



Mississippian volcanism in the south-central Andes: New U–Pb SHRIMP zircon geochronology and whole-rock geochemistry

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ABSTRACT

In the northern extension of the Famatina and the southern Puna (NW Argentina) prominent rhyolitic volcanic rocks traditionally referred to as Ordovician are exposed, resting on metamorphic basement and covered by thick Late Paleozoic siliciclastic successions. We report new U–Pb SHRIMP ages from these rhyolites that show them to be of Mississippian (348–342 Ma) age, thus identifying a previously unknown volcanic event in this portion of western Gondwana. Whole-rock geochemistry and Sr–Nd isotopic analyses suggest a crustal source for these rocks but with a juvenile input ($\epsilon_{Nd}(t)$ between -2.91 and -0.3 , and T_{DM} values between 1.09 and 1.1 Ga). This is different from the Early Paleozoic magmatism of western Argentina where crustal recycling took place without any involvement of mantle material. The Carboniferous magmatism is compatible with an extensional environment developed along the Terra Australis accretionary orogen as a result of tectonic switching processes. These rhyolites may be related to the coeval Mississippian A-type granites exposed to the east, in the Sierras Pampeanas, confirming the regional character of this magmatism.

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1. Introduction

Subduction and protracted magmatism has been recognized at the western margin of Gondwana since the Middle Cambrian (Rapela et al., 1998; Cawood, 2005; Astini et al., 2007; Collo et al., 2009). However, an exception to this trend is the Late Silurian to early Late Carboniferous interval for which a passive margin setting has been suggested (Bahlburg and Herve, 1997). This ~100 m.y. interval is characterized by a scarcity of rocks with typical volcanic arc signatures along the southern Central Andes. Instead, the magmatic activity shifted towards the craton, where it is represented by scattered Late Devonian–Early Carboniferous granites (McBride et al., 1976; Rapela et al., 1982; Grissom et al., 1998; Dahlquist et al., 2006; Grosse et al., 2009). Bimodal dikes and sills have also been recognized within the Precordillera in a more hinterland position (Sessarego et al., 1990; Coughlin, 2000) and minor volcanoclastics occur in the fore-arc in Eastern Chile (Breitkreuz et al., 1989; Charrier et al., 2007), although no clear interpretations of these rocks have been made. After this relative lull, Paleozoic magmatism became pervasive once again with the intrusion of Pennsylvanian arc-type granites and the co-genetic granites and rhyolites of the Permo-Triassic Choiyoi Group (e.g.; Strazzere et al., 2006; Munizaga et al., 2008).

Recent U–Pb and Lu–Hf isotope analysis of detrital zircons and rhyolite and granite pebbles from late Paleozoic accretionary prism successions in central Chile demonstrates the presence of a poorly known Mississippian (here and throughout the text taken as the formal and globally accepted subsystem in replacement of the more ambiguous Lower/Early Carboniferous term; Heckel and Clayton, 2006) magmatic event (Willner et al., 2008). According to these authors, the zircon isotopic data suggest a more primitive basement source probably related to the collision of the controversial Chilenia terrane. However, an unanswered question is the source of the Carboniferous zircons and pebbles.

On the NW border of the Famatina belt and the southern Puna (NW Argentina), ca. 150–250 m thick rhyolites unconformably overlie Precambrian–Early Paleozoic metamorphic basement rocks and underlie thick (>1000 m) late Paleozoic siliciclastic successions represented by Pennsylvanian glacial conglomerates and delta complex deposits (Fig. 1). These rhyolites were previously mapped as Ordovician and included within the Famatinian magmatic arc (Mpodozis et al., 1997; Coira et al., 2005). However, the lack of the Ordovician metamorphism observed in the basement rocks suggests a younger age.

In order to constrain this magmatism we report new U–Pb SHRIMP zircon geochronology for two rhyolite samples. In addition, we present preliminary Sr and Nd isotope data and major and trace element geochemistry of these rocks, which we interpret in the context of the Late Paleozoic evolution of the western margin of Gondwana.

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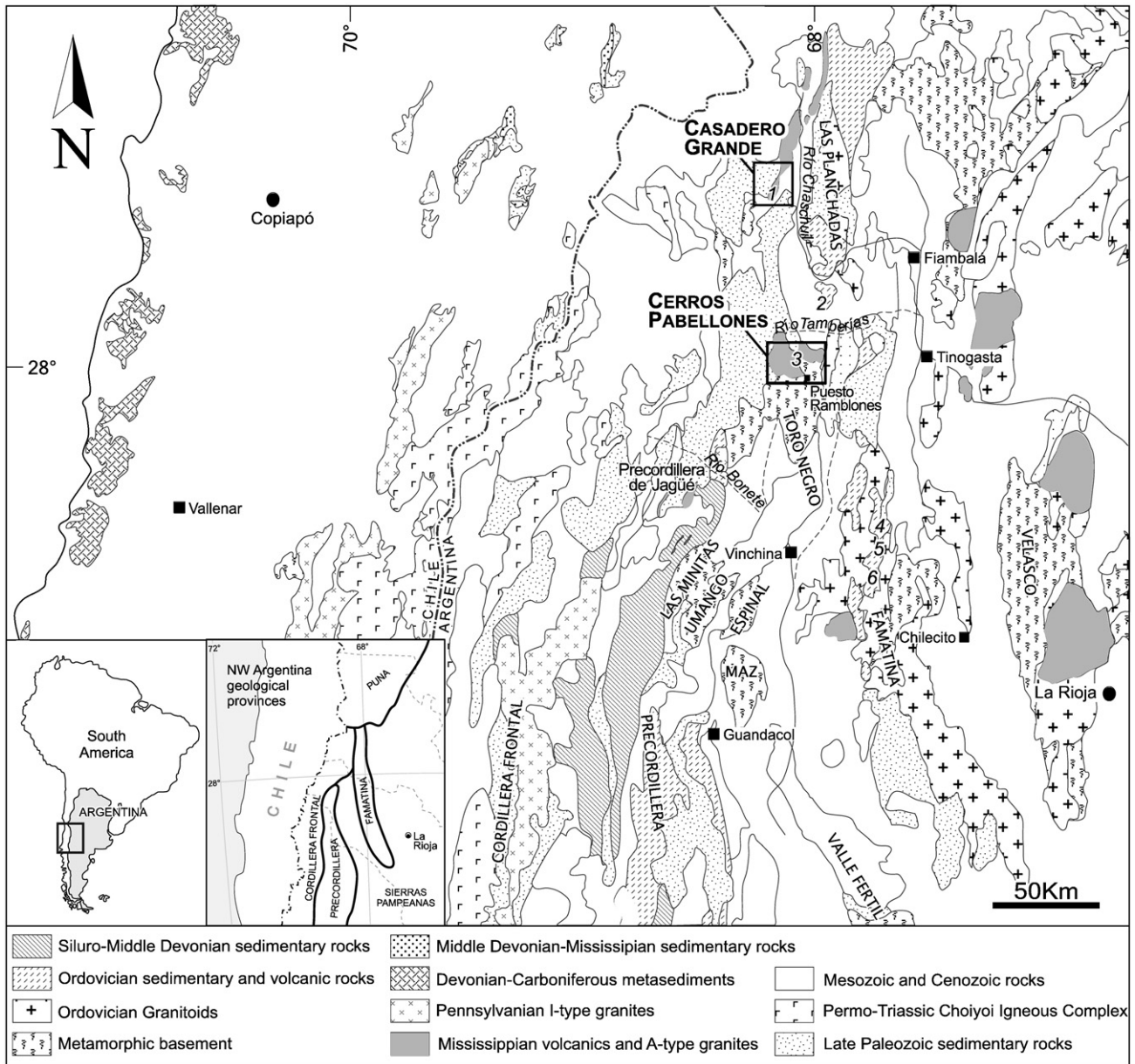


Fig. 1. Simplified geological map of central-western Argentina and central Chile showing the location of the studied areas and the analyzed samples. In gray the Mississippian magmatic record outlined in this paper. Numbers 1 and 3 refer to dated rhyolites of Mississippian age unconformably lapping onto basement; 2, 4, 5 and 6 are the Ordovician rhyolites studied for comparison.

2. Geological setting

The Paleozoic geological record of northwestern Argentina is thought to have been part of the paleo-Pacific accretionary margin of Gondwana known as the Terra Australis Orogen (Cawood, 2005; Adams et al., 2011; Hauser et al., 2011). Owing to its protracted history (~300 m.y.) and areal extent, the record encompasses various sedimentary and igneous accretionary processes related to different tectonic scenarios. Examples of these are the well-known Pampean, Ocoyic and Gondwanic orogenies for which specific accretionary processes have been suggested (cf. Mpodozis and Kay, 1992; Thomas and Astini, 2003; Rapela et al., 2007; Vaughan and Pankhurst, 2008). Each of these processes must have locally increased plate boundary coupling, thereby modifying existing stratigraphies and generating their own signatures.

The Neoproterozoic to Cambrian metamorphic basement of the southern Puna and northwestern Sierras Pampeanas largely consists of

a monotonous schist–gneiss–migmatite association (Allmendinger et al., 1982; Lucassen and Becchio, 2003; Büttner, 2009) intruded by granitic rocks of Ordovician through Mississippian age (Pankhurst et al., 1998a, 2000; Varela et al., 2003; Dahlquist et al., 2006, 2007; Viramonte et al., 2007; Grosse et al., 2009, among others). Volcanic and volcanoclastic facies have also been recorded. Extensive Middle Ordovician rhyolites (the Famatina and Cerro Morado groups) interbedded within marine deposits are exposed in the Famatina Belt at ~29°S (Astini et al., 1995; Astini, 2003; Astini et al., 2007) and extend to the north and northwest into the southern Puna (Viramonte et al., 2007). Another widespread rhyolitic province is the protracted Permo-Triassic Choiyoi Group outcropping along the Cordillera Frontal (Rocha-Campos et al., in press). These extensive igneous rock units have been linked to crustal heating and broad-scale extension during the final assembly of Pangea (Mpodozis and Kay, 1992), most likely recording the termination of the long-lasting Terra Australis Orogen in South America (Cawood, 2005). However, preliminary high-resolution

U–Pb geochronology (Martina et al., 2007) indicated the possibility of recurrent crustal recycling processes embraced within the broad late Paleozoic silicic magmatism along the proto-Andean margin of Gondwana.

The Late Devonian–Mississippian granites in the Sierras Pampeanas have traditionally been included within the Famatinian orogeny (Aceñolaza and Toselli, 1973) and considered to be related to a poorly understood post-orogenic event (McBride et al., 1976; Rapela et al., 1982, 1990; Dahlquist et al., 2005; Grosse et al., 2009; Chernicoff et al., 2010). However, recent regionally constrained geochronological work (e.g., Grissom et al., 1998; Dahlquist et al., 2006; Grosse et al., 2009) has allowed their separation as a new tectonothermal event (Achalán orogeny; cf. Sims et al., 1998). Based on their geochemical signature, these granites can be classified as Fe-rich A-type (Dahlquist et al., 2006) and could be related to crustal extension processes as a result of the post-orogenic collapse of the Famatinian orogen (Grosse et al., 2009). Alternatively, an independent Mississippian tectonic episode was proposed by Dalmayrac et al. (1980) based on various geologic features along the Gondwana margin, including this rather obscure magmatism.

3. Sample collection and petrography

The analyzed samples were collected along the cordilleran region in two areas separated about 100 km (Fig. 1) where a clear mappable relationship between a volcanic and volcanoclastic cover and high-grade metamorphic basement is exposed. The first sample was collected from the Casadero Grande area (27°19'54"S–68°09'55"W) in the southern Puna, near the boundary between Argentina and Chile (Fig. 1). The basement of the region consists of biotite–muscovite orthogneisses with basic intrusions and pegmatitic dikes (Mpodozis et al., 1997). Coarse-grained marbles, calc–silicate schists and partially mylonitized amphibolites are also present. Three U–Pb analyses on titanites provide a metamorphic age of 448 ± 6 Ma for this metamorphic complex (Lucassen and Becchio, 2003). The volcanic rocks unconformably overlie the basement with an attitude of 110°/45°NE and consist entirely of coherent lava flows of rhyolitic composition without macroscopic evidence of metamorphism. The contact between both units is marked by a coarse clast-supported breccia (~12 m) which derived from the local basement. In this area the volcanic section is sharply truncated by rounded clast- to matrix-supported conglomerates with flat-iron striated and polished boulders interpreted to have a glacial origin (Fig. 2a), presumably during the late Paleozoic Gondwana glaciation (Astini, 2009). A thick late Paleozoic succession of deltaic to continental strata, including red beds, overlies the glacial conglomerates. The rhyolite section at Casadero Grande is 130 m thick and can be divided into three depositional units with different textural and structural features suggesting separate lava flows (Fig. 2). Pervasive hydrothermal alteration zones (~10 m thick) also separate each lava flow although no independent criteria indicate the time-gaps they represent. In the field, the rhyolites are aphyric to quartz–phyric and pale pink to cream. Textures vary up section from flow-banded to massive. The basal 4–7 m thick section displays prominent meter-scale open asymmetric to tight isoclinal flow folds suggesting reomorphism and laminar flow as a result of progressive deformation and refolding (cf., McPhie et al., 1993). This is considered typical of vitrophyre facies in rhyolitic flows (cf. Gimeno et al., 2003). This interval also contains a variety of spherulitic textures. Isolated and coalescent spherulites and large lithophysae (0.5 to 10 cm in diameter) indicate both substantial high-temperature devitrification (cf., Logfren, 1971) and pervasive volatile exsolution caused by crystallization (Iddings, 1887; Swanson et al., 1989) or concentrated at outward-propagating crystallization fronts (McArthur et al., 1998) (Fig. 2b). In the thin section the rhyolites are porphyritic and composed essentially of clear, frequently embayed quartz, simple twinned K-feldspar and minor plagioclase as the main

phenocrysts with zircon, biotite, titanite and Fe–Mg oxides as accessory minerals (Fig. 2c). Perthitic and mesh-like textures are common in feldspars suggesting a relatively alkaline composition. The groundmass consists of microcrystalline quartz of two different grain sizes defining the flow-foliation planes.

The second analyzed sample comes from the northwest of the Sierra del Toro Negro (Fig. 1), where massive non-vesicular, porphyritic rhyolites of predominantly pink to reddish colors crop out. This area, referred to as the Cerros Pabellones (28°07'38"S–68°10'36"W), includes two main peaks of ~5000 m (Cerro Pabellón Grande and Cerro Pabellón Chico). The volcanic rocks rest on high-grade metamorphic basement units of the Espinal Formation (Maisonave, 1979) that is thought to be of Mesoproterozoic age (Varela et al., 1996), similar to the basement exposed in Casadero Grande (Martina, 2009). U–Pb dating on titanites from the basement rocks yields an average age of 443 ± 4 Ma, indicating Late Ordovician high-temperature metamorphism (Lucassen and Becchio, 2003). Several 2 to 10 m-wide feeder dikes, mainly of rhyolitic composition, intruded the basement with a general NW–SE trend. The volcanic rocks are stratified at ~10°/78°SE and covered in angular unconformity by black shales and arkosic sandstones of the Middle Carboniferous Agua Colorada Formation. The thickest (~800 m) and most continuous section crops out near Puesto Ramblones (Fig. 2b), where coarse-grained porphyritic rhyolites are interlayered with aphyric flow-banded rhyolites, strongly silicified normal graded ash-fall deposits and minor dacite flows. Phenocrysts in the porphyritic rhyolites consist of euhedral to subhedral plagioclase crystals, quartz, and K-feldspar crystals up to 0.6 cm in length enclosed in a medium to coarse-grained felsic groundmass. A few chloritized and epidotized augite and minor opaque and biotite crystals are also present.

The analyzed sample (FLPDAT) comes from an outcrop located 500 m to the east of the Puesto Ramblones section and consists of a poorly porphyritic, fine grained, massive rhyolite. In the thin section it shows <0.2 cm quartz, plagioclase and sanidine crystal fragments and volcanic lithics set in a formerly glassy fragmental groundmass of highly compacted platy and cusped glass shards and superimposed perlitic fractures (Fig. 2d). The total crystal content is <20%. These rhyolitic rocks may represent welded ash-fall deposits.

For comparison, four rhyolites of certified Ordovician age belonging to the Famatina volcanic arc immediately east of the investigated area were also analyzed. One sample comes from the Cerro Tocino volcanics (28°46'10"S–67°48'37"W) that underlie the Early Ordovician Suri Formation; two samples are from the lower (28°43'15"S–67°47'53"W) and upper (28°43'19"S–67°47'14"W) intervals of the Middle Ordovician Cerro Morado Volcanic Group, and the fourth sample comes from the Las Planchadas Formation (27°54'11"S–68°05'09"W), a time-equivalent unit in the northernmost Sierra de Famatina. The rhyolites of Casadero Grande and Cerros Pabellones analyzed in this paper have traditionally been correlated with those in the Famatina belt (Turner, 1967; Maisonave, 1979; Rubiolo, 2001; Coira et al., 2005). However, nowhere in the Famatina system, do Ordovician volcanic rocks directly overlie basement. The new geochronological data reported in this paper show a clear separation between the two suites, allowing a new magmatic event to be identified.

4. Analytical methods

For geochemical analysis whole-rock powders were crushed and ground in a tungsten-carbide ring vibratory mill. Major and selected trace element abundances were determined on fused glass pellets by XRF spectrometry at the University of Salta. Sr and Nd isotopic analyses were conducted using a Finnigan MAT-262 multicollector mass spectrometer operated in a static multi-collector mode at the Brasilia University following the method described by Gioia and Pimentel (2000). Sample dissolution was done in sealed Savillex capsules. Two initial digestions with HF–HNO₃ were followed by

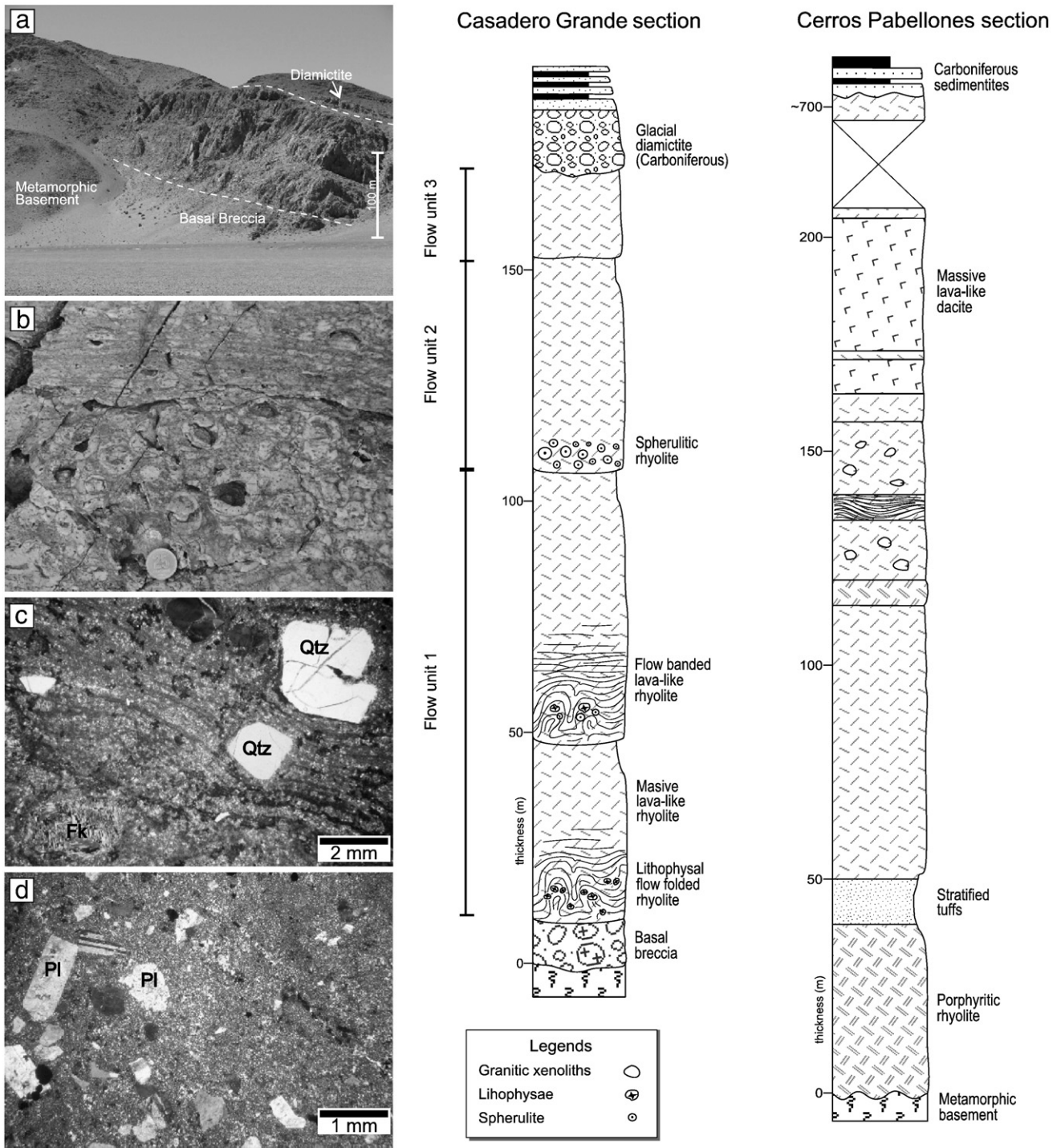


Fig. 2. Stratigraphic profiles of the Puna Catamarqueña and Cerros Pabellones (Sierra del Toro Negro) areas. a) General view of the Casadero Grande section; b) field photograph of a lithophysae-rich and flow-banded rhyolites; c) microphotograph of sample FLPCG showing the flow laminated structure of the rocks; d) fragmented plagioclase phenocrysts in recrystallized tuff sample FLPDAT.

digestion with HCl 6N. The Sr, Sm and Nd elements were separated in Teflon columns by conventional cation exchange techniques. The isotope compositions were measured on Re evaporation filaments of double-filament assemblies. ϵ_{Nd} values were calculated using a present day $^{143}Nd/^{144}Nd$ ratio for CHUR of 0.512638 (cf., [Jacobsen and Wasserburg, 1980](#)). T_{DM} model ages are calculated relative to the depleted mantle model of [DePaolo \(1981\)](#).

Zircon grains were separated from two ~3 kg samples collected from the Casadero Grande and Cerros Pabellones areas by conven-

tional gravimetric and magnetic methods at the University of Brasília. Grains free of inclusions and fractures were handpicked under binocular microscope. Selected zircons were mounted on epoxy resin and then polished to half thickness. U–Pb isotope analyses were performed using the SHRIMP II at the Australian National University, Canberra, following the procedures described by [Williams \(1998\)](#). Data were processed using the SQUID (1.02) and ISOPLOT spreadsheets ([Ludwig, 2001](#)). Data were corrected for common lead using the measured ^{204}Pb .

5. Results

5.1. U–Pb SHRIMP geochronology

Zircon analyses and calculated ages are given in Supplementary Table 1 and illustrated on Concordia plots in Fig. 3. Cathodoluminescence images show that the analyzed zircons are euhedral to subhedral prismatic with lengths of 50 to 250 μm and 2:1 aspect ratio, although many of them are crystal fragments resulting from explosive activity (Fig. 4). Most of the zircon grains are transparent and colorless with concentric variable spaced oscillatory zonation (Fig. 4) typical of magmatic zircons (Corfu et al., 2003). Both dated samples yield a Mississippian age that is similar to the ca. 330–350 Ma U–Pb zircon ages recently reported from granites from the Sierra de Velasco (Dahlquist et al., 2006; Grosse et al., 2009).

A total of 15 analyses were obtained from sample FLPDAT. One analysis is discordant, showing partial Pb loss. The remaining fourteen plot on the Concordia curve. The zircon grains show a relatively wide range in U (38–412 ppm) and Th (45–364 ppm) concentrations with Th/U ratios of 0.35–1.76. Ten of the 14 concordant zircons yield a Concordia age of 348 ± 3 Ma (MSWD = 1.0), which is taken to represent the crystallization age of the rhyolite. Three other analyses (spots 5.1, 14.1 and 16.1) give slightly older ages of ca. 370 Ma and a single analysis yields a concordant age of 1149 ± 13 Ma, suggesting contamination with a Mesoproterozoic continental crust.

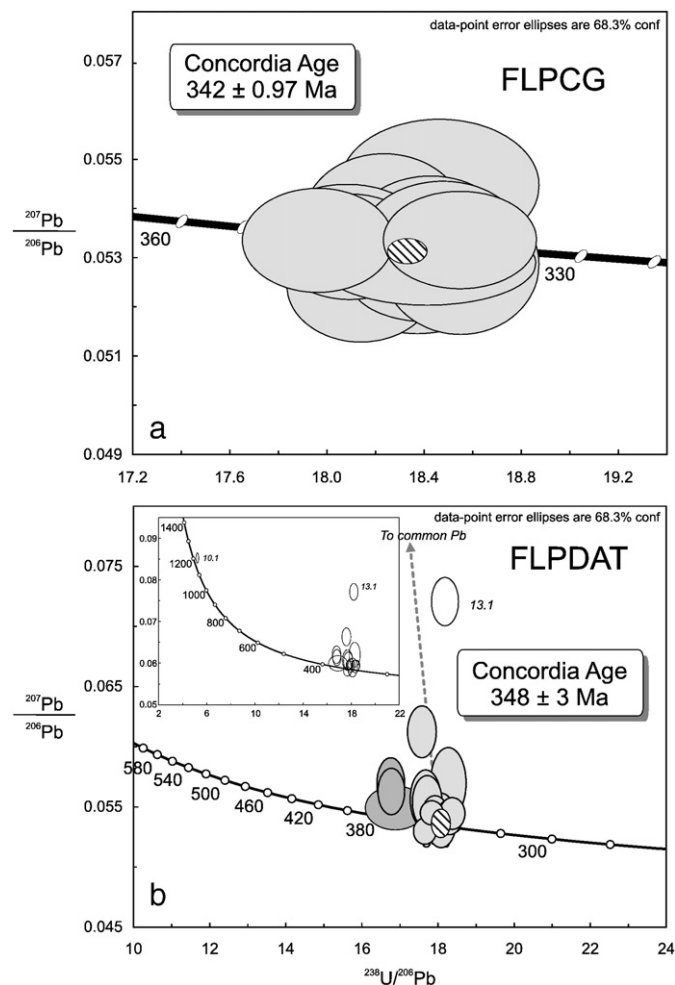


Fig. 3. Tera–Wasserburg diagram of the analyzed rhyolite samples: a) FLPCG (Casadero Grande) and b) FLPDAT (Cerro Pabellones). Striped circles: Concordia age; dark gray: inherited zircons; white: zircon grains with >10% of discordance.

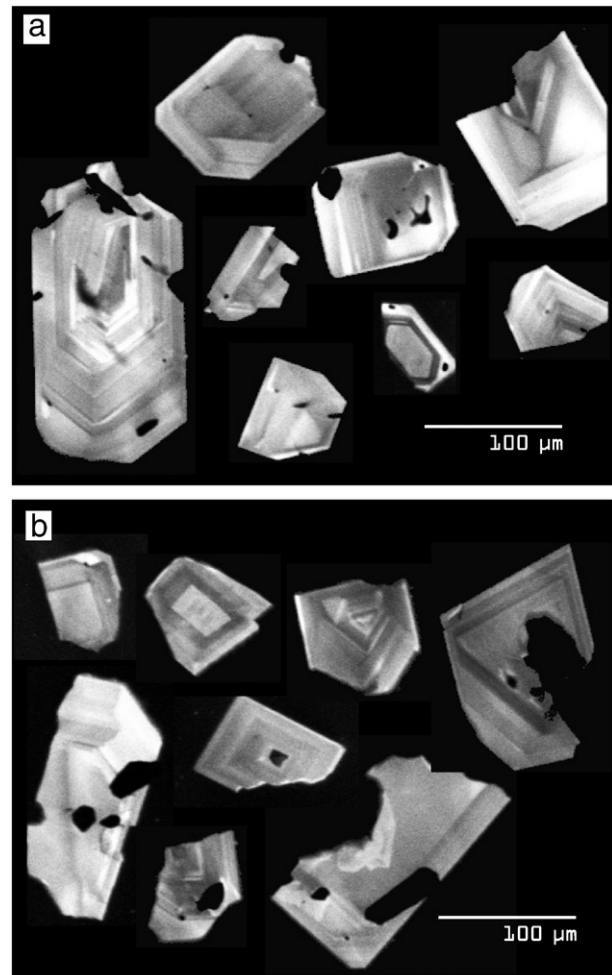


Fig. 4. Cathodoluminescence images of selected zircons from the analyzed rhyolites: a) FLPCG (Casadero Grande) and b) FLPDAT (Cerro Pabellones). Bar scales are 100 μm .

Sixteen zircon grains were analyzed from sample FLPCG. The measured U concentrations vary from 179 to 548 ppm and Th from 80 to 306 ppm. Th/U ratios between 0.46 and 0.63 are typical of an igneous origin (Belousova et al., 2002; Hoskin and Schaltegger, 2003). All analyses form a single tight cluster on the Concordia plot (Fig. 3), yielding the age of 342 ± 1 Ma (MSWD = 1.17), which is interpreted as the crystallization age of the volcanic rocks.

5.2. Sr–Nd isotopic analysis

Sr and Nd isotope data are given in Table 1. The initial ratios were calculated to be 345 Ma. The results are homogeneous and do not show evidence of postmagmatic disturbances. For comparison, the isotope concentrations of the Ordovician rhyolites from the adjacent Famatina belt were also recalculated at 345 Ma.

The Mississippian rhyolites exhibit initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.71433 to 0.71233 and suggest that magma was extracted from a strongly enriched source reservoir with negligible mantle contribution. These values are not unlike those obtained from two of the Ordovician rhyolite samples (0.71327 and 0.72407). The $\epsilon_{\text{Nd}}(t)$ values of -2.91 and -0.33 of the Mississippian rocks are, however, higher than those of the Ordovician rhyolites at 345 Ma, which range between -4.33 and -3.03 . The $\epsilon_{\text{Nd}}(t)$ value for sample FLPDAT (-0.33) is very close to the CHUR (chondrite uniform reservoir) value, indicating a primitive mantle contribution. In this regard, a mafic enclave reported by Grosse et al. (2009) from the Sierras Pampeanas (Sierra de Velasco) to the east shows an even higher $\epsilon_{\text{Nd}}(t)$ value of 0.61.

Table 1

Sr–Nd isotopic data for rhyolite samples FLPDAT and FLPCG and the Ordovician volcanics of Famatina.

| Sample | ppm Rb | ppm Sr | $^{87}\text{Sr}/^{86}\text{Sr}$ | 2 σ error | $^{87}\text{Sr}/^{86}\text{Sr}(t)$ | ppm Sm | ppm Nd | $^{143}\text{Nd}/^{144}\text{Nd}$ | 2 σ error | $^{143}\text{Nd}/^{144}\text{Nd}(t)$ | ϵ_{Nd} | $\epsilon_{\text{Nd}}(t)$ | $T_{\text{DM}}(\text{Ga})$ |
|--------|--------|--------|---------------------------------|------------------|------------------------------------|--------|--------|-----------------------------------|------------------|--------------------------------------|------------------------|---------------------------|----------------------------|
| FLPDAT | 150 | 198 | 0.72511 | 0.00002 | 0.71424 | 10.61 | 57.93 | 0.512295 | 0.000011 | 0.512043 | –6.69 | –2.88 | 1.10 |
| FLPCG | 124 | 126 | 0.72680 | 0.00001 | 0.71246 | 12.444 | 55.121 | 0.512485 | 0.000008 | 0.512179 | –2.98 | –0.36 | 1.09 |
| CMDAT | – | – | – | – | – | 4.46 | 22.04 | 0.512255 | 0.000005 | 0.511979 | –7.47 | –4.20 | 1.3 |
| FLE10 | 59 | 134 | 0.73034 | 0.00004 | 0.72402 | 3.75 | 19.29 | 0.512305 | 0.000008 | 0.512039 | –6.50 | –3.02 | 1.17 |
| CTSC1 | 137 | 46 | 0.75580 | 0.00002 | 0.71291 | 5.72 | 20.13 | 0.512355 | 0.000006 | 0.511967 | –5.52 | –4.43 | 2.51 |
| LPSUR | – | – | – | – | – | 5.68 | 28.46 | 0.512303 | 0.000010 | 0.512030 | –6.53 | –3.19 | 1.21 |

Time corrected $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} values were calculated at 345 Ma. T_{DM} was calculated using the equation of DePaolo (1981). In italics are the Ordovician samples: CMDAT and FLE10 = lower and upper Cerro Morado Group respectively; CTSC = Cerro Tocino Volcanites; LPSUR = Las Planchadas Formation in Sierra de Las Planchadas.

T_{DM} ages of the Mississippian rhyolites range from 1.09 to 1.1 Ga, consistent with the 1149 ± 13 Ma inherited zircon age in sample FLPDAT and slightly younger than the T_{DM} ages of the Ordovician rhyolites, which lie between 1.17 and 1.3 Ga. The 2.51 Ga T_{DM} age of the Cerro Tocino Volcanics contrasts with all the other samples.

Compared with all of the published data from the widespread Ordovician granitoids in the Sierras Pampeanas, the studied Mississippian rhyolites show a more juvenile isotopic signature and younger crustal residence times. The Ordovician intrusives have T_{DM} ages ranging from 1.78 to 1.59 and time corrected $\epsilon_{\text{Nd}}(t)$ values between –8.64 and –5.38, suggesting a Paleoproterozoic crustal source (data according to Pankhurst et al., 1998a, Dahlquist et al., 2007, 2008; Viramonte et al., 2007). Sr isotope values are variable but often more enriched than those from the Mississippian rhyolites. Our Nd results are similar to the contemporaneous San Blas and La Chinchilla granites in the Sierra Pampeanas, which show initial ϵ_{Nd} values between –1.74 and –0.5 and T_{DM} ages between 1.19 and 1.1 Ga (Grosse et al., 2009).

5.3. Geochemistry

The Mississippian volcanic rocks are characterized by their restricted composition, with high SiO_2 (73.55–78.79%) and alkali contents ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 7.98\text{--}8.98\%$), and low MgO, CaO, TiO_2 and P_2O_5 (Table 2). On a total alkali versus silica diagram (Le Bas et al., 1986), the samples fall into the rhyolite field close to the limit between the subalkaline and alkaline series (Fig. 5a). Both samples are potassium rich with $\text{K}_2\text{O}/\text{NaO}$ ratios ranging from 1.09 to 1.17. Based on the K_2O versus SiO_2 variation diagram (Peccerillo and Taylor, 1976), the samples plot in the high-K calc-alkaline series field (Fig. 5b), as do the vast majority of continental margin and intra-continental rhyolites (Hildreth et al., 1999). Their ASI values (molar $\text{Al}_2\text{O}_3/\text{CaO} + \text{K}_2\text{O} + \text{NaO}$) between 1.05 and 1.06, and A/NK ratios of 1.07–1.12, indicate their predominantly metaluminous nature, similar to the analyzed Ordovician rhyolites (Fig. 5c). Both rhyolites show low Zr/Nb (9.96–13.26) and Nb/Th (1.21–2.0) ratios typical of continental crust (cf. Oberc-Dziedzic et al., 2005). This is consistent with the tectonic discrimination diagram of Pearce et al. (1984), on which the Mississippian rhyolites plot in the within plate field, unlike the Ordovician rhyolites, which plot in the volcanic arc field (Fig. 6). This is compatible with all previously published data (Mannheim and Miller, 1996; Fanning et al., 2004; Dahlquist et al., 2008). However, the Mississippian rhyolites display major oxide and some trace element (Sr, Rb and Th) compositions that are very similar to the Puelches rhyolites in the modern southern Andes of Chile (cf. Hildreth et al., 1999). Hence a subduction-related origin cannot be ruled out.

6. Discussion

6.1. Magma source

There is a general consensus that rhyolite lavas can be produced either through fractionation of mantle-derived melts (e.g., Singer et al., 1992; Martin and Sigmarsson, 2007), or by crustal melting in

response to a thermal input (e.g., Oberc-Dziedzic et al., 2005; Yamamoto 2007), or through a combination of assimilation and fractional crystallization (AFC; e.g., McCulloch et al., 1994; Borg and Clynne, 1998). Taking into account the high silica content and apparent lack of rocks of intermediate composition, an origin for the Mississippian rhyolites by crystal fractionation processes is implausible. However, more detailed analyses that include REE are needed in order to develop a reliable petrogenetic model.

The highly radiogenic Sr nature of the Mississippian rhyolites points to considerable crustal contamination or a strongly enriched lithospheric mantle source. Moreover, their Sr isotope ratios are higher than those for island-arc primitive magmas and their differentiated products (e.g., Jicha et al., 2004). The metasedimentary rocks forming the bulk of the Sierras Pampeanas and Famatina are largely bracketed between Mesoproterozoic and Middle–Upper Cambrian (cf. Schwartz and Gromet, 2004; Escayola et al., 2007; Collo et al., 2009), and the Ordovician granites show strong crustal contamination with Sr-isotopic compositions higher than 0.72 (recalculated to 345 Ma; Rapela et al., 1998, Pankhurst et al., 1998a). Therefore, the metasediments

Table 2

Major and trace element geochemistry of the Mississippian and Ordovician rhyolites.

| Sample | FLPDAT | FLPCG | CMDAT | FLE10 | CTSC1 | LPSUR |
|--|--------|--------|--------|--------|--------|--------|
| SiO_2 | 73.55 | 78.79 | 72.82 | 84.01 | 72.32 | 76.14 |
| Al_2O_3 | 13.54 | 11.49 | 12.71 | 8.64 | 15.21 | 13.35 |
| Fe_2O_3 | 1.26 | 0.90 | 2.18 | 0.54 | 0.26 | 1.01 |
| MnO | 0.037 | 0.007 | 0.059 | 0.010 | 0.004 | 0.026 |
| MgO | 0.35 | 0.19 | 0.52 | 0.34 | 0.27 | 0.32 |
| CaO | 0.41 | 0.06 | 1.26 | 0.22 | 0.11 | 0.37 |
| Na_2O | 4.15 | 3.83 | 1.62 | 4.00 | 5.15 | 6.63 |
| K_2O | 4.83 | 4.15 | 6.16 | 0.99 | 5.61 | 1.55 |
| P_2O_5 | 0.11 | 0.03 | 0.08 | 0.04 | 0.04 | 0.03 |
| TiO_2 | 0.26 | 0.15 | 0.25 | 0.10 | 0.13 | 0.13 |
| LOI | 0.72 | 0.48 | 2.02 | 0.92 | 0.17 | 0.61 |
| Total | 99.20 | 100.07 | 99.66 | 99.79 | 99.29 | 100.18 |
| Ba | 1175 | 106 | 682 | 413 | 1119 | 210 |
| Rb | 150 | 126 | 219 | 59 | 137 | 57 |
| Sr | 198 | 124 | 37 | 134 | 46 | 90 |
| Zr | 305 | 498 | 129 | 156 | 202 | 176 |
| Y | 53 | 51 | 34 | 27 | 75 | 36 |
| Nb | 23 | 50 | 6 | 4 | 15 | 7 |
| U | 1 | 1 | 3 | n/d | 2 | 3 |
| Th | 19 | 25 | 14 | 15 | 18 | 18 |
| Co | n/d | n/d | 6 | n/d | n/d | 1 |
| Ni | n/d | n/d | n/d | 3 | 4 | 2 |
| Cr | n/d | 4 | 1 | 3 | n/d | 2 |
| V | 14 | 2 | 23 | 72 | n/d | 10 |
| $\text{Na}_2\text{O} + \text{K}_2\text{O}$ | 8.979 | 7.981 | 7.783 | 4.985 | 10.755 | 8.179 |
| K/Na | 1.165 | 1.085 | 3.804 | 0.246 | 1.090 | 0.233 |
| ASI | 1.058 | 1.055 | 1.094 | 1.074 | 1.032 | 1.006 |
| A/NK | 1.123 | 1.065 | 1.362 | 1.129 | 1.047 | 1.061 |
| Zr/Nb | 13.261 | 9.960 | 21.500 | 39.000 | 13.467 | 25.143 |
| Nb/Th | 1.211 | 2 | 0.429 | 0.267 | 0.833 | 0.389 |
| Th(N) | 223.53 | 294.12 | 164.71 | 176.47 | 211.76 | 211.76 |
| Y(N) | 11.65 | 11.21 | 7.47 | 5.93 | 16.48 | 7.91 |

n/d = not determined.

Italics indicate the Ordovician samples.

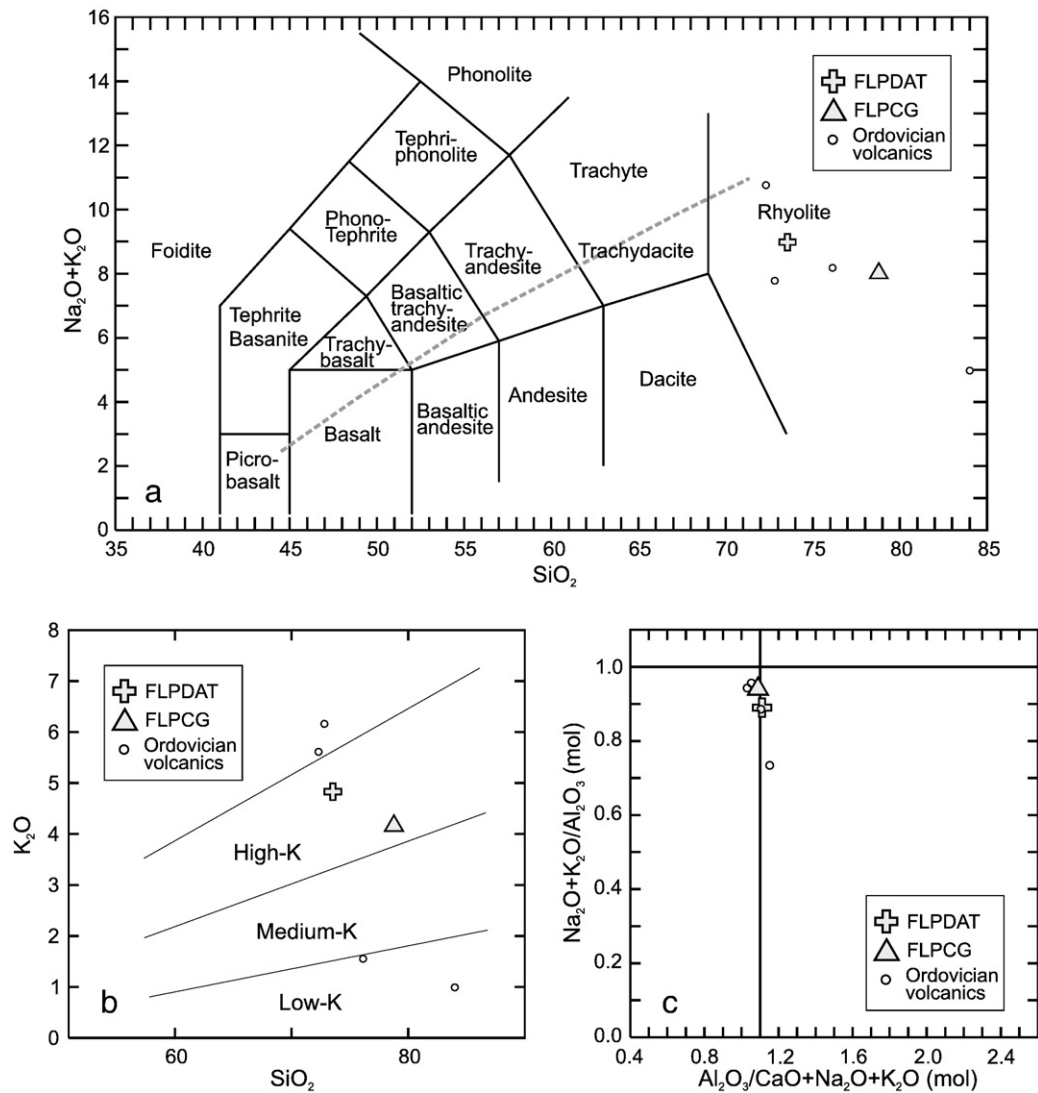


Fig. 5. a) TAS (Le Bas et al., 1986), b) SiO_2 versus K_2O (Peccerillo and Taylor, 1976), and c) ASI versus A/NK (Shand, 1927) diagrams from the Mississippian and Ordovician rhyolites. The boundary between alkaline and subalkaline series (dashed line in a) is after Irvine and Baragar (1971).

that underlie the studied rhyolites could well be a source for the Mississippian magmas. Similar processes have been suggested to explain the extensive Ordovician S-type granites of western Argentina (e.g., Pankhurst et al., 2000; Dahlquist et al., 2007; Viramonte et al., 2007). The presence of a Mesoproterozoic inherited zircon in the Pabellones rhyolite of similar age to that suggested for the underlying Sierra del Toro Negro high-grade metamorphic basement is consistent with at least a partial crustal source for the magmas. An alternative interpretation for the relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios utilizes the mechanism of subduction erosion in the modern Chilean flat-slab (Haschke et al., 2002; Kay et al., 2005).

The lower strontium ratios of the Mississippian rhyolites relative to those of the Pampean metamorphic basement and Ordovician granites can be explained by the addition of a more juvenile component, as previously suggested by Grosse et al. (2008) and Rapela et al. (2008) for the Mississippian granites in the Sierra de Velasco and the Late Devonian Achala batholith in the Sierras de Córdoba. The occurrence of two mafic enclaves with positive ϵ_{Nd} values in the Sierra de Velasco, immediately west of Famatina, could represent the mantle source of the Mississippian magmatism (Grosse et al., 2009). As shown by the ϵ_{Nd} values and Nd-model ages, the parent magma of the rhyolites was probably a hybrid produced by mixing of crustal melts and the hot mantle-derived mafic magmas that induced crustal melting. According

to their isotopic signature, the Mississippian rhyolites have a more primitive value than any of the Mississippian granites within the Sierras Pampeanas, suggesting a larger input from the mantle source. As mentioned above, the ϵ_{Nd} value of the Casadero Grande sample is very close to the CHUR value and thus little crustal contamination would be expected. Alternatively, it could reflect recycling of a more primitive crustal source different from that of the Early Paleozoic magmatism that characterizes the mountain ranges east of the Precordillera. A similar explanation has recently been proposed by Willner et al. (2008) for igneous pebbles in Carboniferous conglomerates in central Chile based on U–Pb and Lu–Hf in zircons. However, this hypothesis fails to account for the fact that the Mississippian magmatism preserved in central-western Argentina appears to be much more widespread than previously thought (Martina and Astini, 2009).

6.2. Regional interpretation and chronology

The volcanic rocks analyzed here have been traditionally included within the Ordovician Las Planchadas Formation (Turner, 1967; Maissonave, 1979; Rubiolo 2001; Coira et al., 2005), but the data we have presented show them to be Mississippian. The arc-type Ordovician volcanism (Toselli et al., 1990; Pankhurst et al., 1998a,b, 2000) lies to the east of the Mississippian volcanic trend (Sierra de Las

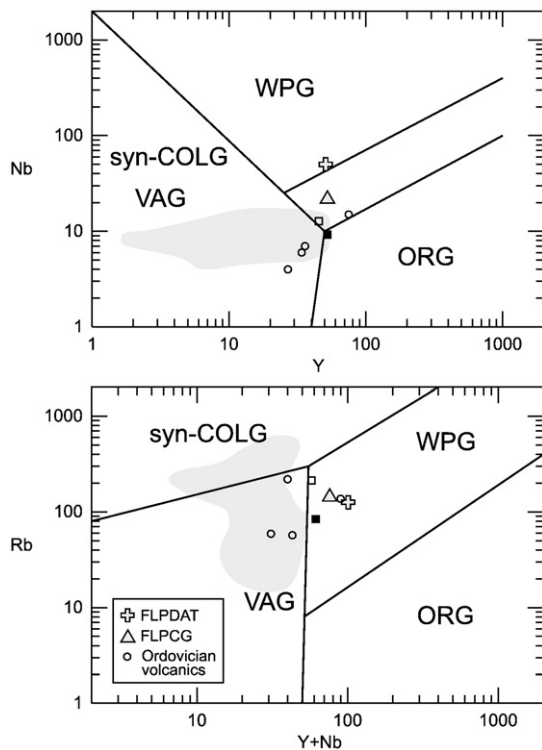


Fig. 6. Y versus Nb and Y + Nb versus Rb tectonic discrimination diagrams (Pearce et al., 1984) for the analyzed rhyolites. The Mississippian rocks plot in the within plate granites field (WPG) unlike the Ordovician samples, which mostly plot in the volcanic arc field (VAG). Gray shaded areas are the Ordovician felsic volcanics of Famatina reported by Mannheim and Miller (1996). Black square from Fanning et al. (2004) and open square for rhyolite from Dahlquist et al. (2008).

Planchadas, Sierra de Narváez and Sierra de Famatina in Fig. 1). The present day areal extent and thickness of the Mississippian rhyolites emphasize the importance of this volcanic event, its outboard position with respect to previous magmatic additions along the Gondwana margin, and its direct overlap onto Grenville basement (Fig. 1).

The geochemical and isotopic signature of the Mississippian rhyolites are comparable to those observed in the San Blas and La Chinchilla granites within the Sierras Pampeanas (Dahlquist et al., 2006; Grosse et al., 2009), including high silica and total alkalis contents, Fe enrichment relative to Mg concentration, primitive Nd values and absence of mafic rocks. These petrological and geochemical similarities, together with their close spatial and temporal relationships, suggest that the two assemblages represent different crustal levels of a same large silicic magmatic event that affected a wide area of the western margin of Gondwana and partly overlaps previous magmatic cycles.

According to the data presented here, the Mississippian volcanism represents an independent magmatic episode that differs from both the earlier well-known Ordovician Ocolytic arc magmatism and the Permo-Triassic Choiyoi rhyolite province but is of comparable size and magnitude. The Mississippian rhyolites can be grouped with the largely coeval granites in the Sierras Pampeanas (Sims et al., 1998; Grosse et al., 2009; Dahlquist et al., 2010). The importance of this volcanic event has been recently highlighted by Willner et al. (2008) who recognized an important penecontemporaneous igneous detrital zircon population in the Pennsylvanian Chilean accretionary prism. These authors also reported crystallization ages from rhyolite and granite pebbles of the overlying Huentelauquén Formation, which they concluded have an identical source. The bulk of the magmatic zircons in the detrital population and the rhyolite and granite pebbles, show positive $\varepsilon_{\text{Hf}}(t)$ values, indicating a juvenile input like that proposed for the rhyolites studied here. According to Willner et al.

(2008) the magmatism is the product of melting of Mesoproterozoic crustal sources within the Cordillera Frontal. However, the correspondence between the data in Willner et al. (2008) and the Mississippian rhyolite/granite data reported here, which together cover a belt ~150 km in width and more than 250,000 km² in area, point to the foreland region of Argentina as the most likely source for the Chile detrital input.

6.3. Tectonic setting

Attempts to elucidate the Late Paleozoic tectonic evolution of the Central Andes has always been hampered by the poorly preserved Middle Devonian to Mississippian record. The lack of representative foreland stratigraphic successions and a broad unconformity recorded in the Andean region gave rise to the so-called Chanic unconformity, which was initially linked to the collision of Chilenia with the western margin of Gondwana (Ramos et al., 1986). Since then, other hypotheses have been proposed to explain this unconformity, including the combined result of eustatic and glacial effects (e.g., González-Bonorino, 1992). While the collisional hypothesis implies a dominantly contractional stress regime, an extensional setting was proposed by Astini (1996) who suggested that the cordilleran region and the present Andean foreland were being uplifted and exposed to erosion during the Mississippian. Bahlburg and Herve (1997), on the other hand, postulated a passive margin setting for northern Chile and northwestern Argentina based on the apparent sedimentological continuity and absence of magmatism and metamorphism along the northern termination of this segment of the Andes. However, the latest tectonic reconstructions suggest an active continental margin setting at least since the earliest Pennsylvanian (e.g., Charrier et al., 2007; Willner et al., 2005, 2008). Evidence for subduction comes from the presence of accretionary prism metasedimentary rocks of Mississippian age (~325 Ma U–Pb detrital zircon ages and ~340 Ma Lu–Hf mineral isochron on garnet amphibolite) along the central Chile coast (Rebolledo and Charrier, 1994; Hervé et al., 2007; Willner et al., 2004, 2005, 2009; Richter et al., 2007).

According to our geochronological, isotopic and geochemical results, the rhyolites studied within the Argentine Andes likely represent the source of the magmatic activity recorded in the exposed Late Paleozoic fore-arc basins of Central Chile, and while the geochemical signature is not definitive, it precludes a passive margin scenario. Rhyolite lava flows with similar geochemical signatures have been described in the Andes of central Chile where cessation of overthrusting along the eastern margin of the arc may have locally created neutral or extensional stress components, favoring storage of crustal partial melts (Hildreth et al., 1999). Modern possible analogues are recorded in the eastern Cascade Range (Hildreth, 2007) and Trans-Mexican Volcanic Belt (e.g., La Primavera, Los Azufres and Los Humeros volcanoes; Ferriz and Mahood, 1986), where rhyolites have been developed along the inboard margin of the volcanic chain where extensional faulting is actively impinging on the arc.

Crustal melting recorded by Mississippian rhyolites and co-genetic granites that extend more than 200 km east from the modern arc within the Andean broken foreland region, requires crustal extension and asthenospheric upwelling (responsible of the thermal perturbation and magma generation). Worldwide, there seems to be a common temporal and spatial association between major granitic magmatism and lithospheric extension (Clemens, 2003). Extensional stress regimes related to convergent margins have been widely recognized in the geological literature (e.g., Cawood and Buchan, 2007) and incorporated within the context of protracted accretionary orogens (Collins, 2002a). Such regimes occur when the plate convergence rate is less than the rate of subduction and, as a consequence, roll-back or retraction of the subducted slab occurs (Uyeda, 1982; Royden, 1993). An alternative model including an event of slab break-off (Davies and von Blanckenburg, 1995) related to the aftermath of Chilenia docking

against Gondwana is also likely and compatible with extension in an upper-plate context. However, regardless of the plate dynamics needed to trigger lithospheric extension within these settings (Doglioni, 1995; Cawood and Buchan, 2007), unusually high temperatures are required for partial melting of relatively refractory source rocks like those of the lower crust, implying thermal and/or mass input from the underlying mantle. In such a scenario it is possible for large volumes of mafic material to provide the heat source for crustal melting. In turn, the production of relatively large volumes of crustal felsic magmas could well have acted as a barrier to the rise of mafic magmas (cf. Pankhurst et al., 1998b; Riley et al., 2001), which would remain stored in the lower parts of the crust. We discard a hypothesis of lithospheric delamination as the possible tectonic setting for extension because thick fossiliferous marine strata bracket the volcanic interval in various places preventing the possibility of major crustal uplifting that seems a requirement in both present day (Kay and Kay, 1993) and past examples (Bird, 1979).

Tectonic switching (Collins, 2002b) in the retro-arc region of the Terra Australis accretionary margin along western Gondwana could account for crustal extension through associated heat softening and silicic magmatism operating for ca. 20 Ma. Similar examples have been suggested to explain the widespread Mesozoic silicic magmatism in Western Gondwana (Mpodozis and Kay, 1992; Pankhurst et al., 1998b), the Mesoproterozoic metaluminous A-type rhyolites of the St. Francois Mountains (Menuge et al., 2002) and the Quaternary subduction-related rhyolites of NE Japan arc (Yamamoto, 2007; Isozaki et al., 2010).

Asthenospheric mantle upwelling within the Sierras Pampeanas can be inferred from the Mississippian high-temperature conditions originally proposed by McBride et al. (1976). Additional lines of evidence appear to confirm this hypothesis. U–Pb geochronological data from apatite within basement shear zones that show a metamorphic thermal peak age of 342 ± 2 Ma (Höckenreiner et al., 2003) are compatible with this event. Fission-track analysis and various other cooling age indicators (e.g., Jordan et al., 1989; Coughlin et al., 1998; Höckenreiner et al., 2003) point to important unroofing in western Argentina during the late Paleozoic, also compatible with regional thermal doming in the Mississippian. Similarly the absence of a Mississippian stratigraphic record within the Sierras Pampeanas and the eastern Precordillera suggests protracted exposure at this time (Charrier, 1986; González-Bonorino, 1991). In contrast, >2000 m of alluvial conglomerates and shallow-marine strata of Mississippian age (Astini et al., in press) precedes the widespread development of silicic magmatism in the Precordillera de Jagüé (Fig. 1), suggesting that major extension and crustal stretching took place to the west. This distribution is compatible with broad-scale asymmetric models of crustal extension (Astini et al., 2009).

7. Conclusions

A new volcanic event of predominantly rhyolitic composition is recognized in the south-central Andes of Argentina. Based on U–Pb SHRIMP zircon data the magmatic event is constrained to the Mississippian. Geochemical data classify these rocks as calc-alkaline K-rich rhyolites, whereas ASI and A/NK values show them to be predominantly metaluminous. Preliminary isotopic geochemistry suggests mixing of a Mississippian juvenile source and a Mesoproterozoic crustal component for the parental magmas, similar to the Mississippian A-type granites in the Sierras Pampeanas immediately to the east.

This magmatism questions a typical passive margin setting for the southern Central Andes during the Carboniferous. Although not conclusive, the isotopic and geochemical data are more compatible with an extensional environment. This interpretation is consistent with generalized high-temperature crustal conditions recorded by the widespread (>250,000 km²) magmatism in the foreland region, and the observed stratigraphic and structural relationships across the

Gondwana margin. In terms of the evolution for the Terra Australis accretionary orogen, a major tectonic switching episode with crustal extension seems the most likely explanation for both magmatic and sedimentary additions during the Mississippian.

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