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Late Miocene ignimbrites at the southern Puna–northern Sierras Pampeanas border (~27°S): Stratigraphic correlation

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ABSTRACT

New field observations and petrographic and geochemical data of pyroclastic deposits exposed along the Las Papas valley (border between southern Puna and northern Sierras Pampeanas, Argentina) and further north, lead us to propose a new stratigraphic correlation and classification of the late Miocene volcanism in this area. We redefine the Las Papas, Las Juntas, Aguada Alumbrera and Rosada ignimbrites and define the Agua Caliente and Del Medio ignimbrites. The whole set of ignimbrites are rhyolites and less frequently dacites of calc-alkaline affinity. In the present contribution we divide ignimbrites into the Agua Negra and Rincón groups, based mainly on their geochemical signature. The Agua Negra Group is formed by the Las Papas and Las Juntas ignimbrites, indurated and welded, lithic-rich, with crystal-poor pumices and crystal-rich matrix. The Rincón Group comprises the Agua Caliente, Aguada Alumbrera, Rosada and Del Medio ignimbrites, with variable welding degrees, lithic and crystal content.

The greater enrichment of crystals in the matrix in comparison with the crystal content in pumices indicates significant elutriation during flow transport and thus volume estimations are to be considered lower bounds for the actual erupted volume. The total minimum estimated volume for the ignimbrites of the Agua Negra and Rincón groups is 2.8 km^3 (2.3 km^3 DRE). Field relationships and new analytical data indicate that the different acid ignimbrites that crop out in this small area are related to at least two different magma chambers. The widespread Quaternary volcanism in this area covers the older deposits, thus making it difficult to recognize the volcanic centers that produced these late Miocene ignimbrites.

1. Introduction

From Oligocene to Present the Altiplano-Puna plateau (Central Andes of South America), accounts for a profuse magmatic history with a high increment registered since the Miocene (e.g., Coira et al., 1993; Guzmán et al., 2014) forming the so-called Central Volcanic Zone (CVZ; Thorpe et al., 1984). In the southern Puna (~24–28°S), the Miocene to Recent volcanism is represented by effusive and pyroclastic products related mostly to calderas, stratovolcanoes, domes and scoria cones (e.g., Coira and Kay, 1993). Between 67° and 69°W the pyroclastic flow deposits of the southern Puna were characterized by their low-volume and poor crystal content (Schnurr et al., 2007) with the exceptions of ignimbrite deposits from Cerro Galán and Luingo calderas which are crystal-rich and large-volume deposits (e.g., Sparks et al., 1985; Guzmán and Petrinovic, 2010; Guzmán et al., 2011). However, recent studies (e.g., Guzmán et al., 2014) show that the features of ignimbrites within the southern Puna are highly variable in space and time, thus no simple characterization can be derived.

Most detailed studies of the Cenozoic volcanism developed in the Puna plateau have been concentrated to the north of 24°S latitude, while the south area was mainly the subject of regional studies. For this contribution we have studied several ignimbrite deposits exposed in the eastern part of the Cordillera de San Buenaventura, which comprises a group of high ranges that separate the southern Puna from the northern Sierras Pampeanas and Cordillera Frontal. The ignimbrites studied between 26°45′ and 27°10′S constitute, at present, the southernmost outcrops of ignimbrites recognized so far in the transition of these geological provinces. This study deepens the results obtained previously in the specific area of research and surroundings (Seggiaro et al., 2001; Montero-López et al., 2010a,b, 2011). To enrich the

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knowledge of the volcanic history of the southern rim of the Puna we present a new stratigraphic subdivision of the late Miocene ignimbrites cropping out on the southeastern part of the Cordillera de San Buenaventura, based on field relations, petrography and geochemical composition, as well as previous published ages.

2. Regional geological setting

The Altiplano-Puna plateau is characterized by a high elevation above 3.5 km asl and constitutes the second largest plateau of the world after the Tibet. The Andean plateau has a thick crust (55–75 km; e.g., Yuan et al., 2000; Heit et al., 2007) in response to the shortening associated to the convergence geometry of the Nazca-South American plates (e.g., Isacks, 1988; Allmendinger and Gubbels, 1996). The southern Puna border (approximately 27°S at these longitudes) (Fig. 1) coincides with the transition of a normal subducted segment (30°) north of 24°S to a flat subducted segment south of 27°S (e.g., Baranzagi and Isacks, 1976; Jordan et al., 1983; Allmendinger, 1986).

The Cordillera de San Buenaventura is composed mainly of Plio-Pleistocene dacitic and andesitic domes and stratovolcanoes emplaced on the central and western parts of the range (Seggiaro et al., 2001). Whereas the eastern part of the range is formed by basement rocks with variable degrees of metamorphism and some igneous intrusions of the Proterozoic–early Paleozoic (Rubiolo et al., 2001) covered by volcanic and sedimentary deposits. The latter comprises the Plio-Pleistocene Punaschotter conglomerates (Penck, 1920). The most recent volcanic deposits present in this eastern part of the range, are as young as Pleistocene–Holocene (Arnosio et al., 2008; Montero-López et al., 2010a) and correspond to ignimbrites erupted from the Cerro Blanco calderas (Seggiaro et al., 2001; Arnosio et al., 2005; Báez et al., 2015) northward of the study area. Besides the Cerro Blanco ignimbrites, there is a series of pyroclastic flow deposits of late Miocene age (Montero-López et al., 2011) which constitute the focus of the present contribution. These ignimbrite deposits crop out along an inter-montane valley (Las Papas valley) that drains to the Fiambalá Basin (immediately to the south) (Fig. 1b), a basin with a major high

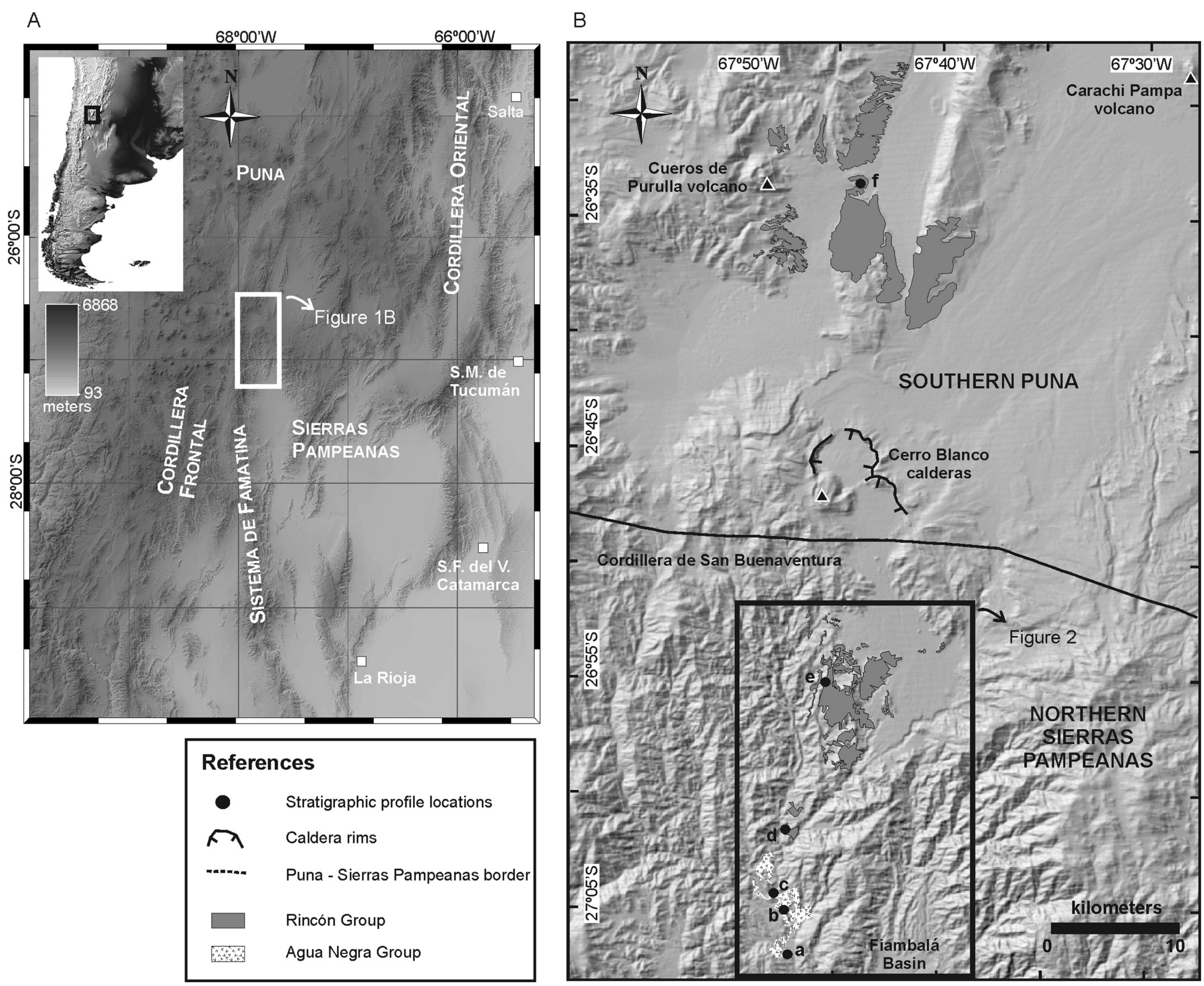

Fig. 1. A – Digital Elevation Model (DEM) from the northwest of Argentina showing the location of the Puna plateau. B – Digital Elevation Model (DEM) of the study area showing the outcrops of the Agua Negra and Rincón Groups The black box shows location of the study area. Stratigraphic profile locations of Fig. 3 are shown as black circles.

accumulation rate of Neogene and Quaternary sediments, flanked by reverse-faulted ranges typical of the Sierras Pampeanas.

3. Neogene stratigraphy

The neogene stratigraphy of the Las Papas valley is complex because many ignimbrites with comparable field characteristics crop out in a small area. Moreover, their petrography and geochemistry is similar. However, the sum of field studies, petrography, mineral chemistry, whole-rock geochemistry and absolute ages enables to distinguish them into six different units (Fig. 2). All the pyroclastic units are massive and have low volumes, with variable welding degrees and pumice and lithic contents. Stratigraphic sections of selected sites are shown in Fig. 3 and modal analyses of petrographic thin sections of each pyroclastic unit are shown in Fig. 4.

Montero-López et al. (2011) separated the ignimbrites of the Las Papas valley into the Las Papas Ignimbrite and Las Juntas Ignimbrite; subdividing the latter in lower and upper members. We here redefine the stratigraphic units and also define two new ignimbritic units, based on the new data available. Even though overall characteristics of ignimbrites are approximately similar, the geochemical signatures (mostly minor and trace elements) enabled to divide them into two groups: Agua Negra Group (Las Papas and Las Juntas ignimbrites) and Rincón Group (Agua Caliente, Aguada Alumbrera, Rosada and Del Medio ignimbrites).

3.1. *Agua Negra Group*

3.1.1. *Las Papas ignimbrite*

This unit was originally described by Montero-López et al. (2011). It crops out along the right margin of Las Papas valley (Fig. 2), with a thickness between c. 5 m and c. 70 m. The base of this ignimbrite has not been observed. It consists of a massive purplish-gray indurated deposit, with high to medium welding degree and with strong columnar jointing (Fig. 5a). The crystal content is low in the pumices (<15 vol.%) and high in the matrix (≤40 vol.%) and the lithic content is high (<28 vol.%). Lithics comprise subangular to subrounded fragments, varying between 0.2 and 11 cm in size, and with compositions of mainly amphibolite and lesser amount of granitoid, volcanic rocks, schist and sandstone. The pumice content reach 27 vol.% (Fig. 4) and consists of two types: a) black-colored crystal-rich fiamme (<9 cm), generally with flattening ratios of 12:1 and b) brownish-white crystal-poor fiamme (<23 cm; with flattening ratios up to 15:1); both of them have perlitic fracture and a flame-like shape (Gifkins et al., 2005). The mineral association of both pumice types is plagioclase, K-feldspar, quartz, biotite, zircon and opaque minerals (Fig. 4). This ignimbrite yielded an age of 9.24 ± 0.03 Ma (^{40}Ar/^{39}Ar in biotite, Montero-López et al., 2014).

3.1.2. *Las Juntas ignimbrite*

We redefine this unit, including only those deposits previously grouped in the Lower Member of Las Juntas Ignimbrite (Montero-López et al., 2011).

Las Juntas Ignimbrite covers the Las Papas Ignimbrite; it crops out all along both margins of the Las Papas valley (see Fig. 2). The maximum recognized thickness of this unit is 50 m. It is white, massive and moderately indurated, with low degree of welding and high lithic content (40 vol.%) which gradually decrease towards the top of the unit (Fig. 5b). The lithic fragments (c. 1.2 cm) are subangular to subrounded, primarily of amphibolite and minor amounts of granitoid, schist, quartzite and volcanic rocks. The content in pumices is moderate (19 vol.%) (Fig. 4); while crystal content is low in pumices (5 vol.%) and moderate in the matrix (23 vol.%). Two types of pumices were recognized: a) brownish-white fragments, around 0.3 cm in size, slightly flattened and rich in crystals of plagioclase, K-feldspar, quartz, apatite and opaque minerals and b) white pumices, 0.02–4 cm in size and without crystals. Minerals within the matrix are quartz, plagioclase, K-feldspar, biotite, amphibole, pyroxene, apatite, zircon, muscovite and opaque minerals (Fig. 4). This unit provided an age of 8.47 ± 0.02 Ma (^{40}Ar/^{39}Ar in biotite, Montero-López et al., 2014).

3.2. *Rincón Group*

3.2.1. *Agua Caliente ignimbrite*

Montero-López et al. (2010a) defined the Aguada Alumbrera Ignimbrite (see below) dividing it in a lower and upper part separated by a sedimentary deposit. However, new field observations permitted to redefine this unit. Thus, the lower part of the former Aguada Alumbrera Ignimbrite (i.e., the one below the sedimentary deposit) belongs to the Agua Caliente Ignimbrite, whereas the part above the sedimentary deposit remains as the Aguada Alumbrera Ignimbrite (see below).

Here we grouped pink-colored pyroclastic deposits without previous detailed studies which crop out to the northeast of the Las Papas valley (Fig. 2). Despite the contacts with other units are not seen in the field, we infer it is below the Aguada Alumbrera Ignimbrite based on the stratigraphic relations (Fig. 5c). The deposits consist of massive, indurated, unwelded, white-grayish-colored ignimbrites that in some sectors acquire a pinkish color linked to weathering. Its pumice and lithic content gradually diminishes from base (pumices: 40 vol.%; lithics: 30 vol.%) to top (pumices: 20 vol.%; lithics: 7 vol.%). Pumices are white, generally small (3 mm) but some fragments reach 4 cm long; they are subrounded and contain biotite, K-feldspar and opaque minerals. The lithics are subangular to subrounded fragments of rigid basement rocks (amphibolite, quartzite and granitic rocks) and volcanic rocks, mainly of 0.5–1.5 cm with some clasts as large as 6 cm. The deposit is poor to moderate in crystal content (2 vol.% in pumice and 18 vol.% in matrix); minerals in the matrix are quartz, plagioclase, K-feldspar, biotite, amphibole, pyroxene, zircon, muscovite and opaque (Fig. 4). The age of this unit is unknown.

3.2.2. *Sedimentary deposit*

The Agua Caliente and Aguada Alumbrera ignimbrites are separated by a 10 m-thick conglomeratic succession. It is a brown-colored conglomerate deposit in a sandy matrix, strongly consolidated and with a coarse stratification and intercalations of sand beds. Lithic fragments in the conglomerate deposit are mainly amphibolite, schist, quartzite and volcanic rocks. The clasts are subangular to subrounded, they are usually 1.6–2.6 cm long, but some fragments reach 15 cm. This deposit is unconformably overlain by the ignimbrites of the Aguada Alumbrera unit. We link this sedimentary event to an alluvial-fan or a fluvial environment.

3.2.3. *Aguada Alumbrera ignimbrite*

As previously explained this ignimbrite is redefined here and represents only the former upper member of the Aguada Alumbrera Ignimbrite of Montero-López et al. (2010a). The deposits of this unit are, by far, those with the greatest areal extent. They are concentrated in the surroundings of Aguada Alumbrera lake (Fig. 2) but some deposits are widely scattered, cropping out to the east of the Las Papas village.

Montero-López et al. (2010a) distinguished two units within the Aguada Alumbrera Ignimbrite: Blanquecina and Rojiza, being the Blanquecina Unit further subdivided into the upper and lower members. The Rojiza Unit was only observed to the east of the Aguada Alumbrera lake, covering an area of 4.9 km^2. This unit

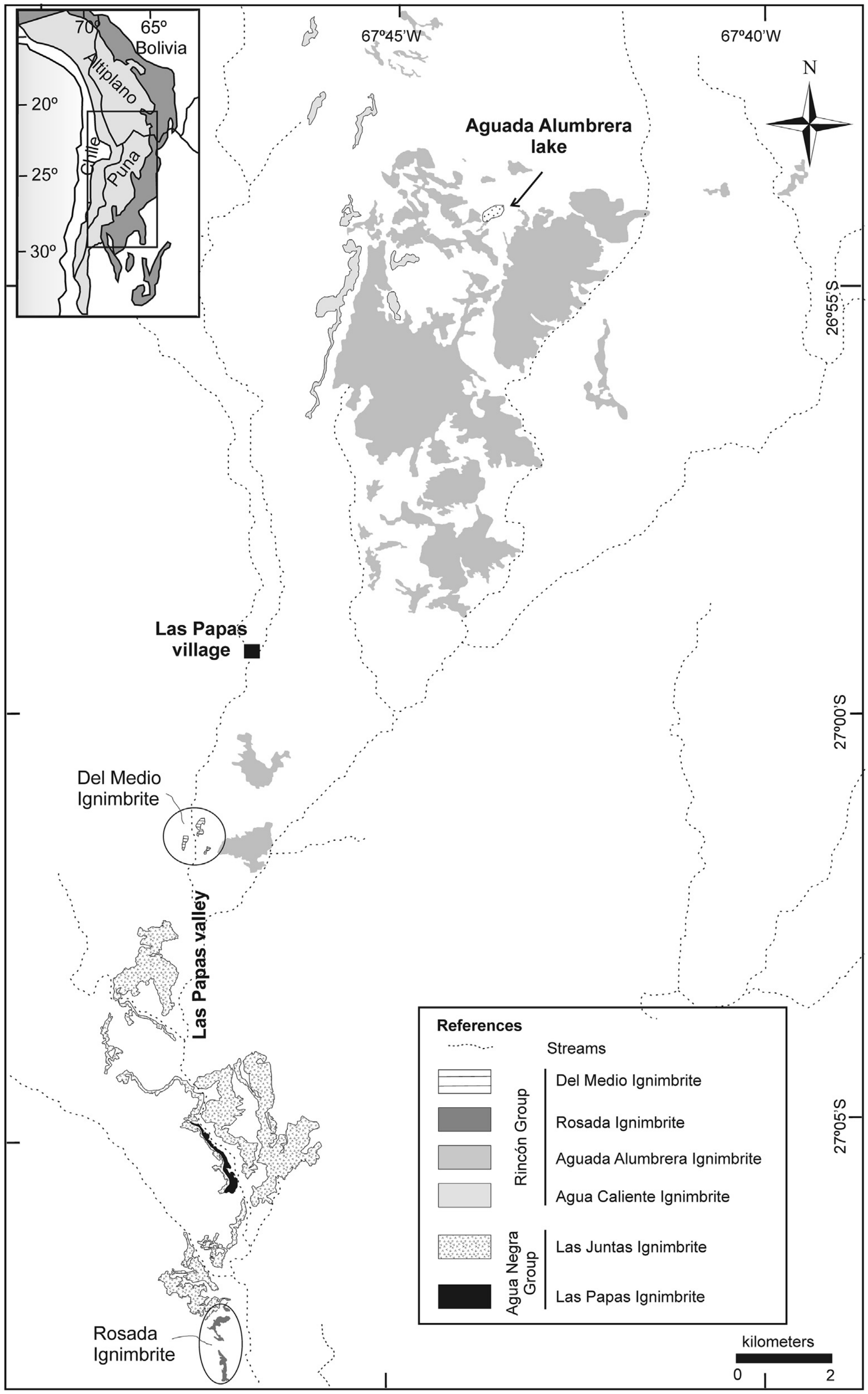

Fig. 2. Geological map of the study area between southern Puna and northern Sierras Pampeanas with the distribution of the late Miocene ignimbrites.

consists of massive, red-colored crystal and lithic-rich deposits, with a minimum thickness of 40 m (Montero-López et al., 2010a). The pumices are white in color, slightly flattened (3 cm, flattening ratio: 3:1) and with crystals of plagioclase, quartz, biotite, amphibole and opaque minerals. The lithic fragments are sub-angular and correspond to metamorphic and volcanic rocks. In this study, we focused our attention in the more widely distributed Blanquecina Unit, of 31.4 km^2.

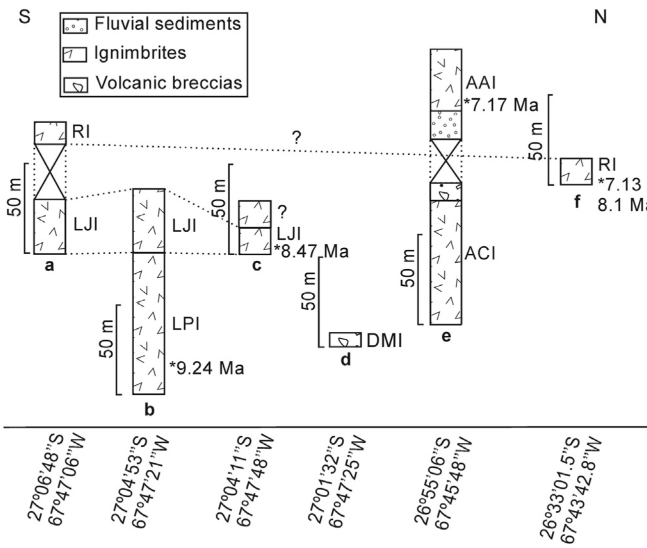

Fig. 3. Stratigraphic profiles of the ignimbrite units studied along the Las Papas valley, southern Puna–northern Sierras Pampeanas border. LPI: Las Papas Ignimbrite; LJI: Las Juntas Ignimbrite; ACI: Agua Caliente Ignimbrite; AAI: Aguada Alumbrera Ignimbrite; DMI: Del Medio Ignimbrite; RI: Rosada Ignimbrite.

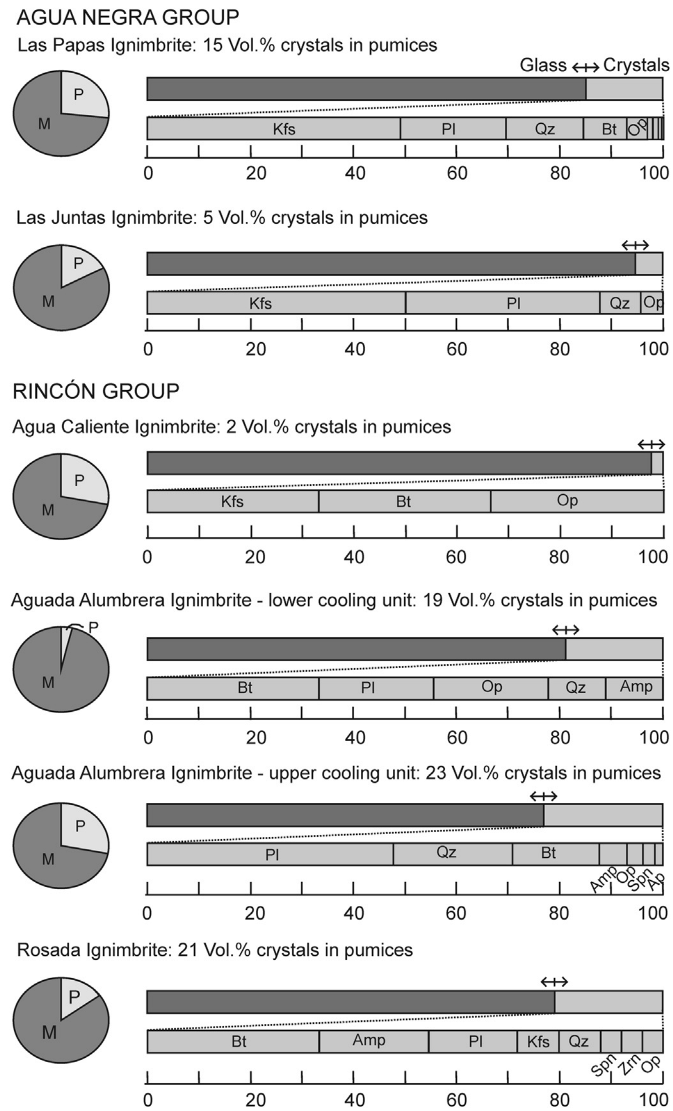

Fig. 4. Modal analyses of the ignimbrites from the Agua Negra and Rincón groups. Pie charts show the percentage (vol.%) of pumice (P) and matrix (M) in the whole rock. Bar charts present crystal contents in pumices. Kfs: K-feldspar; Pl: plagioclase; Qz: quartz; Bt: biotite; Amp: amphibole; Op: opaque minerals; Zrn: zircon; Ap: apatite; Spn: sphene.

The Blanquecina Unit (i.e., former upper member of Montero-López et al., 2010a) has a minimum thickness of 100 m and comprises two cooling units, both indurated, with moderate welding and coarse columnar jointing (Fig. 5d). The lower cooling unit is gray with moderate to high crystal content (19 vol.% in pumice and >31 vol.% in matrix) and poor in pumice (<5 vol.%). Pumices (<3 cm) are pink-colored probably as a result of their alteration and some fragments are slightly flattened; they contain crystals of biotite, plagioclase, quartz and amphibole (Fig. 4). The lithic fragments (<10 vol.%) are subangular, generally 0.3 cm long; they are amphibolite, schist, quartzite, granitoid and volcanic rocks. The upper cooling unit is a white massive pyroclastic deposit with moderate to high crystal content (23 vol.% in pumice and 37 vol.% in matrix). Lithic fragments (10 vol.%; c. 1 cm) are subangular amphibolite, schist, granitoid, sandstone and volcanic rocks. Pumices (<28 vol.%; c. 5 cm) are white-colored and rich in crystals of plagioclase, quartz, biotite, amphibole, opaque minerals, sphene and apatite (Fig. 4). Minerals present in the matrix of both cooling units are quartz, plagioclase, K-feldspar, biotite, amphibole, pyroxene, sphene, zircon, apatite and opaque minerals. Montero-López et al. (2010b) reported ages between 7.14 ± 0.19 Ma ($^{40}Ar/^{39}Ar$ in hornblende) and 7.17 ± 0.02 Ma ($^{40}Ar/^{39}Ar$ in biotite) for the Blanquecina Unit of the Aguada Alumbrera Ignimbrite.

3.2.4. *Rosada ignimbrite*

The Rosada Ignimbrite (Seggiaro et al., 2001) is redefined by grouping the Upper Member of the Las Juntas Ignimbrite (Montero-López et al., 2011) and the outcrops of the Rosada Ignimbrite described in Montero-López et al. (2010a) in the Cueros de Purulla area (see Fig. 1b). Although the outcrops at the surroundings of Cueros de Purulla and the ones at the southern part of the Las Papas valley are c. 40 km apart, they show similarities in the field (with the exception of the color of the deposits), petrography and geochemistry. Seggiaro et al. (2001) describe two different pyroclastic flows forming the Rosada Ignimbrite. Field characteristics of the outcrops at the southern part of the Las Papas valley are similar to the Rosada Ignimbrite upper flow of Seggiaro et al. (2001).

The pyroclastic deposits at the Las Papas valley (Fig. 2) are gray, massive, indurated, devitrified and with a high welding degree (Fig. 5e). The base of this deposit is not exposed, having a minimum thickness of 5 m. The deposit shows marked columnar jointing; it is moderate to rich in crystal content (21 vol.% in pumice and 53 vol.% in matrix) and lithic-poor (3 vol.%). The lithic fragments (c. 0.2 cm) are subangular and comprise mainly amphibolite, and lesser amounts of schist and volcanic rocks. The pumice content is moderate to high (16–34 vol.%) with two types of fiamme fragments with flame-like shape in the sense of Gifkins et al. (2005): a) white-brownish-colored, small (<1 cm, flattening ratio of 5:1) and without crystals, and b) brown-colored (4.5 cm, flattening ratio: 3:1) and rich in crystal content; both fiamme form stretched bands. The crystals within pumice and matrix are the same comprising biotite, amphibole, plagioclase, quartz (crystalline and pink), K-feldspar, sphene, zircon, opaque minerals and apatite (Fig. 4). Several absolute age determinations were performed in samples from the Rosada Ignimbrite: 6.3 ± 0.2 Ma, K/Ar in biotite (Kraemer et al., 1999); 7.13 ± 0.03 Ma, $^{40}Ar/^{39}Ar$ in biotite (Montero-López et al., 2010a); 7.3 ± 0.5 Ma and 8.1 ± 0.5 Ma, K/Ar in biotite (Kay

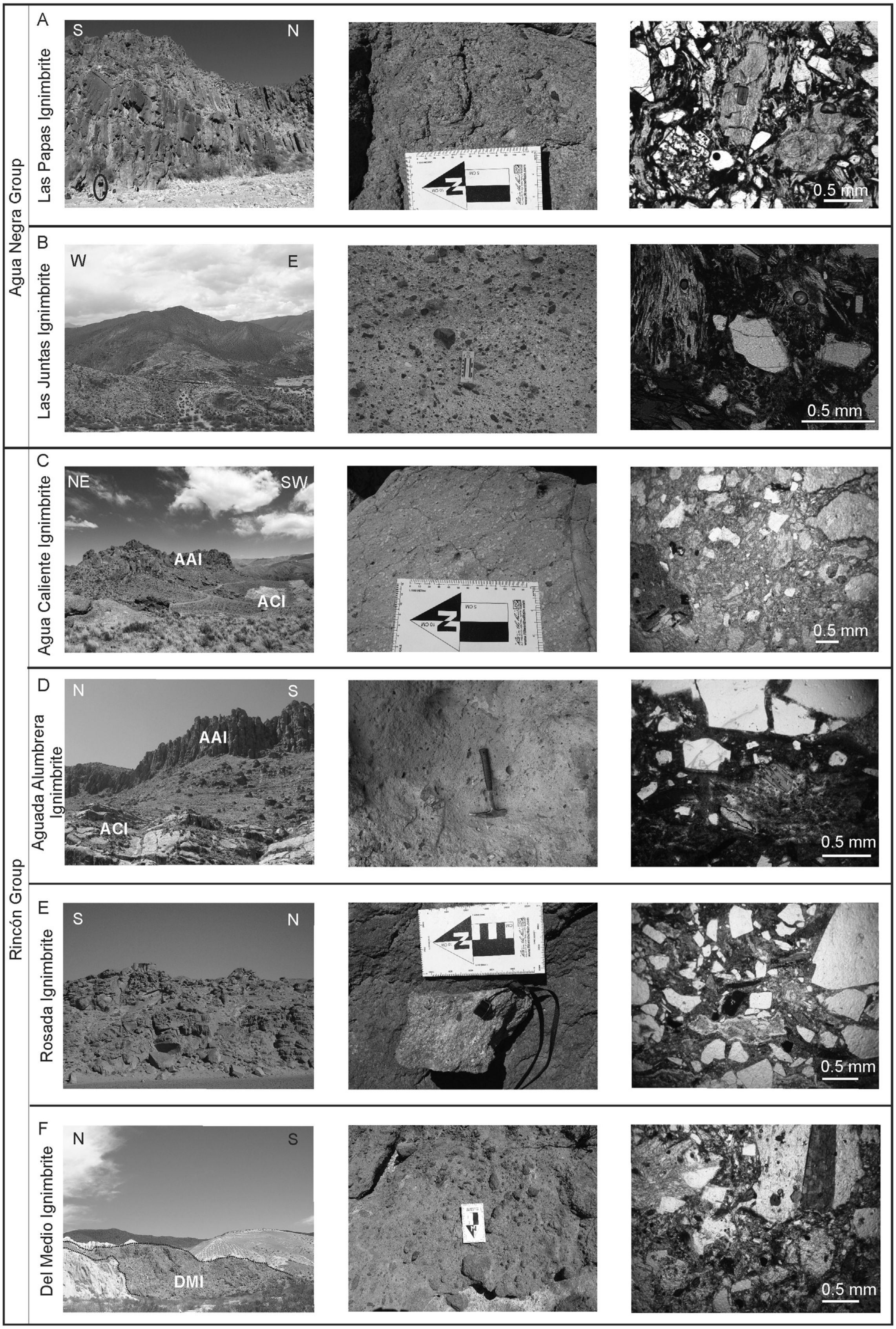

Fig. 5. Photos of the field outcrops and micro-photographies of A – Las Papas Ignimbrite, B – Las Juntas Ignimbrite, C – Agua Caliente Ignimbrite (ACI); D – Aguada Alumbrera Ignimbrite (AAI), E – Rosada Ignimbrite and Del Medio Ignimbrite (DMI). The first column to the left is a view of the field outcrop of each unit and the middle column shows a detailed view of these outcrops. The column to the right is a microscale view of thin section by microscope; white bar measures 5 mm.

et al., 2006). The significance and reliability of these age determinations were discussed in Montero-López et al. (2010a) considering an acceptable age range for this unit between 7.13 and 8.1 Ma.

3.2.5. Del Medio ignimbrite

A pyroclastic lithic breccia has been recognized in both margins of the central section of the Las Papas valley. As this unit was not previously documented and because of having particular features that make it different from other ignimbrites of the area, we define it as a new unit, the Del Medio Ignimbrite (Fig. 2). It consists of a gray, massive, lithic-rich, pumice-poor (5–10 vol.%) deposit with a pyroclastic matrix (Fig. 5f). The lithic fragments belong to lava clasts of phenoandesitic composition; whereas the composition of pumices and matrix is slightly more felsic. The deposit shows reverse coarse-tail grading with a 25–30 vol.% of lithic fragments in the lower part of the sequence which increase towards the top where they reach 70 vol.%. The lithic fragments are subangular to subrounded and are as big as 35–40 cm and as small as <1 cm, but the most frequent size is 5 cm. Pumices are white, subrounded fragments with plagioclase, K-feldspar, biotite, amphibole, apatite and opaque minerals; crystals in the matrix are the same of those in pumices. At present, there is no age reported for this unit.

4. Volume of the ignimbrites

To constrain the magnitude of the late Miocene eruptions in the border between southern Puna and northern Sierras Pampeanas, we performed volume estimations of the pyroclastic deposits. Since much of the ignimbrites are covered by Quaternary volcanic deposits, the volume estimations have to be considered minimum values.

Based on the mapping in a GIS platform we constructed a solid digital model delimited by two surfaces (upper and lower surfaces of known elevation values) obtained from a 90 m resolution SRTM digital elevation model (DEM). Limitations of this method are the uncertainties in the way elevation contours were obtained, as well as the necessary homogenization of paleo-topography in those sectors covered by volcanic facies.

Nevertheless, we were able to obtain what we consider to be adequate minimum volume estimations. The calculation shows a minimum volume of 2.79 km^3 (2.26 km^3 DRE). From this, we could discriminate between a minimum volume of 0.04 km^3 (0.03 km^3 DRE) for the ignimbrites of the Agua Negra Group and 2.75 km^3 (2.23 km^3 DRE) for those of the Rincón Group. Dense Rock Equivalent (DRE) is based on a calculated mean density of 2.04 kg/m^3 for the ignimbrites of the Agua Negra Group and 2.03 kg/m^3 for those of the Rincón Group (see Appendix A). The VEI (Volcanic Explosivity Index, Newhall and Self, 1982) of the eruptions responsible for the formation of these ignimbrites is difficult to constrain as no volume differentiation of each of the ignimbrites is possible to perform. However, given their areal coverage and medium thicknesses, it is possible that most of them had VEI around 2–3; the only one that could have reached a greater explosivity with a VEI of c. 5 may be the one of the Aguada Alumbrera Ignimbrite.

Taking into account the volume estimations and the area covered by the outcrops, it is possible to get an average thickness for the units, being of 6.5 m for the Las Papas and Las Juntas ignimbrites (Agua Negra Group) and 29 m for the other ignimbrites (Rincón Group). Here, we have not considered the outcrops of the Rosada Ignimbrite described in the literature to the west of the Peinado lineament (e.g., Seggiaro et al., 2001) since there is no detailed study of those deposits. But, if the outcrops to the west of the area considered in this work (i.e., to the west of Peinado area) belong to the Rosada Ignimbrite the resulting total volume would be increased. Moreover, it should be noted that the ignimbrites from the Agua Negra Group are the oldest of the studied units and most of them are buried by the younger volcanic deposits, and therefore, the estimated volume may be much lower than the actual erupted volume.

5. Geochemistry

We have performed new major and minor elements analysis for 8 whole rock ignimbrite samples by XRF and trace elements analysis by ICP-MS at the ACME Laboratories (Canada); analytical methodology is explained in Appendix A. The results of major, minor and rare earth elements of this contribution plus those previously obtained (Kay et al., 2006; Montero-López et al., 2010a, 2011) are given in Table 1.

The composition (on a volatile free basis) of most of the pyroclastic rocks studied in this contribution is calc-alkaline rhyolite (70–76% SiO_2), whereas some samples belonging to the Rosada Ignimbrite and to the Del Medio Ignimbrite are dacites (64–68% SiO_2) (Fig. 6). All the ignimbrites are peraluminous to metaluminous rocks with high alkalis content ($K_2O + Na_2O > 6\%$). Major elements are not quite useful for discriminating the different units studied in this contribution. However, bivariation diagrams may indicate fractionation of crystals such as biotite (Ba vs SiO_2) and apatite (P_2O_5 vs SiO_2).

The magnesium number (Mg#) is low in all the studied units (Mg# = 22–32), indicating an elevated crystal fractionation. The Las Papas Ignimbrite has lower values (then more fractionated) than the rest of the ignimbrites. From chondrite-normalized multielement (Thompson, 1982) (Fig. 7a) and rare earth elements diagrams (Sun and McDonough, 1989, Fig. 7b; Table 1), two non-cogenetic groups are clearly distinguished corresponding to the Rincón Group (Agua Caliente, Aguada Alumbrera, Rosada and Del Medio ignimbrites) and the Agua Negra Group (Las Papas and Las Juntas ignimbrites). The similarity of the trend shown by the Aguada Alumbrera and Rosada ignimbrites is clear in the multielement diagram, being very close to the behavior of the Agua Caliente and Del Medio ignimbrites. On the other hand, the Agua Negra Group internally shows variations in Ba and Rb in the multielement diagram that can be related with biotite and feldspar fractionation; this last one also is in agreement with the observed Sr anomaly. Moreover, the variation on concentration of Y, MREE, and HREE can be ascribed to the fractionation of hornblende and apatite. The Nb–Ta depletion seen in the multielement diagram is a typical feature of subduction-related rocks of continental arc signature. Although both groups, Agua Negra and Rincón, show this anomaly, it is less marked in the Agua Negra Group. Also, the concentration of P and Ti varies from one unit to another, being Agua Negra Group the one with more depleted values that could be related with variable fractionation of minerals such as apatite, Fe–Ti oxides, and sphene.

The Agua Negra Group presents a smooth rare earth elements slope (La/Yb_N: 2.5–3.7) and a marked Eu negative anomaly (Eu/Eu^*: 0.18–0.19) indicating feldspar fractionation and low fractionation of both LREE (La/Sm_N: 1.44–2.27) and HREE (Gd/Yb_N: 1.37–1.44). Although both ignimbrites of this group show approximately equivalent REE patterns (i.e., parallel patterns), the Las Juntas Ignimbrite shows a greater enrichment in all the REE that may indicate an overall greater fractionation that does not correlate with the SiO_2 composition. On the other side, the Rincón Group shows a steeper REE pattern (La/Yb_N: 17.1–21.2), with more enrichment of the LREE (La/Sm_N: 5.11–6.91) than the HREE (Gd/Yb_N: 1.61–2.20). Eu/Eu^* varies from 0.66 to 0.74 in the Rincón Group, except for the Del Medio Ignimbrite that have a slight Eu anomaly (Eu/Eu^*: 0.88). All the ignimbrites from the Rincón Group

Table 1
Major and trace element analyses from ignimbrites of Agua Negra and Rincón groups.

	Agua Negra Group						Rincón Group							
Unit	Las Papas Ignimbrite		Las Juntas Ignimbrite				Agua Caliente Ignimbrite	Aguada Alumbrera Ignimbrite		Rosada Ignimbrite				Del Medio Ignimbrite
Sample	LP-7	PA-015A	LP-10	LP-6	LP-11	PA-017	PA-006	PA-004	LH-25	Pu-14	PA-018	SAF58	SAF60	PA-011
Location	27°04′52.4″S/ 67°47′21.4″W	27°04′52.6″S/ 67°47′21.1″W	27°05′31.8″S/ 67°46′49.6″W	27°04′42.9″S/ 67°4′33.4″W	27°06′29.3″S/ 67°48′19.3″W	27°06′48.2″S/ 67°47′05.6″W	26°55′06.1″S/ 67°45′48.2″W	26°54′10.2″S/ 67°45′22.3″W	26°53′46.3″S/ 67°40′58.2″W	26°33′01.5″S/ 67°43′42.8″W	27°06′52.9″S/ 67°47′07.8″W	26°26.66′S/ 67°41.35′W	26°33.81′S/ 67°44.41′W	27°01′32.2″S/ 67°47′25.1″W
SiO_2	74.58	71.90	69.96	68.83	72.21	70.1	68.40	73.30	69.76	68.0	69.50	66.83	68.78	62.30
Al_2O_3	12.79	13.23	14.62	14.23	14.31	14.28	13.39	11.44	14.16	14.79	14.23	3.09	3.49	15.59
Fe_2O_3	0.91	2.09	1.96	1.76	0.58	2.79	1.76	2.63	2.72	3.41	3.48	14.91	15.1	4.97
MnO	0.04	0.10	0.16	0.06	0.15	0.17	0.02	0.06	0.03	0.06	0.05	0.04	0.05	0.08
MgO	0.43	0.59	0.94	1.90	0.88	0.96	0.69	0.93	1.00	1.45	1.07	1.3	1.57	2.11
CaO	0.76	0.73	1.59	2.39	0.88	1.53	1.79	2.06	2.32	2.95	2.52	3.21	3.22	4.22
Na_2O	3.52	3.77	3.58	3.38	4.01	3.80	1.90	1.94	3.24	3.89	3.80	5.61	3.82	3.82
K_2O	4.45	4.22	4.45	3.43	4.37	3.68	4.49	3.91	4.17	3.87	3.82	3.51	2.9	2.95
P_2O_5	0.04	0.06	0.09	0.08	0.05	0.08	0.06	0.10	0.11	0.17	0.15	0.14	0.16	0.23
TiO_2	0.10	0.12	0.22	0.33	0.15	0.27	0.25	0.34	0.40	0.49	0.44	0.55	0.58	0.69
LOI	2.40	2.61	3.00	4.49	3.33	2.86	6.38	2.70	2.00	0.80	2.60	0.2	0.1	2.38
Ba	185.10	73.00	71.40	327.00	142.00	109.00	753.00	524.00	585.30	675.00	627.00	678.00	627.00	591.00
Rb	142.00	199.90	349.80	148.00	341.00	319.00	345.80	124.90	132.20	139.70	132.60	111.00	124.00	124.70
Sr	52.00	25.60	57.30	470.00	27.00	80.00	752.30	396.50	388.30	461.90	378.70	421.00	374.00	494.10
Y	13.00	19.50	32.10	19.00	38.00	27.80	14.20	12.30	12.60	18.30	12.50	12.00	16.00	12.90
Zr	61.00	45.80	47.90	129.00	50.00	64.10	118.30	122.00	133.20	155.30	129.70	179.00	139.00	143.40
Nb	13.70	26.10	48.30	15.00	50.00	41.70	13.10	13.70	16.80	18.70	15.30	18.00	17.00	14.20
Th	13.90	15.80	17.50	23.00	17.00	16.70	16.40	17.30	19.60	19.30	18.80	16	15.4	15.30
Pb	1.90	3.70	1.00	–	–	2.80	6.20	11.90	1.20	1.20	4.20	13.00	14.00	1.40
Ga	14.60	17.80	24.70	–	–	23.60	15.60	14.00	16.50	19.70	17.00			19.20
Zn	9.00	11.00	14.00	–	–	63.00	21.00	25.00	21.00	11.00	26.00	48.00	50.00	33.00
Cu	1.80	6.00	8.90	–	–	11.00	7.80	11.70	10.80	11.40	18.30	18.00	16.00	12.20
Ni	–	5.00	15.00	13.00	17.00	6.50	4.00	7.80	13.00	7.10	10.20	12.00	11.00	10.20
V	–	12.00	37.00	52.00	23.00	40.00	25.00	42.00	46.00	63.00	55.00	34.00	66.00	94.00
Cr	–	–	–	4.00	5.00	–	–	–	–	–	–	19.00	20.00	–
Hf	2.20	1.80	2.40	–	–	2.30	3.20	4.00	3.70	4.40	3.50	3.8	4	3.90
Cs	18.50	19.50	17.40	–	–	18.20	739.30	8.10	7.10	4.70	8.10	1.3	4.2	45.80
Sc	3.00	–	9.00	–	–	–	–		6.00	7.00	–	6.8	7.4	–
Ta	1.10	2.30	4.00	–	–	4.00	1.00	1.30	1.40	1.50	1.50	1.5	1.5	1.10
Co	74.70	2.20	74.90	43.00	55.00	5.70	2.60	5.60	44.10	44.50	6.50			12.70
Be	–	4.00	–	–	–	5.00	4.00	3.00	2.00	2.00	3.00			<1
U	4.20	6.80	13.30	3.00	10.00	11.90	4.40	3.00	4.30	5.00	4.60	4.3	4.5	3.80
W	–	1.10	–	–	–	3.20	0.70	<0.5	266.30	289.30	0.70			0.90
Sn	1.00	1.00	4.00	–	–	4.00	<1	<1	1.00	1.00	<1			<1
Mo	0.10	0.60	0.10	–	–	0.30	0.20	0.30	0.10	0.10	0.60			0.10
Au	–	<0.5	–	–	–	0.70	3.10	2.80	2.40	2.60	0.90			1.20
La	14.40	7.90	8.10	–	–	10.30	37.30	33.30	33.70	41.00	39.70	36.7	36.3	33.30
Ce	30.20	19.90	23.10	–	–	26.20	71.60	61.70	68.00	82.40	73.80	70.6	71.4	64.30
Pr	3.10	1.92	2.90	–	–	3.12	6.85	5.84	7.01	8.46	7.00			6.46
Nd	9.70	7.00	10.60	–	–	9.40	24.90	18.10	23.40	29.00	23.90	25.8	24.7	23.10
Sm	2.00	2.25	3.60	–	–	3.81	3.82	3.11	3.72	4.71	3.77	4.58	4.69	4.21
Eu	0.25	0.14	0.22	–	–	0.25	0.72	0.65	0.68	0.90	0.80	0.92	0.91	1.08
Gd	1.90	2.57	4.00	–	–	4.28	2.92	2.56	2.38	3.37	2.90			3.37
Tb	0.40	0.55	0.90	–	–	0.89	0.49	0.39	0.39	0.55	0.43	0.43	0.479	0.49
Dy	2.00	3.06	5.00	–	–	5.26	2.57	2.04	1.76	2.60	2.52			2.73
Ho	0.30	0.67	0.90	–	–	0.98	0.51	0.41	0.36	0.49	0.49			0.49
Er	1.10	1.86	2.50	–	–	2.60	1.46	1.21	1.13	1.48	1.32			1.35

(*continued on next page*)

Table 1 (*continued*)

Unit	Agua Negra Group						Rincón Group							
	Las Papas Ignimbrite		Las Juntas Ignimbrite				Agua Caliente Ignimbrite	Aguada Alumbrera Ignimbrite		Rosada Ignimbrite				Del Medio Ignimbrite
Tm	0.20	0.25	0.40	–	–	0.38	0.21	0.20	0.17	0.22	0.21			0.19
Yb	1.10	1.55	2.30	–	–	2.46	1.26	1.26	1.22	1.62	1.38	1.41	1.52	1.27
Lu	0.20	0.24	0.30	–	–	0.39	0.21	0.20	0.16	0.24	0.23	0.161	0.177	0.19
Ba/La	12.85	9.24	8.81	–	–	10.58	20.19	15.74	17.37	16.46	15.79	18.5	17.3	17.75
La/Ta	13.09	3.43	2.03	–	–	2.58	37.30	25.62	24.07	27.33	26.47	24	25	30.27
$(La/Yb)_N$	9.40	3.66	2.50	–	–	3.00	21.23	18.96	19.81	18.15	20.64			18.81
$(La/Sm)_N$	4.58	2.27	1.44	–	–	1.75	6.30	6.91	5.85	5.62	6.80			5.11
$(Gd/Yb)_N$	1.46	1.37	1.44	–	–	1.44	1.92	1.68	1.61	1.72	1.74			2.20
Eu^*	11.14	13.61	21.67	–	–	22.86	19.59	16.39	17.95	23.59	19.38			21.96
Eu/Eu^*	0.39	0.18	0.18	–	–	0.19	0.66	0.70	0.70	0.69	0.74	0.75	0.7	0.88
Reference	Montero-López et al. (2011)	This work	Montero-López et al. (2011)	This work	Montero-López et al. (2011)	This work	This work	This work	Montero-López et al. (2010a)	Montero-López et al. (2010a)	This work	Kay et al. (2006)	Kay et al. (2006)	This work

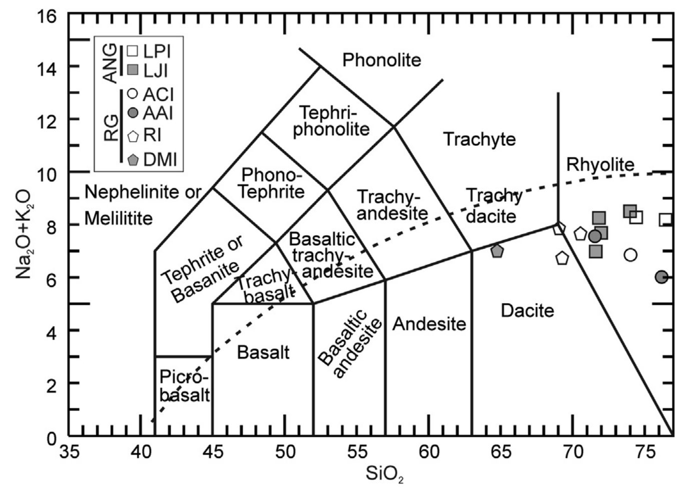

Fig. 6. Total Alkali Silica diagram TAS (Le Maitre et al., 1989) showing the classification of rocks of the Agua Negra and Rincón groups. Irvine and Baragar (1971) curve, in dots, indicates the alkaline and sub-alkaline fields. AGN: Agua Negra Group: LPI: Las Papas Ignimbrite; LJI: Las Juntas Ignimbrite; RN: Rincón Group: ACI: Agua Caliente Ignimbrite; AAI: Aguada Alumbrera Ignimbrite; DMI: Del Medio Ignimbrite; RI: Rosada Ignimbrite.

show approximately similar REE patterns, and the differences between them can be related with variable percentages of fractional crystallization, but also in some cases, with variable mineral phases involved in the crystallization processes. In this regard, the Aguada Alumbrera Ignimbrite shows a spoon-shaped pattern in the MREE and HREE that may be related with the presence of amphibole during crystallization. Furthermore, the small Eu anomaly in the Del Medio Ignimbrite indicates a much lesser feldspar fractionation in comparison with the other ignimbrites of the Rincón Group.

6. Physical parameters: amphibole thermobarometer

The mineral chemistry data published by Montero-López et al. (2010a, 2011) are taken here in order to perform temperature calculations. For this, we have used the methodology described by Ridolfi et al. (2010) for subduction-related calc-alkaline compositions in amphibole phenocrysts; we take into account only the data from crystal cores. The Agua Negra Group (Las Papas and Las Juntas ignimbrites) classify as Mg-hornblende and hornblende-tschermakite (Table 2), where the Al# (>0.21) indicates that these amphiboles are xenocrysts, i.e., inferred to represent in the sense of Ridolfi et al. (2010) mantle or crustal material, which is in total synergy with the fact that amphiboles of these samples are present only in the matrix. Therefore, the temperatures estimated for these amphiboles (see Table 2) do not represent pre-eruptive temperatures of these rocks. The results range between 857 and 877 °C for the Las Papas Ignimbrite and 896–912 °C for the Las Juntas Ignimbrite.

Amphiboles from the Rincón Group (samples from Aguada Alumbrera and Rosada ignimbrites) are much more useful for interpreting pre-eruptive temperatures as they are present in pumices and as they are not included in the xenocryst group in the sense of Ridolfi et al. (2010). They classify as Mg-hornblende and, less frequently, as Mg-hastingsite. The calculations performed in phenocrystal cores indicate temperatures between 809 °C and 889 °C, at a pressure of 1–2 kbar that correspond to a depth of 3.9–7.5 km for the Aguada Alumbrera Ignimbrite and temperatures between 873 and 942 °C and a pressure of 1.7–3.4 kbar compatible with a depth of 8.0–12.1 km for the Rosada Ignimbrite. However,

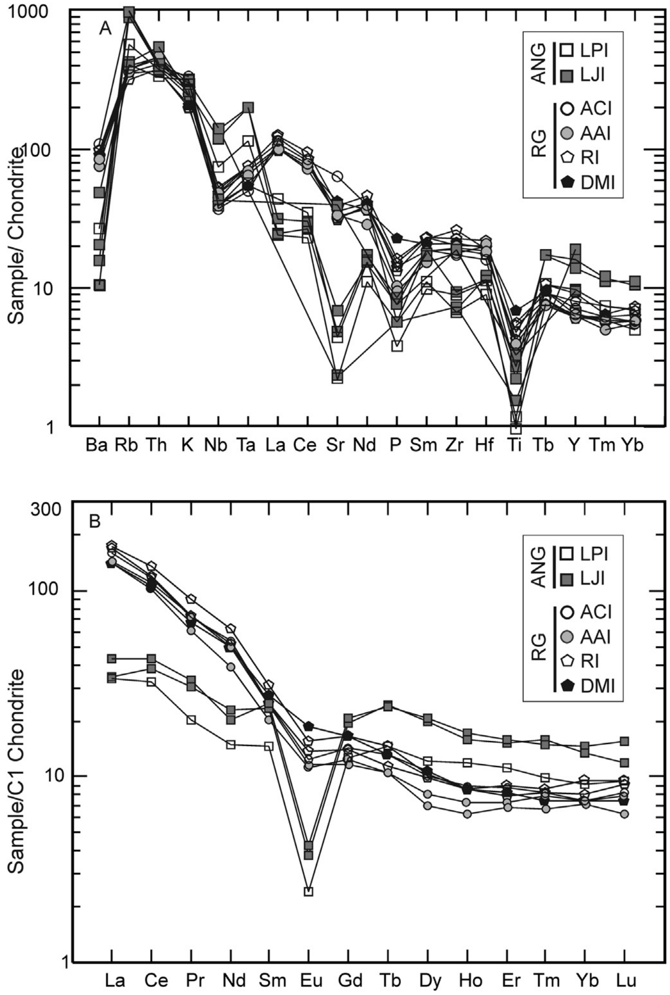

Fig. 7. A – Multielement diagram normalized to chondrite (Thompson, 1982); B – Rare earth elements diagram normalized to chondrite C1 (Sun and McDonough, 1989). AGN: Agua Negra Group: LPI: Las Papas Ignimbrite; LJI: Las Juntas Ignimbrite; RN: Rincón Group: ACI: Agua Caliente Ignimbrite; AAI: Aguada Alumbrera Ignimbrite; DMI: Del Medio Ignimbrite; RI: Rosada Ignimbrite.

even though temperature estimates have good precision, estimates of pressure do not, given that the studied rocks are crystal-rich, meaning that the error involved in these calculations may reach up to 24%. Although, the apparent differences between the Aguada Alumbrera and Rosada ignimbrites may be not so great, in any case they imply the presence of shallow to intermediate magma chamber/s in the crust, being the magmas of the Rosada Ignimbrite hotter than those of the Aguada Alumbrera Ignimbrite.

Ridolfi et al. (2010) also allow estimating water concentrations on the melts before eruptions, on the basis of amphiboles mineral analysis. These calculations were only possible to be performed in rocks from the Rincón Group (Aguada Alumbrera and Rosada ignimbrites) ranging mostly between 4.2 and 4.8 (wt.%); they should be quite accurate, with uncertainties around 0.4 wt.% (Ridolfi et al., 2010) as almost all of them are Mg-hornblendes.

7. Discussion

All of the pyroclastic units studied in this work are calc-alkaline rhyolites to rhyodacite–dacites. Together, the field characteristics, petrography and geochemical composition lead to discriminate six stratigraphic units. Geochemical features show two clearly different patterns (evident mostly by trace elements) that may indicate two distinct magma evolution histories and thus we propose that the whole set of units studied in the present contribution were erupted from at least two different sources. However, no evidence of vents was found in the surroundings of the main ignimbrite outcrops owing probably to the widespread Quaternary volcanic deposits (mainly related to the explosive activity of Cerro Blanco calderas), that cover an area of about 314 km^2 in this region (Guzmán et al., 2014). We hence interpret that the vents of the late Miocene ignimbrites were buried by this recent volcanism.

As noted previously, trace elements are very different in the Rincón and Agua Negra groups. In particular, the profile developed in the multielement and rare earth elements diagrams of the Agua Negra Group (see Fig. 7) are not so frequently seen in the southern Puna, we can cite few examples: a) 2nd volcanic cycle of the Cerro Blanco Volcanic Complex (Montero-López et al., 2010a) but much more enriched in REE; b) some ignimbrites further west in the Salar de la Isla area (e.g., San Andrés and Juncalito ignimbrites, Siebel et al., 2001; Schnurr et al., 2007). As the Agua Negra Group has this particular or at least not so frequent pattern, we tried to model their evolution from different sources, searching in a first attempt the basement rocks of the region. The rocks that may best fit a simple fractional crystallization process (expectable as no particular petrographic evidence indicates other evolution processes) are gabbroic ones. Complete geochemical data is available only for gabbroic rocks further southeast of the study area which seems to be compositionally different to the ones located in the area of study

Table 2
Results of the amphibole thermobarometer calculation.

	Unit	Sample	Label	Amphibole	Specie	T (°C) ± σ_{estim}	P (MPa) ± σ_{estim}	Depth (km)	ΔNNO	$logfO_2$ ± σ_{est}	H_2O_{melt} (wt.%)
Agua Negra Group	Las Papas Ignimbrite	LP-7	LP7-164	a-core	Xenocryst	873 ± 56	–	–	–	–	–
	Las Papas Ignimbrite	LP-7	LP7-184	b-core	Xenocryst	857 ± 56	–	–	–	–	–
	Las Juntas Ignimbrite	LP-10	LP10-129	a-middle	Xenocryst	912 ± 56	–	–	–	–	–
	Las Juntas Ignimbrite	LP-10	LP10-130	a-core	Xenocryst	896 ± 56	–	–	–	–	–
	Las Juntas Ignimbrite	LP-10	LP10-131	a-middle	Xenocryst	906 ± 56	–	–	–	–	–
Rincón Group	Aguada Alumbrera Ignimbrite	C5-7	C5-7-219	a-core	Mg-Hbl	885 ± 22	195 ± 22	7.38	0.28	−11.9 ± 0.4	4.2 ± 0.4
	Aguada Alumbrera Ignimbrite	C5-7	C5-7-250	c-core	Mg-Hbl	809 ± 22	104 ± 11	3.93	1.12	−12.6 ± 0.4	4.3 ± 0.4
	Aguada Alumbrera Ignimbrite	C5-7	C5-7-263	d-middle	Mg-Hbl	846 ± 22	141 ± 16	5.34	0.87	−12.0 ± 0.4	4.2 ± 0.4
	Aguada Alumbrera Ignimbrite	C5-7	C5-7-272	e-core	Mg-Hbl	889 ± 22	198 ± 22	7.47	0.52	−11.6 ± 0.4	4.8 ± 0.4
	Rosada Ignimbrite	Pu-14	Pu14-754	a-core	Mg-Hst	942 ± 22	338 ± 37	12.77	−0.31	−11.4 ± 0.4	5.9 ± 0.9
	Rosada Ignimbrite	Pu-14	Pu14-760	b-core	Mg-Hbl	873 ± 22	173 ± 19	6.54	0.53	−11.8 ± 0.4	4.3 ± 0.4

(e.g., Complejo básico-ultrabásico Tramontana, Seggiaro et al., 2001). Nevertheless, a first attempt using a gabbronorite (sample S.104) from DeBari (1994) in the Fiambalá gabbroic intrusion as the parental magma, leads to approximately similar compositions to the ones of Agua Negra Group by about 90% of fractional crystallization. No exact numerical modeling can be provided due to the lack of data of partition coefficients of mineral phases such as sphene, apatite or zircon. Even a very low percentage of these minerals in the parental magma can highly influence the resulting trace element concentrations of the evolved rock.

On the other hand, the Rincón Group shows REE patterns that are very frequent in volcanic rocks of the southern Puna. Without the knowledge of isotopic data, and given that the REE and multi-element patterns developed by these rocks are very common, the potential source for these rocks is very difficult to estimate. Trace elements for this group indicate some fractionation of feldspars, and an apparent absence of garnet in the source given the positive correlation between Ce vs Yb, so that the depletion in MREE and HREE may be related with the presence of amphibole (among other possibilities). The relatively high fractionation of LREE instead may be related either with crustal assimilation or with low percentages of partial fusion.

For the above-mentioned, we infer the presence of at least two generating magma chambers of the silicic melts. One magma chamber could have erupted the ignimbrites from the Agua Negra Group (Las Papas and Las Juntas ignimbrites), and the other, the ignimbrites from the Rincón Group (Agua Caliente, Aguada Alumbrera, Rosada and Del Medio ignimbrites). The minimum volume erupted during these volcanic events is estimated in 0.03 km^3 DRE for the Agua Negra Group and 2.23 km^3 DRE for the Rincón Group. Since most of the ignimbrites from both groups have poor crystal content in the pumices, but are moderate to crystal-rich in the matrix, we assume that much of the fines were elutriated during their transport. Despite the volume calculated for the ignimbrites of the Agua Negra Group is low, the units represent a strong evidence of the existence of a km-paleorelief between the southern Puna–northern Sierras Pampeanas border as early as 9 Ma (Montero-López et al., 2014). Therefore, the data set presented here provides a proxy of the geochemical signature of explosive magmatism during the construction of the southern edge of the Andean plateau.

To the present state of knowledge, the Las Papas Ignimbrite is the oldest of the pyroclastic deposits cropping out in this area (Montero-López et al., 2014). We thereafter interpret that the pyroclastic deposits of the Agua Negra Group have been erupted in an initial magmatic cycle with the more acid composition. The geochemistry shows high silica content, LILE (Cs, Rb) and Th that could be a proxy of more evolved composition of the original liquid. Whether both ignimbrites, Las Juntas and Las Papas, were erupted from the same magma chamber is difficult to assess, but their overall geochemical signature is quite similar. The main differences between these ignimbrites are their small variation in REE concentrations and SiO_2 (wt.%); but the intriguing fact is that on one hand the degree of enrichment in REE indicates more evolved melts for the Las Juntas Ignimbrite but on the other hand the SiO_2 (wt.%) is lower in comparison with the Las Papas Ignimbrite. This apparent incompatibility may be linked also with analytical problems, e.g., the impossibility of separation of all lithic fragments, or different alteration in these rocks that may affect mostly the major elements (note that samples from the Las Juntas Ignimbrite have generally high LOI values), that may lead to these slight differences, however further studies that are out of the scope of this contribution, need to be carried out to solve this problem.

Two ignimbrites from the Rincón Group (Rosada and Aguada Alumbrera ignimbrites) have absolute ages ranging from 8.1 to 7.13 Ma (Kay et al., 2006; Montero-López et al., 2010a). All the rocks belonging to this group show similar REE patterns, and differences in their mineralogical composition, texture, color and induration degree. Nevertheless, there are variations in the absolute REE concentrations and in the silica content that leads to a compositional variation from dacites (Rosada and Del Medio ignimbrites) to rhyolites (Agua Caliente and Aguada Alumbrera ignimbrites). Therefore, linking all these ignimbrites to the same magmatic chamber is possible, but the differences between them may involve a series of processes, such as differences in fractional crystallization. The differences between these two ignimbrites are similar to those found between the Las Papas and Las Juntas ignimbrites, and thus may be related to the same causes.

8. Conclusion

The acid ignimbrite units studied in this work constitute the southernmost expressions of the late Miocene volcanism of the Puna plateau reported until present, emplaced on the transition zone between steep-slab (southern Puna) and flat-slab (northern Sierras Pampeanas) segments of the Central Andes. The differences observed among each ignimbritic unit as induration degree, texture, lithic content, crystal content, size and type of pumices, as well as the variations evidenced by the REE geochemistry allowed to distinguish six different pyroclastic units. All the studied ignimbrites are peraluminous to metaluminous calc-alkaline rocks, mainly of rhyolitic and subordinately dacitic composition. They consist principally of massive deposits with variable induration degree, crystal-rich and variable pumice content (mostly between 16 and 40 vol.%, but only 5 vol.% in the lower cooling unit of Aguada Alumbrera Ignimbrite), with poor to moderate crystal content in the pumice fragments. The geochemical signature enables to separate the ignimbrites in two groups, the Agua Negra and the Rincón groups, indicating that at least two magma chambers were responsible for the eruption of this set of ignimbrites. The volcanic centers that erupted these ignimbrites were not recognized as they are probably covered by extended younger volcanic deposits. Pre-eruption temperature estimates for the Aguada Alumbrera and Rosada ignimbrites of the Rincón Group give a range between 809 °C and 942 °C and their pressure estimates are 1.0–3.4 kbar indicating their eruption from a shallow to intermediate magma chamber in the crust.

The volume estimates indicate that the erupted material was relatively low, with a minimum value of 0.04 km^3 (0.03 km^3 DRE) for the Agua Negra Group and 2.75 km^3 (2.23 km^3 DRE) for the Rincón Group. These low volumes are in accordance to the general behavior of other small explosive eruptions in the southern Puna for this period (e.g., Guzmán et al., 2014). These ignimbrites represent an insignificant volume in the CVZ magmatism, however, they have an important geodynamic meaning because the oldest ignimbrites of Agua Negra Group (i.e., Las Papas and Las Juntas ignimbrites) are filling a paleotopography along the Las Papas valley.

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Appendix A. Analytical techniques

We estimated the density of the Agua Negra and Rincón groups using a hydrostatic weighing technique. Unaltered bulk matrix samples were selected for the procedure. The method consisted of recording the displaced volume when a sample portion of known weight had been introduced in a volumetric flask. This flask is connected to a pipette through a rubber tube. The procedure consisted of adding a known volume of distilled water to the flask, and then introducing a cube of rock sample (previously weighted and covered with paraffin in order to seal it) then observing the displaced volume of water.

Results indicate densities of 2.04 kg/m^3 for the Agua Negra Group and 2.03 kg/m^3 for the Rincón Group. The density increase is clearly proportional to the increment in the degree of welding in each pyroclastic unit.

Considering that the average density of rhyolites is around 2.51 kg/m^3 with these results we obtained conversion factors of 0.81 for both groups for calculating DRE volumes.

Rocks samples were processed and analyzed at the ACME laboratory (Canada). They were crushed, milled (1 kg to 80% passing 10 mesh, split 250 g and pulverized to 85% passing 200 mesh) and fused with $LIBO_2$. Major elements were determined by X-ray fluorescence, having a detection limit of 0.01%. Loss on ignition (LOI) is by weigh difference after ignition at 1000 °C. Rare earth elements (REE) and other trace elements (ppm) were quantitatively and qualitatively determined by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer). Rare Earth and refractory elements were determined by ICP mass spectrometry following a Lithium metaborate/tetraborate fusion and nitric acid digestion of a 0.2 g sample. In addition a separate 0.5 g split is digested in Aqua Regia and analyzed by ICP Mass Spectrometry to report the precious and base metals. Detection limits are 0.1–0.01 ppm for REE and of 0.1–1 ppm for other trace elements.

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