these ages were found in all studied samples (8–40%). Zircons of these ages are abundant in southern South America, evidencing the uplift and denudation of the Pampean-Brasiliano orogenic belts. (4) Ordovician-Early Devonian: Zircon grains of these ages are recorded in samples Hor 27 (with more than 50%), Hor 46 and Hor 81 (in between 3 and 10%). These grains probably derived from the erosion of the igneous rocks from the Late Famatinian magmatic arc, well known in western-central Argentina. The Devonian ages are abundantly registered on magmatic zircons from sample Hor 27.

The younger detrital zircon ages (ca. 410 Ma) recorded on the sample Hor 27 allows to constrain the age of deposition of the La Horqueta Formation to the Silurian-Devonian limit.

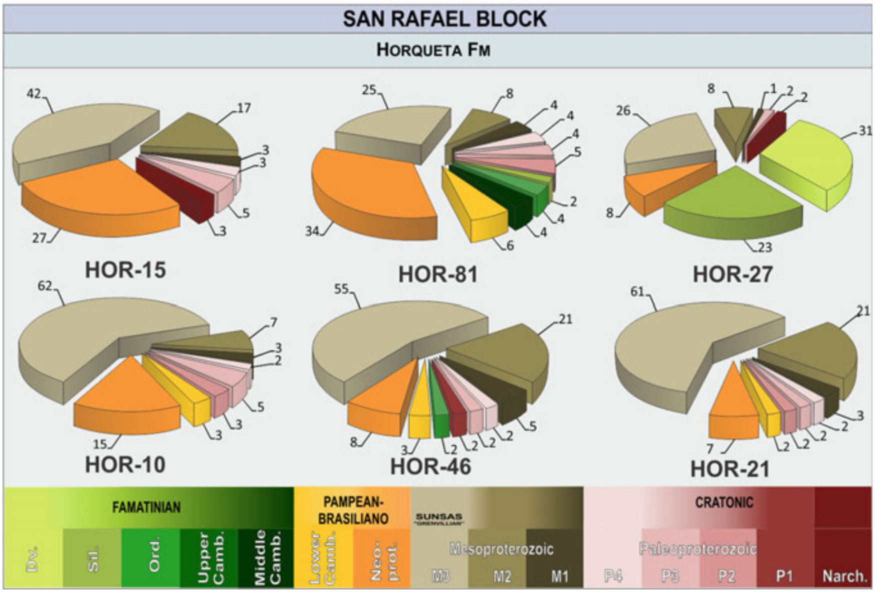


**Fig. 11** Percentage representation 'pie diagrams' of the U-Pb detrital zircon ages in terms of the main orogenic cycles defined for South America

## 4 Concluding Remarks

The La Horqueta Formation is a marine metasedimentary sequence that has been folded, cleaved and faulted by a main regional deformational event with southeast vergence that was coeval with a regional metamorphic event of very low to low-grade. Studies performed on samples from La Horqueta Formation in its type section area indicate that the regional metamorphism affecting this unit attained high anchizone-epizone and intermediate P facies series.

The Rb-Sr whole-rock age obtained from Los Gateados sector is 371 ± 62 Ma, with IR: 0.7165 ± 0.0034, while from La Horqueta type section yielded an age of 379 ± 15 Ma, with IR: 0.7151 ± 0.0026. These ages constrain the metamorphic and the main deformational event to the Devonian and linked it to the Chanic Orogenic phase.

Based on U-Pb isotopic data the La Horqueta Formation received a minor sedimentary input from cratonic sources such as the Rio de la Plata craton, which contribute with the older ages, then an important source from Cuyania terrane basement (Mesoproterozoic ages) and finally a younger source from Pampean and Famatinian orogenic belts. The U-Pb detrital zircon ages constrain the age of sedimentation to the Silurian-Devonian limit.

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