

# Hybridization between I-type and S-type granites in the Ordovician Famatinian magmatic arc, Tafí del Valle, Tucumán, NW Argentina

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## ABSTRACT

In the Tafí del Valle region, in northwestern Argentina, several intrusive bodies of lower Paleozoic age were emplaced in the metasedimentary Puncoviscana Formation, belonging to the Sierras Pampeanas. Four intrusive bodies outcrop in the study area: La Ovejería, El Infiernillo, Loma Pelada and Los Cuartos. La Ovejería and El Infiernillo intrusive bodies represent the I-type magmatism according to their major element contents and show cotectic evolutions similar to those described by Famatinian I-type batholiths. These moderately peraluminous adakitic trondhjemites have characteristic high Sr/Y ratios and low Fe<sub>2</sub>O<sub>3</sub>+MgO+MnO+TiO<sub>2</sub> contents. They are related to high-pressure conditions at the source, where dehydration melting of basaltic rocks may be involved and garnet is retained in the residue leading to generation of HREE depleted melts. The Loma Pelada granites show characteristics of S-type magmatism (low CaO and MgO, and high SiO<sub>2</sub> and K<sub>2</sub>O contents) typical of granites segregated in the last stages of magmatic differentiation, or anatetic granites. They show an increasing peraluminosity due to garnet entrainment and they are related to the anatetic melts generated in the Puncoviscana Formation. Both the Loma Pelada and Los Cuartos granitoids include samples with intermediate geochemical characteristics that range between those of the El Infiernillo and La Ovejería and the regional metasedimentary rocks. These characteristics could be explained by assimilation processes involving the I-type intrusive magmas and the metasedimentary host rocks or by hybridization processes between trondhjemitic I-type magmas as La Ovejería and El Infiernillo and anatetic S-type melts.

KEYWORDS

Hybridization. Lower Paleozoic. Sierras Pampeanas. Tafí del Valle. La Ovejería pluton.

## INTRODUCTION

I-type and S-type granitic classification (Chappell and White, 1974) constitutes a general primary framework to distinguish worldwide magmatism based on geochemical characteristics with significant implications in the source nature and tectonic setting. Straightforward petrologic and geochemical evidences as Aluminium Saturation Index (ASI), CaO and alkalis content, diagnostic mineral phases or enclaves are used to distinguish granitic typologies (Chappell and White, 2001). More controversial evidences are obtained from trace elements and isotopic data, which compositional ranges are overlapped between S- and I-type granitoids (*e.g.* Hyndman, 1984). From its origin, the I-type and S-type classification involves an important petrogenetic significance that includes the nature of source rocks, P-T conditions during the melting process and tectonic setting (Chappell and White, 1974, 1992; Chappell *et al.*, 2000; King *et al.*, 2001). However, the results of a simple interpretation of this classification are called into question (*e.g.* Frost *et al.*, 2001), and hybrid terms are usually invoked when a mixed source or assimilation and hybridization processes are involved. Precisely, orogenic belts are paradigmatic examples of the coexistence of S- and I-type end members and transitional or hybrid granitoids (Miller and Bradfish, 1980; Chappell, 1996; Gonçalves *et al.*, 2016; Tung *et al.*, 2016).

The Famatinian arc in northern Argentina represents the best preserved paleo-magmatic arc system formed at the Gondwana active margin during Ordovician times. Several Mountain alignments in the Pampean region of northern Argentina are characterized by large exposures of granite batholiths that were mostly formed during the Paleozoic (Rapela *et al.*, 1992; Pankhurst and Rapela 1998; Pankhurst *et al.*, 2000; Rossi *et al.*, 2002). From West to East: Sierra de Valle fértil (Otamendi *et al.*, 2009b; Castro *et al.*, 2014), Sierra de Famatina (*e.g.* Alasino *et al.*, 2014), Sierra de Fiambalá (De Bari, 1994; Pankhurst *et al.*, 2000), Sierra de Velasco (Grosse *et al.*, 2011) and Sierra de Ancasti (Dahlquist *et al.*, 2012). These batholiths, among others, comprise lower to middle crustal fragments conformed by a voluminous arc-related magmatism and its metasedimentary host-rocks. Western I-type calc-alkaline and eastern S-type crustal-derived Ordovician batholiths are spatially and chronologically related with transitional hybrid granitoids in the Famatinian Belt (*e.g.* Grosse *et al.*, 2011). The transition from I-type to S-type implies a compositional continuum related with an increasing participation of crustal metasediments towards the continental interior, as it has been proposed in other arcs (*e.g.* De Paolo, 1981; Brown *et al.*, 1984; Gray, 1984; Liew and Hofmann, 1988; Collins, 1996).

This study concerns the magmatism emplaced in a retro-arc context in the active margin of Gondwana, as proposed by Buttner (2009). In the Tafí del Valle region, located to the northeast of the Famatinian Belt, Ordovician I-type and S-type granitoids are emplaced in the thick low- to medium-grade metasediments of the Puncoviscana Formation (Fm.). The study of in-situ processes occurred in deep-generated calc-alkaline magmas and emplaced in an anatetic crustal domain are crucial to understand the role of assimilation and hybridization from the petrological and geochemical variability in the granitoids.

## GEOLOGICAL SETTING

The Famatinian magmatic arc extends over 1500km along a NNW-SSE trending belt, from ~22°S to ~33°S. It is characterized by a widespread Ordovician magmatism forming an outer I-type dominated belt to the West, and an inner S-type dominated belt to the East (Toselli *et al.*, 1996; Pankhurst *et al.*, 2000) (Fig. 1).

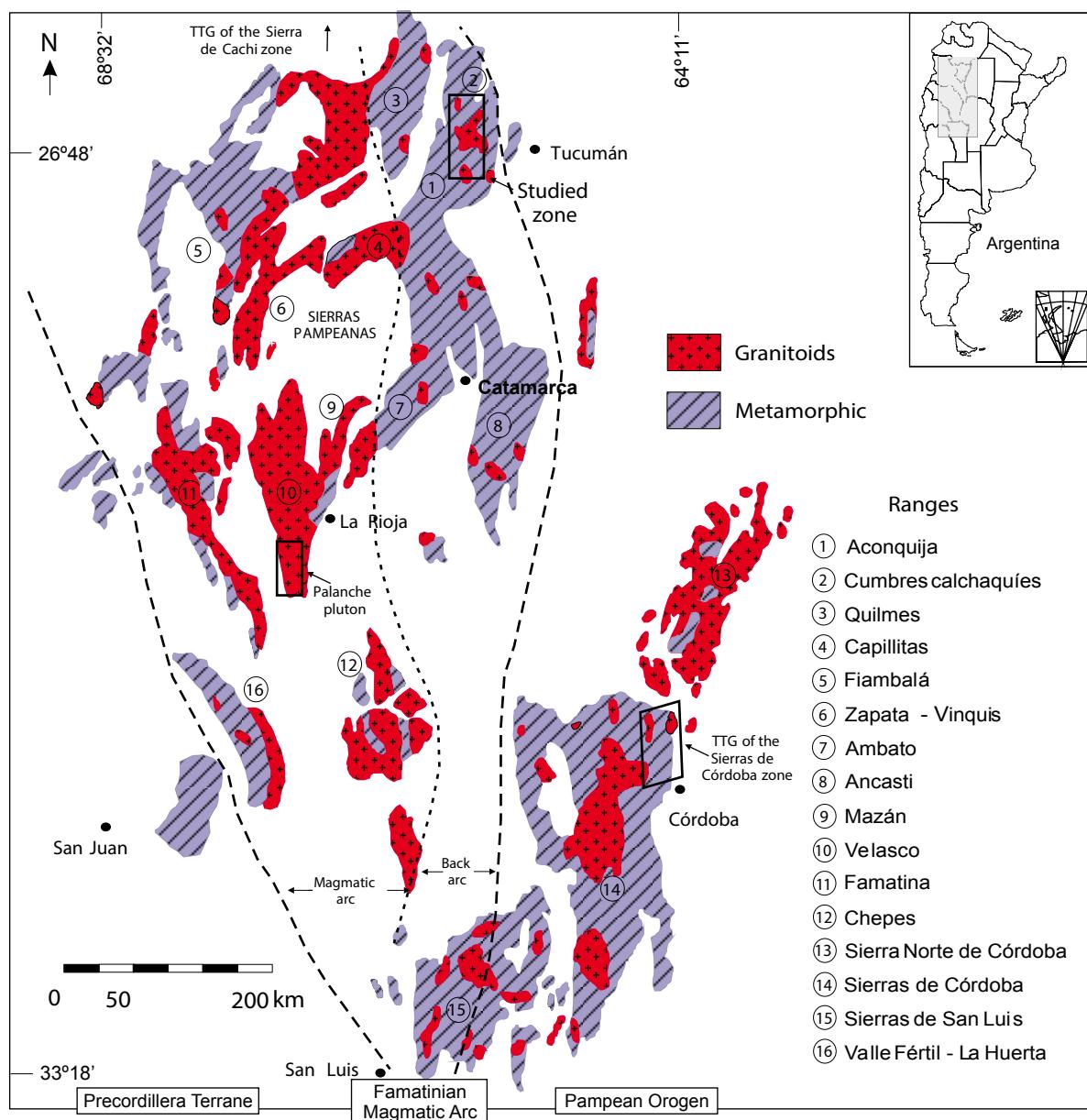
To the East, basement units were mainly affected by the Pampean orogeny, which was characterized by late Neoproterozoic sedimentation and Ediacaran to Cambrian deformation, magmatism and metamorphism (Rapela *et al.*, 2007). The Sierras Pampeanas consist of several blocks exhumed during the Neogene by high angle reverse faults with N-S azimuth (González Bonorino, 1950a; Jordan and Allmendinger, 1986; Isacks, 1988). In the Sierras Pampeanas, the I-type belt is mainly represented by the ranges of Famatina (*e.g.* Aceñolaza *et al.*, 1996; Saavedra *et al.*, 1998), southern La Rioja (Chepes, Los Llanos and Ulapes) (*e.g.* Pankhurst *et al.*, 2000), southern of Velasco (Bellos *et al.*, 2015) and Valle Fértil (*e.g.* Otamendi *et al.*, 2009b; Castro *et al.*, 2014). The S-type belt includes the Mountain ranges of Fiambalá (*e.g.* Grissom *et al.*, 1998), Capillitas (*e.g.* Rossi *et al.*, 2002), Mazán (*e.g.* Schalamuk *et al.*, 1989; Toselli *et al.*, 1991) and central and northern Velasco (Rossi *et al.*, 2005; Grosse *et al.*, 2011).

Three orogenic events were involved in the origin and evolution of the Sierras Pampeanas (Sims *et al.*, 1998; Aceñolaza *et al.*, 2000; Rapela *et al.*, 2001; Höckenreiner *et al.*, 2003; Buttner *et al.*, 2005; Steenken *et al.*, 2008): the Pampean event (Late Neoproterozoic-Lower Cambrian), the Famatinian event (Upper Cambrian-Lower Devonian) and the Achalian event (Middle Devonian-Lower Carboniferous); this latter one is not represented in the study area. The Pampean and Famatinian orogens are interpreted to be the result of the subduction, continental collision and accretion of several terranes along the Gondwana margin (Ramos *et al.*, 1986; Ramos, 1988, 1995, 2008; Willner, 1990; Dalla Salda *et al.*, 1992; Kraemer *et al.*, 1995; Rapela et

*al.*, 1998, 2001, 2007; Omarini *et al.*, 1999). Especially for NW Argentina, these orogens could have resulted from the continuous evolution of an intracratonic mobile belt along the continental margin of Gondwana with the subsequent crustal thickening and magmatic activity (Lucassen *et al.*, 2000), followed by an extensional high thermal period in the Early Ordovician (Büttner *et al.*, 2005).

The Cumbres Calchaquíes and the Sierra de Aconquija belong to the northwestern Pampean Ranges (Caminos, 1979) (Fig. 1). These Mountain ranges show vast exposures

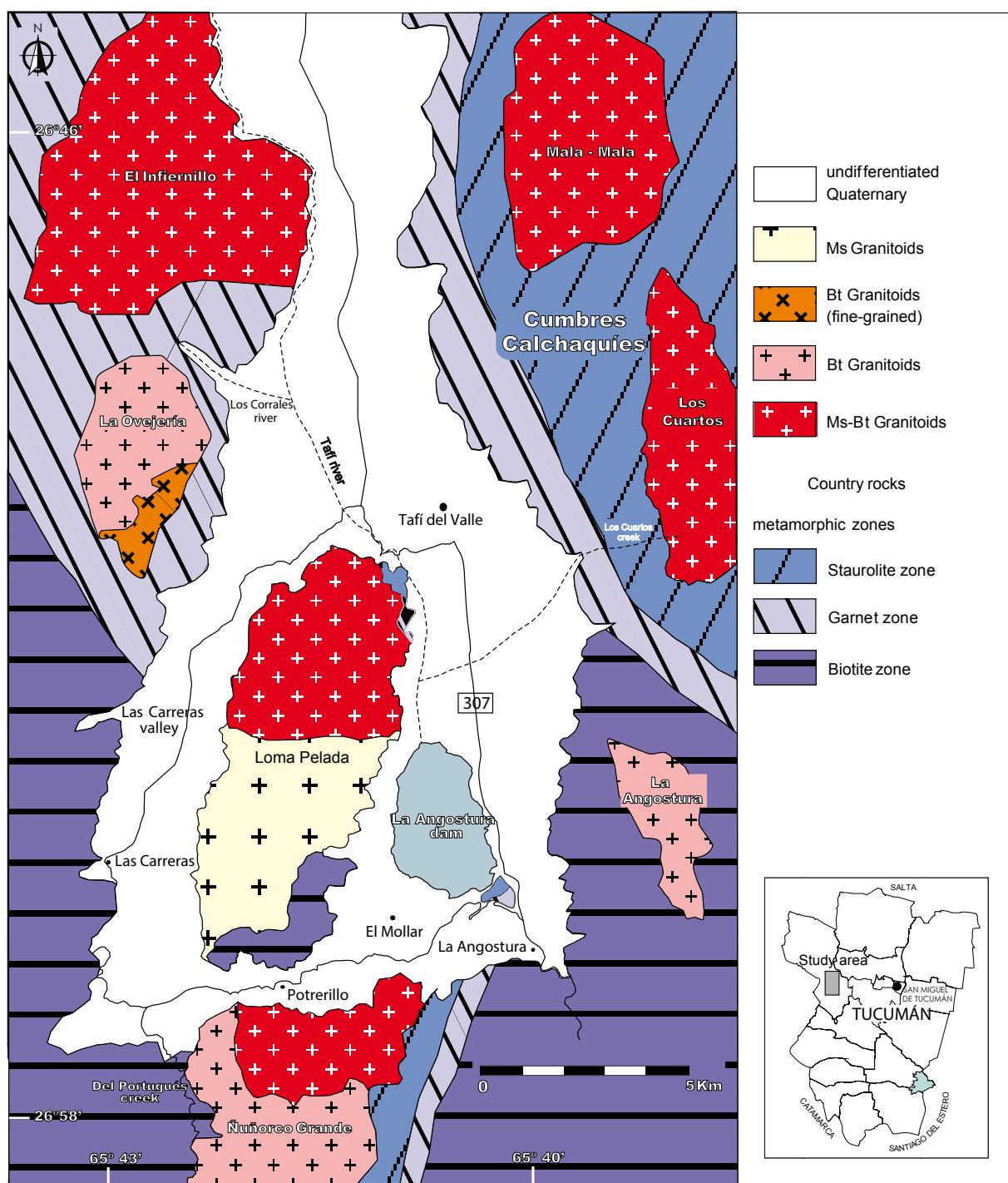
of the metamorphic basement (Puncoviscana Fm.: Turner, 1960) that hosts the Lower Ordovician magmatism. In the study area, the Puncoviscana Fm. is mainly formed by low to medium metamorphic grade biotitic schists (Toselli and Rossi de Toselli, 1973). Andalusite and staurolite domains are described in the Cumbres Calchaquíes and extensive migmatization domains are present to the West of the Sierra de Aconquija (Fig. 1) (González Bonorino, 1950a, b, 1951; Toselli and Rossi de Toselli, 1998; Masetti, 2010). In Tafí del Valle region, the metamorphic basement of the Cumbres Calchaquíes is intruded by granitic plutons called Loma Pelada, Los Cuartos, La Ovejería and El Infiernillo



**FIGURE 1.** General geological scheme of the central part of the Sierras Pampeanas, NW Argentina. Limits of Precordillera terrane, Famatinian magmatic arc and the Pampean orogen are represented by dashed lines.

that represent the Famatinian magmatism in the region (Fig. 2). These bodies do not show mutual contacts. The contacts with the host rocks, where observed, are sharp and transitional (schlieren textures and enclaves are present to the east of Los Cuartos and Loma Pelada).

The available geochronological data of the studied intrusive units is scarce. Los Cuartos granite yields ages from  $479 \pm 9$  to  $456 \pm 21$  Ma (K/Ar on biotite, González *et al.*, 1973) and the Loma Pelada granite gives  $470 \pm 10$  Ma (Rb/Sr, Sales *et al.*, 1998).



**FIGURE 2.** Geological map of Tafí del Valle area, Province of Tucumán, Argentina. The studied granitoids are represented. Mineral abbreviations in the legend are from Kretz (1983).

## PETROGRAPHY AND SAMPLE DESCRIPTIONS

To obtain a first hand classification of the studied granites we have considered the classification of Chappell and White (2001) (Fig. 3). Most samples of the Los Cuartos granite present higher  $K_2O$  and  $FeO$  contents than La Ovejería and El Infiernillo tonalites and granodiorites, and are located in the S-type granites field. Besides, metapelitic xenoliths are recognized in the Los Cuartos granites. La Ovejería and El Infiernillo samples are mostly located in the I-type granites field, although some of them are plotted together with Loma Pelada granites in an intermediate location between S- and I-type granites (Fig. 3). La Ovejería, El Infiernillo, Los Cuartos and Loma Pelada lack diagnostic minerals as hornblende for I-type and garnet or cordierite for S-type granites. The studied granites are posttectonic as shown by its discordant contacts with the host rocks foliation and the lack of internal deformation.

### The metamorphic basement

Three low to medium grade metamorphic assemblages are identified in the host basement: biotite zone schists ( $Bt+Qtz+Chl+Ms+Ab$ ), garnet zone schists ( $Grt+Qtz+Bt+Ms+Ab$ ) and staurolite zone schists ( $St+Grt+Bt+Ms+Ab$ ) (mineral abbreviations by Kretz, 1983). These metamorphic zones show a complex relation with the deformational phases described in the region and are related with regional metamorphism (Toselli and Rossi de Toselli, 1973; Willner, 1990). Where the contact area between the plutons and the host-rocks is accessible, a pervasive contact metamorphism is not observed in the basement rocks.

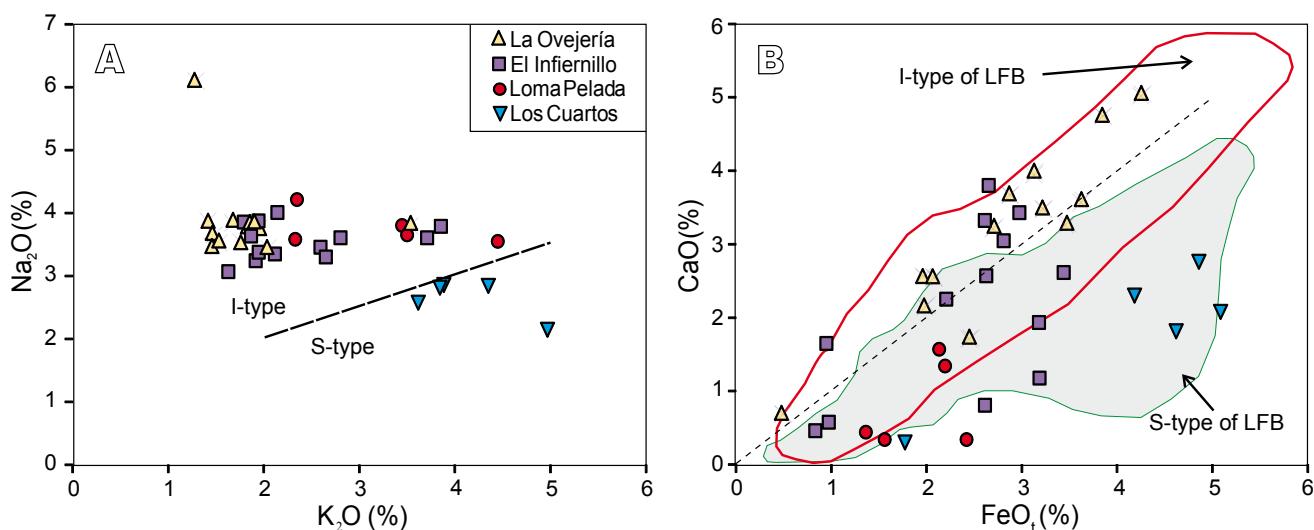
In general, the host rock of the granitoids corresponds to banded schists (Fig. 4A) with alternating of lepidoblastic and granoblastic layers. The first ones are composed by fine-grained muscovite (0.2mm) with a strong preferred orientation; biotite and anhedral quartz (0.1mm) are scarce. Granoblastic layers are constituted by larger grains of anhedral quartz (0.2-0.3mm), scarce plagioclase ( $An_{55}$ ) and lamellae of preferentially oriented muscovite. Larger and poikiloblastic grains of biotite (0.5mm) without preferred orientation are conspicuous, locally with chlorite overgrowth.

In the Garnet zone, this mineral is euhedral to subhedral and forms up to 0.5mm poikiloblast, limpid, immersed in the matrix. In the higher zone, Staurolite presents subhedral to euhedral porphyroblasts (up to 40mm), with characteristic pleochroism. It is strongly poikiloblastic and altered to sericite; garnet is present as inclusions in it. The assemblage next to the metamorphic peak is biotite + muscovite + plagioclase + garnet + staurolite + quartz.

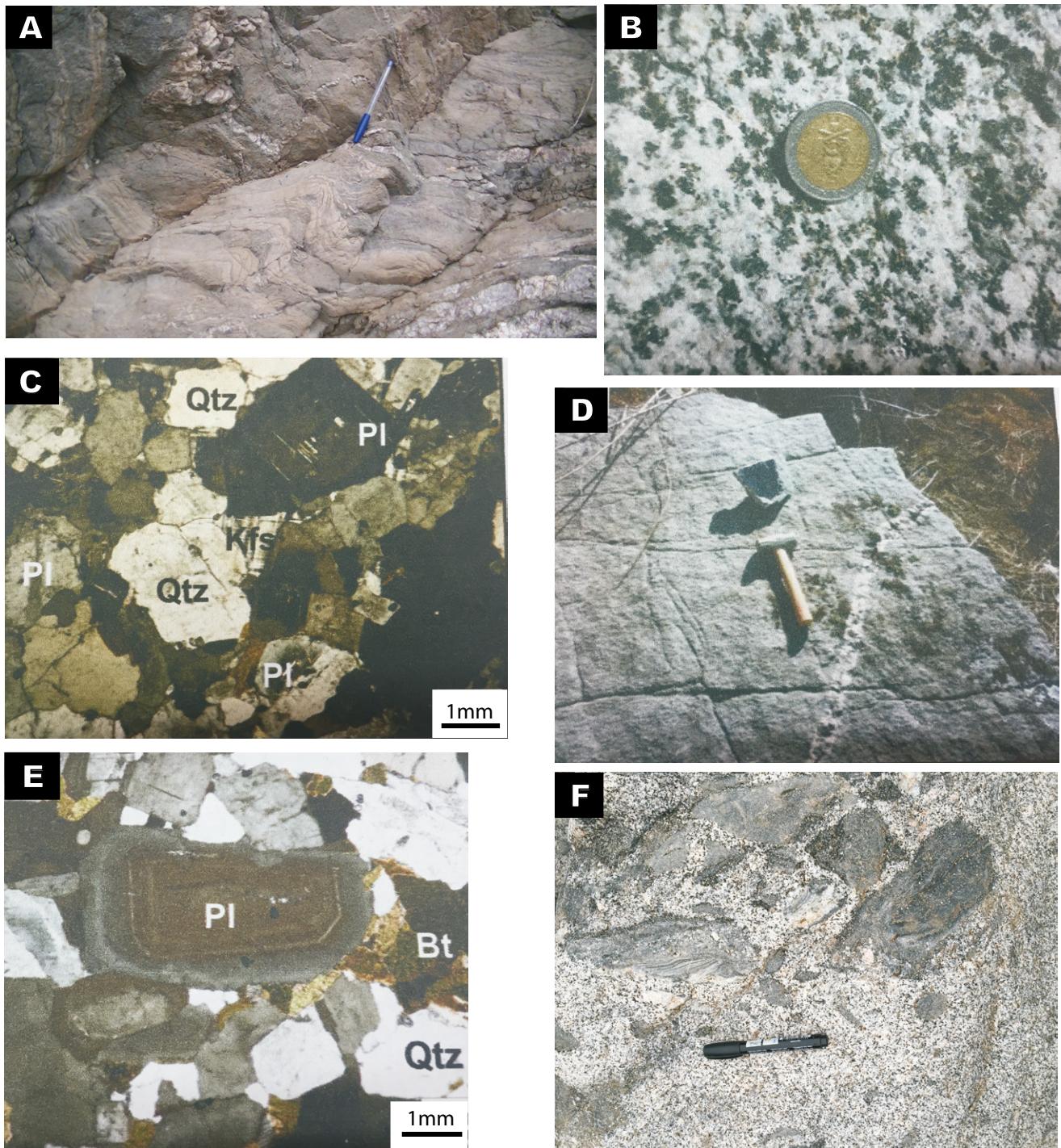
### I-type granites

#### *La Ovejería Tonalite*

La Ovejería Tonalite is located on the eastern margin of the Sierra de Aconquija. It forms an elongated N-S trending body of 4.4km length and 1.5km width (average) and intrudes biotite and biotite + garnet schists (Fig. 2). Two tonalitic facies were recognized according to their grain size. In the North sector a medium grain size facies (Fig. 4B) consists of plagioclase, quartz, scarce microcline, biotite, turmaline and epidote. Medium grain size tonalites show



**FIGURE 3.** A)  $Na_2O$  vs.  $K_2O$  diagram for the intrusive bodies of the Tafí del Valle region. Dashed line is the limit of I- and S-type granites proposed by Chappell and White (1974). B)  $CaO$  vs. total  $FeO$  diagram (Chappell and White, 2001). The line represents compositions with equal wt.%  $CaO$  and total  $FeO$ . The area marked by a red line represents the I-type granites and the grey area the S-type granites of the Lachlan Fold Belt (LFB).



**FIGURE 4.** A) Granitoid host-rocks are comprised by Bt-, St- and Grt-bearing banded schists. La Ovejería pluton: B) tonalitic medium-grained facies where C) microcline is presented in small late crystallization crystals ( $N^+$ ). D) Tonalitic fine-grained facies of the La Ovejería. E) Thin section of fine-grained facies showing zoned plagioclase crystals ( $N^+$ ). F) Los Cuartos granite presents a significant interaction with abundant host-rock xenoliths.

equigranular and xenomorphic texture (Fig. 4C). Plagioclase is the most abundant mineral phase (60-67 vol%). It presents large (up to 3.5 mm) anhedral and zoned crystals and small (up to 2.5 mm) subhedral crystals. Quartz (20-23 vol%) is anhedral, fractured and forms interstitial grains; microcline is presented in scarce and small crystals (1-3 vol%), whereas

biotite (9-14 vol%) constitutes anhedral flakes. Pistacite is anhedral and associated to altered biotite or plagioclase. Turmaline is locally abundant.

A fine grained-size facies is observed in the southern sector (Fig. 4D) consisting of plagioclase, quartz, very

scarce microcline, biotite and scarce titanite. This facies shows an inequigranular and xenomorphic texture (Fig. 4E). Plagioclase (56-64vol%) constitutes subhedral and zoned crystals; quartz (24-29vol%) and small microcline (<2vol%) are present as anhedral crystals; titanite forms anhedral and fractured grains. Pistacite and muscovite are present in biotite (10-15vol%) alteration areas.

La Ovejería tonalite is cut by several 2m wide granitic dykes. These show medium grain size and inequigranular texture and consist of microcline, quartz, plagioclase and muscovite. Microcline is present as crystals of up to 4mm. Quartz conforms anhedral grains and as inclusions in microcline. Anhedral to subhedral plagioclase is scarce. Muscovite is abundant as interstitial sheets or as inclusions in microcline.

### ***El Infiernillo Granodiorite***

This pluton is located to the North of the La Ovejería Tonalite. It covers an area of 100km<sup>2</sup> approximately and intrudes biotite or biotite + garnet schists (Fig. 2).

Two compositional facies are recognized. A facies of granodioritic composition comprises the center of the intrusive body. A second one of dominant tonalitic composition crops out at the border zone. The contact between the two facies is sharp and, occasionally, the tonalites are present as enclaves in the granodiorites. Both facies show an equigranular texture. The granodioritic facies shows plagioclase (42vol%), quartz (24-47vol%) and K feldspar (10-15vol%); biotite (3-18vol%) and muscovite (0-12vol%) are the accessory minerals. Plagioclase is present either as coarse, zoned and deformed crystals or as smaller undeformed crystals. Quartz presents undulate extinction and biotite presents kink band structures. The tonalitic facies presents plagioclase (60-80vol%), quartz (15-40vol%), scarce and intergranular K feldspar (5vol%). Lisiak (1990) and Toselli (1992) described tourmaline in the granodioritic facies and epidote in the tonalitic ones.

### **S-type and hybrid granites**

#### ***Loma Pelada Granite***

The Loma Pelada Granite is located in the central part of the Tafí del Valle. It constitutes an elongated N-S trending body that crops out along 40km<sup>2</sup> (Fig. 2) and intrudes biotite or biotite + garnet schists.

The intrusive rocks consist of biotitic-muscovitic granodiorites, biotitic monzogranites and pegmatitic and quartz-tourmaline bearing dykes. The largest outcrops of this body correspond to the granodiorite facies, that shows zoned crystals of plagioclase (43vol% average), exhibiting an andesine core mantled by an oligoclase

rim. Sericitic and clinzoisite alteration is frequent. Myrmekites are common in the contact between plagioclase and K feldspar (13vol% average). Biotite is the predominant mafic mineral (4vol% average) and muscovite is present in larger sheets (3vol% average). The muscovite monzogranite constitutes the South area of the Loma Pelada Granite. It forms dikes that cut the granodioritic facies. Plagioclase (33vol% average) is homogeneous and shows oligoclase-albite composition. Microcline is interstitial (21vol% average), with characteristic Pericline-Albite twins. Muscovite (9vol% average) and scarce garnet are also present.

### ***Los Cuartos Granite***

Los Cuartos Granite crops out to the West of the Cumbres Calchaquíes. It is an elongated N-S trending body of 2x7km and intrudes medium metamorphic grade biotite or biotite and garnet schists (Fig. 2). It consists of biotite and muscovite monzogranites and granodiorites that crop out in the South and northwest sector. In the North part of the body tonalites are present. The main body is cut by pegmatitic tourmaline-bearing monzogranitic dykes. The contacts between the different facies are sharp and the presence of xenoliths with different grades of assimilation is recognized in several outcrops (Fig. 4F). Plagioclase (20-34 vol%) forms subhedral deformed and strongly zoned crystals (up to 2.5mm). Occasionally, megacrysts of 6-8mm are recognized. Muscovite and epidote are common secondary minerals. Microcline (7-23vol%) is present as anhedral crystals of 0.3-3.5mm, with deformed twins and perthitic and myrmekitic textures. Quartz crystals (32-50vol%) of 0.2-4.0mm size show undulose extinction with rutile and biotite inclusions. Biotite is the mafic mineral (4-15vol%) and it is present in brown sheets (of up to 2mm) with inclusions of zircon and prismatic apatite. Muscovite is scarce (2-6vol%). Titanite constitutes subhedral crystals up to 0.7mm in size.

## **GEOCHEMISTRY**

### **Comparative data and analytical techniques**

Trace elements from 13 samples of the two facies from La Ovejería granitoids were analyzed (Table I, Appendix I). Trace elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at the University of Huelva by ICP-MS with an HP-4500 system, following digestion in an HF+HNO<sub>3</sub> (8:3) solution, drying and further second dissolution in 3ml HNO<sub>3</sub>. The average precision and accuracy for most of the elements was determined by repeated analyses of the SARM-1 (granite) and SARM-4 (norite) international rock standards, and are in the range 5-10% relative. Major element analyses from La Ovejería,

Los Cuartos, El Infiernillo and Loma Pelada granitoids (available in the Electronic Appendix at [www.geologica-acta.com](http://www.geologica-acta.com)) were extracted from Lisiak (1990) and Saavedra *et al.* (1984), López and Bellos (2010), López *et al.* (2012).

We used previously studied coeval granitoids of the Sierras Pampeanas as comparative data, which represent the geochemical diversity of the regional lower Paleozoic magmatism. Metaluminous I-type granitoids are represented by the Palanche pluton (southern part of the Sierra de Velasco) (Bellos *et al.*, 2015), whereas the examples for the peraluminous S-type magmatism are the Sierra de Chepes and Mazán granites, and the inner area of the Palanche pluton (Dahlquist *et al.*, 2005, Grosse *et al.*, 2011, Toselli *et al.*, 2014).

### Major and trace element description

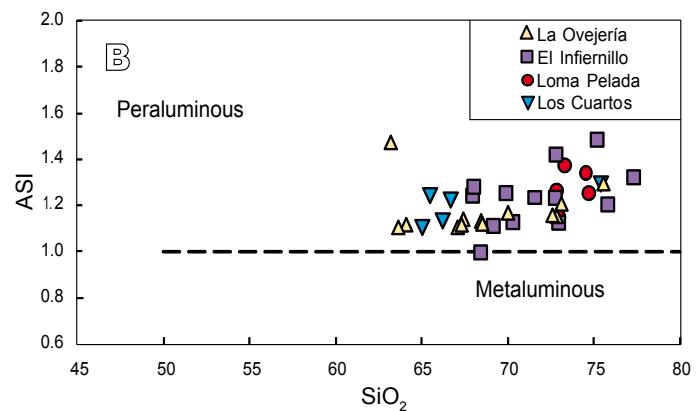
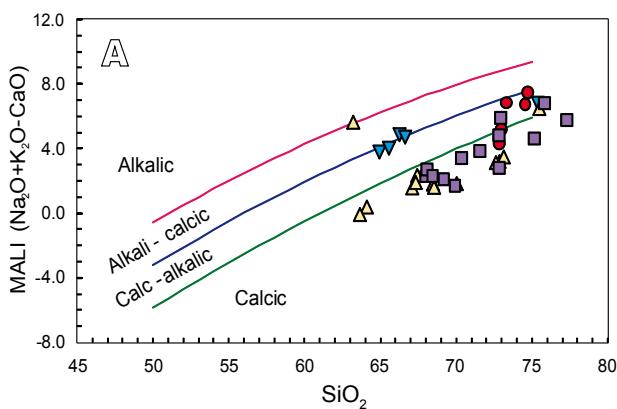
According to the classification scheme of Frost *et al.* (2001), the intrusive units of La Ovejería, El Infiernillo and Loma Pelada are calcic, whereas the granodiorite samples from El Infiernillo and Loma Pelada evolve to the calc-alkalic field. On the other hand, Los Cuartos granite samples project to the boundary between the calc-alkalic and alkali-calcic series (Fig. 5A). All rock samples are peraluminous (Alumina Saturation Index > 1) and show a wide compositional range ( $\text{SiO}_2$  between 63 wt.% and 77 wt.%) (Fig. 5B, Table I). Granodiorites from Los Cuartos show  $\text{SiO}_2$  contents between 64 and 67 wt.%, while granites of Loma Pelada are grouped between 73 and 75 wt.%  $\text{SiO}_2$ , close to the most evolved samples from La Ovejería and El Infiernillo. In the Harker diagrams (Fig. 6), linear trends for La Ovejería and El Infiernillo samples show negative correlations for  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$  and  $\text{CaO}$  oxides vs.  $\text{SiO}_2$  (Fig. 6A-E).  $\text{Na}_2\text{O}$  shows a flat trend (Fig. 6G) and a positive correlation between  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  is observed, with a slight dispersion in the high silica samples (Fig. 6F), which are coincident with  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{FeO}$  poor Loma Pelada granites. Los Cuartos samples are separated from the general trends described

by the other units. These samples show higher contents of  $\text{FeO}$ ,  $\text{MgO}$  and  $\text{K}_2\text{O}$ , and lower of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{Na}_2\text{O}$  in comparison with La Ovejería and El Infiernillo samples.

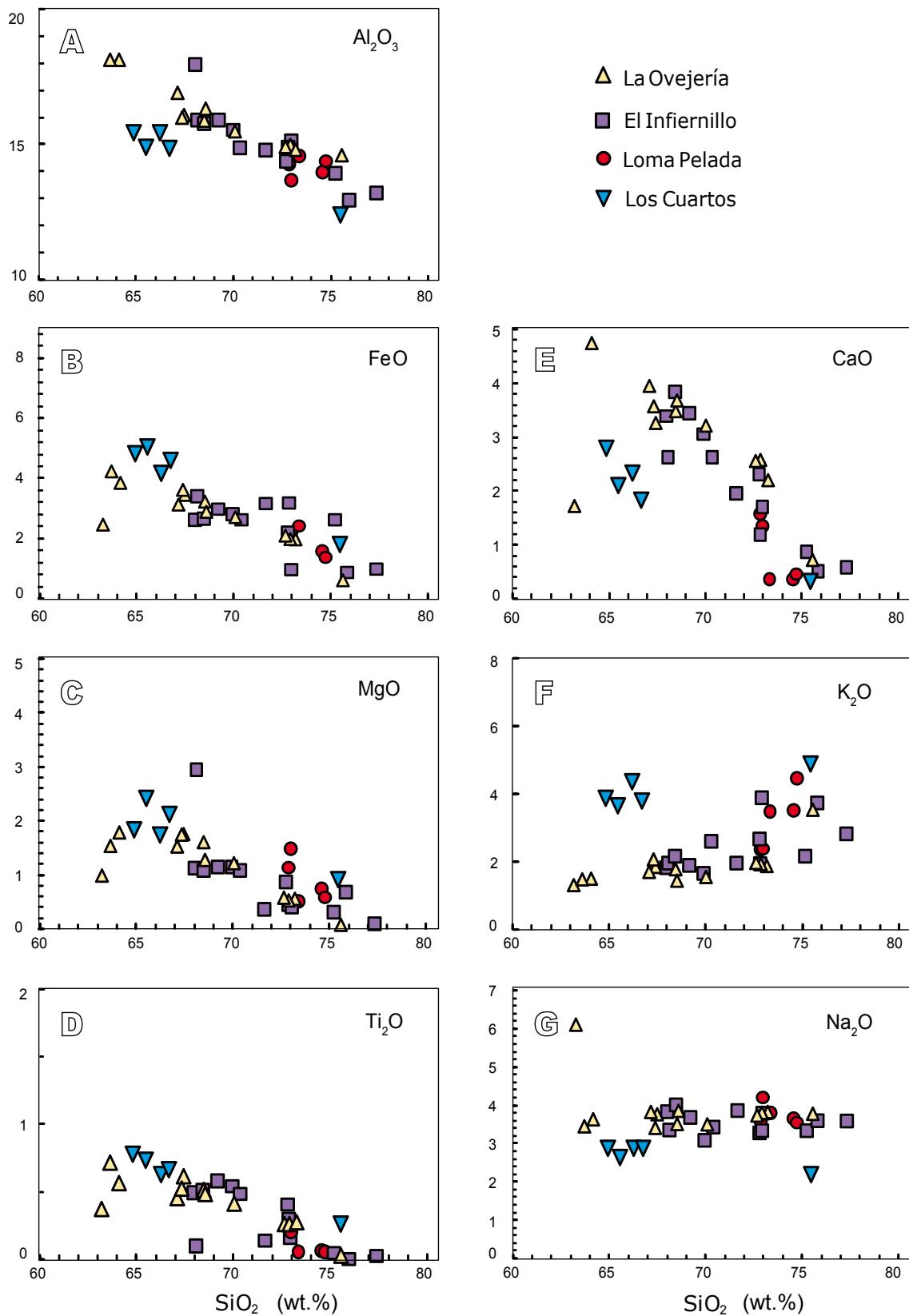
In the Ab-Or-An diagram (O'Connor, 1965; Fig. 7A), a continuous evolution from tonalite to granite fields is observed among samples of the La Ovejería, El Infiernillo, and Loma Pelada. Los Cuartos samples, which show higher Or proportions, are mostly located between the granodiorites and monzogranites field. According to the  $\text{SiO}_2\text{-Na}_2\text{O}+\text{CaO}\text{-FeO}_t\text{+MgO}$  diagram (Johannes and Holtz, 1996) (Fig. 7B), samples from the La Ovejería, El Infiernillo and Loma Pelada intrusive bodies are defined as trondhjemites. They present low  $\text{FeO}$  and  $\text{MgO}$  contents with  $\text{Fe}_2\text{O}_3\text{+MgO+MnO+TiO}_2 < 5\%$ .

Figure 8 shows the variation of selected trace elements vs.  $\text{SiO}_2$ . La Ovejería and El Infiernillo granites present similar Rb, Y and Ba contents, although a greater scattering is observed in El Infiernillo samples (Fig. 8A; C; E). The Loma Pelada rocks are separated in two groups, one of them is plotted together with the La Ovejería and El Infiernillo granodiorites, whereas a second group shows higher Rb values and lower Sr, Zr and Ba contents (Fig. 8A; B; D; E). Sr content decreases with  $\text{SiO}_2$  in the La Ovejería samples (from 334 to 20 ppm), while the low Rb and Y content is consistent with the trondhjemitic characteristics of the La Ovejería and El Infiernillo granitoids. Los Cuartos samples have higher contents in Rb, Ba, Zr, and Y (24–35 ppm). In addition, they show lower Sr values in comparison with the samples with similar  $\text{SiO}_2$  contents.

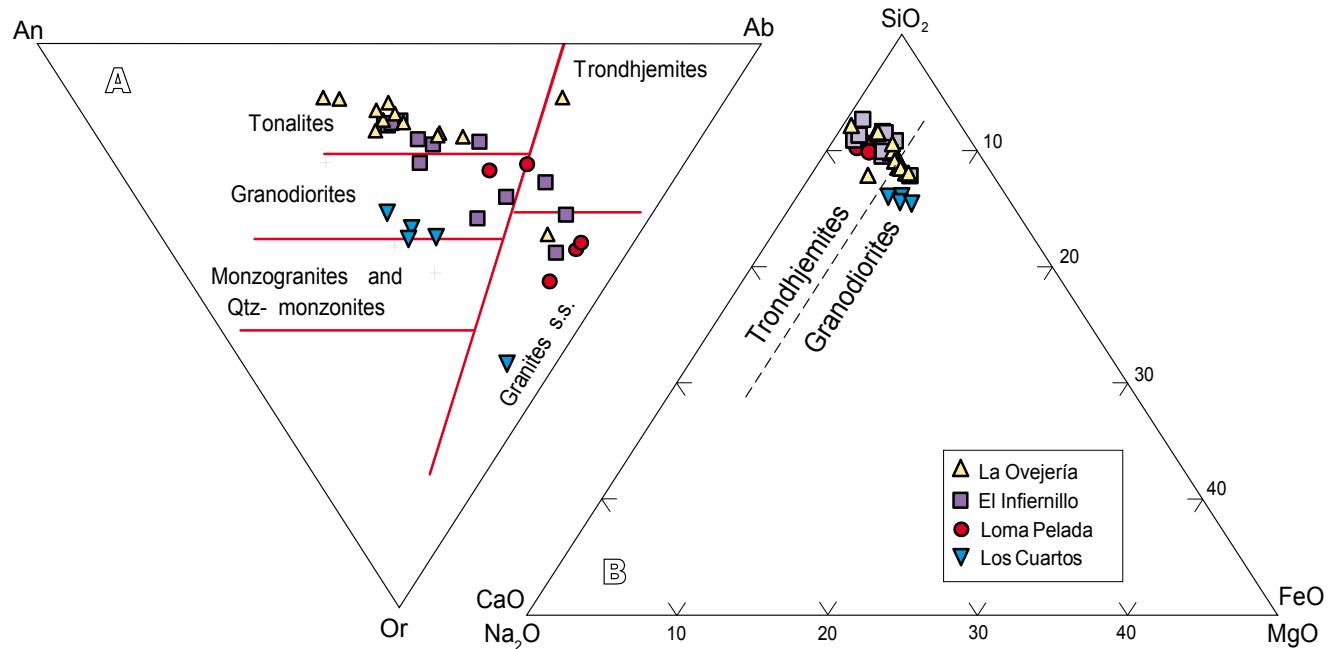
Chondrite-normalized REE plots (Nakamura, 1974) of tonalites and granodiorites of the La Ovejería are shown in Figure 9. In general, subparallel patterns can be observed, with slight negative and positive (5 samples) Eu anomalies. In both cases the patterns generated are almost flat ( $\text{Eu/Eu}^* \sim 0.70\text{-}1.29$ , average = 0.98).  $\text{La}_{\text{N}}/\text{Yb}_{\text{N}}$  ratio ranges from 6.63 to 17.46 (average 11.80). In general,



**FIGURE 5.** General compositional characteristics of granitoids: A) MALI vs. silica diagram; B) ASI vs.  $\text{SiO}_2$  diagram (Frost *et al.*, 2001).



**FIGURE 6.** Silica variation diagrams (Harker) plotting granitoids of the Tafí del Valle area. Linear trends are described by La Ovejería and El Infiernillo samples. Granitoids of Loma Pelada are grouped between 73 and 75 wt.%  $\text{SiO}_2$ . Los Cuartos samples are separated from the general trends described by the other units (see further explanations in the text).



**FIGURE 7.** A) Classification of O'Connor (1965) and B)  $\text{SiO}_2\text{-Na}_2\text{O}+\text{CaO}\text{-FeO}_t\text{+MgO}$  diagram of Johannes and Holtz (1996). See text for details.

La Ovejería samples are enriched in LREE, showing an almost flat pattern for the HREE.

Trace elements of the La Ovejería granitoids are compared with other S and I-type regional granitoids (Fig. 10). In general, La Ovejería granitoids show lower trace element contents than the comparative I- and S-type granitoids. Sr anomalies are positive for three tonalitic samples, a similar behavior than Eu in REE diagrams for these samples (Fig. 9). However, others granitoids of the La Ovejería present negative Sr anomalies. Flat patterns of Tb, Y, Tm and Yb are similar to the comparative granitoids, although a lower HREE content is observed in the La Ovejería granites.

### Comparative projections

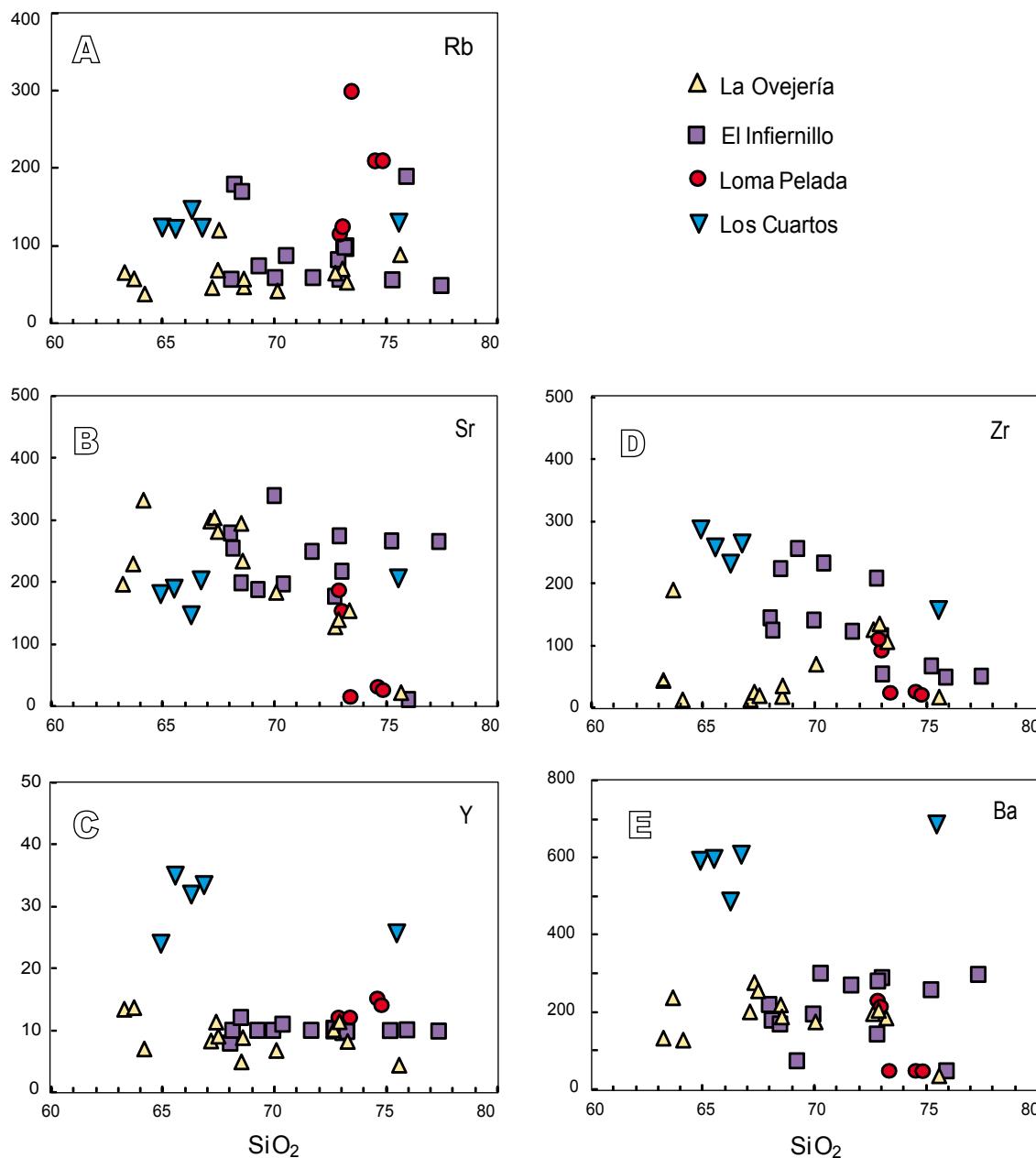
The new trace element data of the La Ovejería intrusive unit, along with the significant geochemical data from El Infiernillo, Loma Pelada and Los Cuartos granitoids allow a comparison of the lower Paleozoic granitoids of the Tafí del Valle region with the regional coeval magmatism. In order to constrain the petrogenetic considerations and the geochemical variations occurred during the emplacement stage of these magmas, models obtained by the Rhyolite-MELTS program (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; Gualda *et al.*, 2012) and experimental examples of magmatic evolutions have been used (Figs. 11 and 12).

$\text{MgO}$  vs.  $\text{CaO}$  and  $\text{K}_2\text{O}/(\text{K}_2\text{O} + \text{CaO})$  diagrams (Fig. 11A; B) highlight the geochemical differences between the granitoids of the La Ovejería and El Infiernillo regarding to

Loma Pelada and Los Cuartos granodiorites and granites. La Ovejería and El Infiernillo samples follow a linear trend similar to the I-type granitoids (Palanche) that matches the cotectic evolution (LLD: Liquid Line of Descent, Castro, 2013). The model liquid compositions of an initial dioritic composition with 1 and 2 wt.% of  $\text{H}_2\text{O}$  and 0.7 and 1.5 GPa were plotted. The resulting trend fits quite well with the evolution of the main group of samples of the La Ovejería and El Infiernillo (Fig. 11A; B). However, some samples of these intrusive units show crossed trends from this cotectic path, noting an enrichment in  $\text{MgO}$  with a  $\text{CaO}$  decrease (Fig. 11A) and an increase of  $\text{K}_2\text{O}$  (Fig. 11B). These trends settle on the field of regional metasedimentary rocks (Puncoviscana Fm.), suggesting the interaction with country rocks.

Samples from Loma Pelada and Los Cuartos intrusive units show two distinctive locations in the geochemical variation diagrams. A first group, mainly corresponding to Loma Pelada samples, is plotted with the leucogranites, with very low  $\text{CaO}$  and  $\text{MgO}$  contents, and highly enriched in  $\text{K}_2\text{O}$ , coincident with the most evolved S-type regional granitoids (Velasco, Mazan and Chepes). Moreover, a second group, mainly corresponding to Los Cuartos granites, is placed in an intermediate position between the granodiorites of the La Ovejería and El Infiernillo and the  $\text{MgO}$  rich S-type granitoids, together with the field of the host metasedimentary rocks.

Regarding to the  $\text{Sr}$  vs. peraluminosity relations, most of La Ovejería samples show a slight increase of

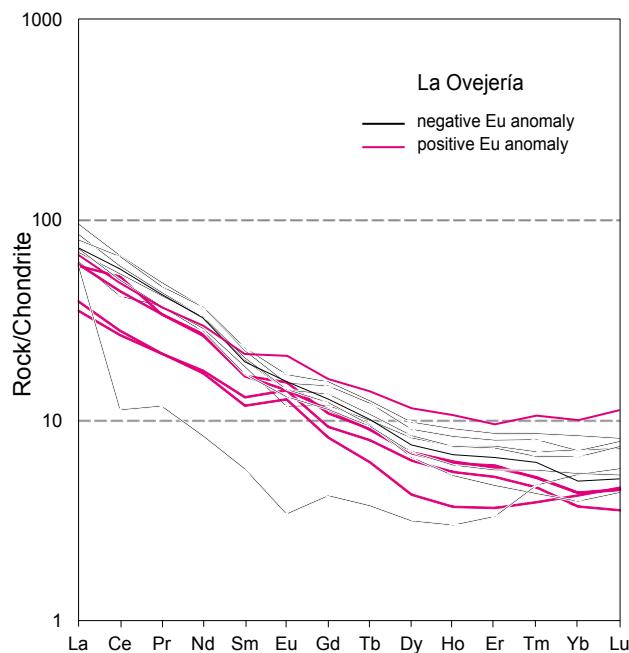


**FIGURE 8.** Variation diagrams of some trace elements vs. SiO<sub>2</sub>. La Ovejería and El Infiernillo granites present similar trends, although a greater scattering is observed in the El Infiernillo samples. The Loma Pelada samples are separated in two groups. Los Cuartos samples present trace elements contents that differ from those trends pointed by the La Ovejería and El Infiernillo granitoids.

peraluminosity with decreasing Sr, which coincides with an evolution by Cpx+Pl (+Grt) fractionation (Fig. 11C). The rest of the studied granitoids (El Infiernillo, Loma Pelada and Los Cuartos) present much higher peraluminosity compared with the values observed in La Ovejería samples (ASI=1.15 approximately), and show no correlation with the Sr contents. The Sr/Y ratio (Fig. 11D) shows a similar behavior in La Ovejería and El Infiernillo granitoids. The increase of Sr/Y vs. Y in these samples is remarkable and matches the trends pointed by the modeled dioritic composition for 0.7 and 1.5GPa. The high Sr content and

the strong depletion of the more refractory elements can be related to the presence of garnet at the source, because garnet would retain the Y and the most refractory elements (Moyen, 2009). Higher Sr/Y ratios coincide with lower SiO<sub>2</sub> contents and higher Eu/Eu\* values (Fig. 11D). La<sub>N</sub>/Yb<sub>N</sub> vs. Yb<sub>N</sub> diagram (Fig. 11E) confirms the moderate LREE/HREE ratios observed in Figure 8, which are positively correlated with SiO<sub>2</sub> contents.

Figure 12 shows a projection in the pseudoternary system defined by Opx-An-Or (Fe+Mg+Mn; Ca; K).



**FIGURE 9.** Chondrite-normalized (Nakamura, 1974) REE plots. Tonalites and granodiorites of La Ovejería in general show subparallel patterns, with slight negative Eu anomaly, although 5 samples show positive Eu anomaly. In both cases the patterns generated are almost flat ( $\text{Eu/Eu}^* \sim 0.70\text{--}1.29$ , average = 0.98).  $\text{La}_N/\text{Yb}_N$  ratio ranges from 6.63 to 17.46 (average 11.80).

La Ovejería and El Infiernillo samples are plotted between the areas typically occupied by trondhjemites (close to the An apex) and the less evolved granitoids of the calc-alkaline systems used for comparison. The best fit regarding to the conditions of the experimental examples are undersaturated between 0.7 and 1.5 GPa, with parental compositions very similar to primary andesitic magmas in the less evolved samples. However, some granitoids of this group follow paths not described by cotectic trends of granotonatites (Castro, 2013), and point to the compositions of S-type granitoids and regional metasediments. A second group is projected very close to the Or apex and leucogranites, trending toward the location of the host rocks (Fe+Mg+Mn) with increasing peraluminosity. Finally, a third group is recognizable by an intermediate location between I-type magmas trends and S-type granitoids together with the composition of the host metasediments.

## DISCUSSION

New geochemical data obtained from the La Ovejería granitoids and the previously studied samples in the Tafí del Valle region allow us to propose a new scheme for the late Paleozoic regional magmatism. All these granitic units were emplaced in a retro-arc environment,

during the development of the Famatinian magmatic arc at the western margin of Gondwana, as the result of the subduction of the paleo-Pacific oceanic Plate (Pankhurst and Rapela, 1998; Lucassen and Franz, 2005; Miller and Söllner, 2005; De los Hoyos *et al.*, 2011). To the West, this arc is dominantly conformed by calc-alkaline I-type granitoids, with small S-type associated bodies (Saal *et al.*, 1996; Toselli *et al.*, 1996; Saavedra *et al.*, 1998; Dahlquist *et al.*, 2005; Otamendi *et al.*, 2009a, 2009b, 2012, Bellos *et al.*, 2015). To the East, the S-Type peraluminous granites are predominant, and large batholiths were emplaced eastwards at lower pressures in a thicker crust (Toselli *et al.*, 2000, 2005; Báez and Basei, 2005; Grosse and Sardi, 2005; Grosse *et al.*, 2009). The granitoids of the La Ovejería, El Infiernillo, Loma Pelada and Los Cuartos are located to the East of the Famatinian Arc.

According to the geochemical characteristics found out in this study, La Ovejería and El Infiernillo tonalites and granodiorites show  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  and  $\text{CaO}/\text{FeO}$  ratios that mostly coincide with the I-type granites (Fig. 3). Major elements variation diagrams as  $\text{MgO}$  vs.  $\text{CaO}$  and  $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{CaO})$  show cotectic evolutions that relate these granitoids with regional I-type magmatism (Fig. 11A; B). However, significant differences with the typical I-type granitoids of the Famatinian Arc are observed. They are weakly to moderate peraluminous ( $\text{ASI}=1.1\text{--}1.4$ ) (Fig. 5B). Hornblende is absent in these rocks and scarce titanite is observed only in some tonalitic facies of the La Ovejería body. Samples from the La Ovejería intrusive unit show a strong enrichment in  $\text{Sr/Y}$  with respect to  $\text{Y}$  (Fig. 11D). This, together with the moderate LREE/HREE ratio and the low  $\text{Yb}_N$  content (Fig. 11E) are characteristic of the adakitic signature. Interestingly, La Ovejería and El Infiernillo granitoids are classified as trondhjemites according to their low  $\text{Fe}_2\text{O}_3+\text{MgO}+\text{MnO}+\text{TiO}_2$  contents. Low  $\text{Rb}$ , moderately peraluminous trondhjemites have been experimentally related to the dehydration partial melting of basaltic rocks at depth, where garnet is retained in the residue (Rapp and Watson, 1995; Frost *et al.*, 2016), leading to generation of HREE depleted melts (Defant and Drummond, 1990). MELTS models (Fig. 11) and experimental (Fig. 12) liquid evolutions for dioritic magmas under high pressure and water undersaturated conditions are coincident with these source conditions suggested for the origin of La Ovejería and El Infiernillo trondhjemites.  $\text{Cpx+Pl+Grt}$  or  $\text{Cpx+Grt}$  can be implied in the fractionation and evolution of these magmas (Fig. 11). Nevertheless, the  $\text{Sr/Y}$  and the  $\text{Eu/Eu}^*$  ratios decreases with the  $\text{SiO}_2$  content (Fig. 11D), while  $\text{Y}$  values remain almost constant (Fig. 8D). These, together with the high  $\text{Sr}$  contents and the positive Eu anomaly observed in the silica-poor less evolved tonalitic samples of La Ovejería, may suggest the absence of Pl in the

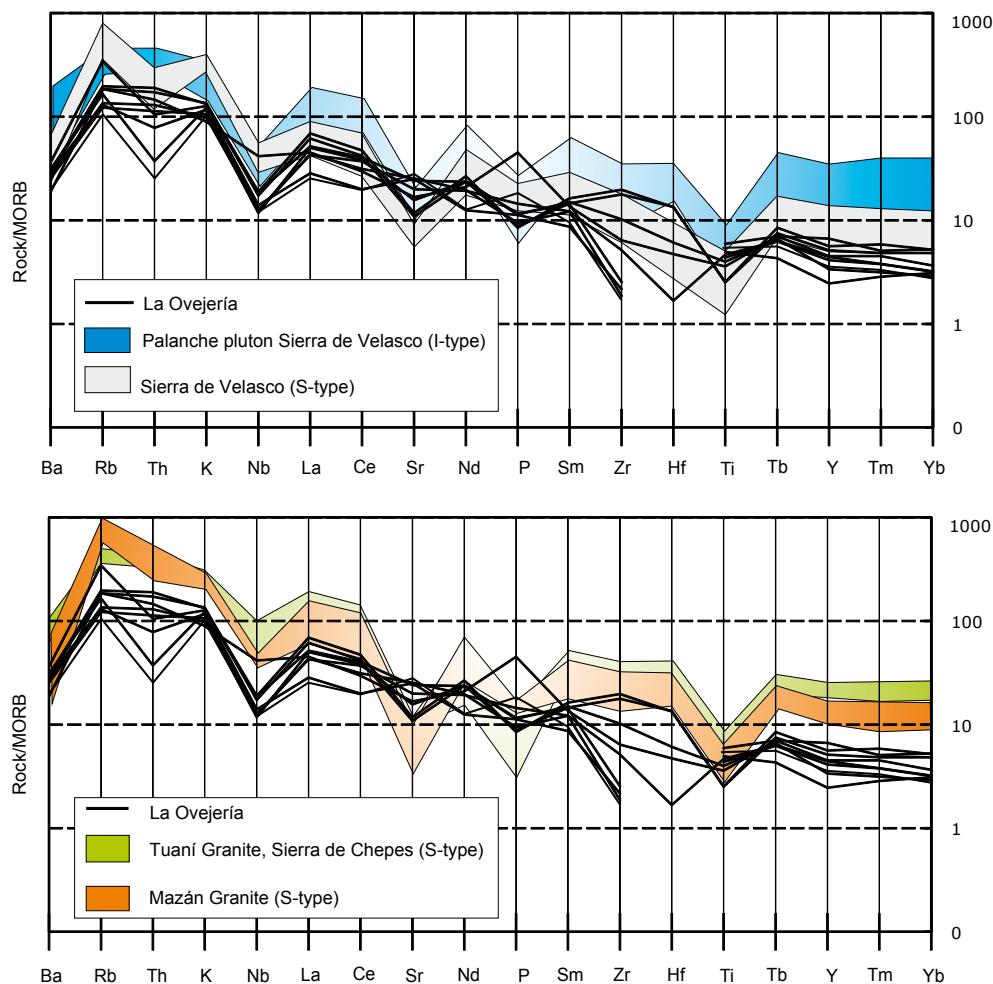
source, but the subsequent Pl fractionation between the CaO and Sr rich tonalites and granodiorites.

Some samples of both El Infiernillo and La Ovejería intrusive units show crossed trends regarding to the cotectic linear evolution described by most samples (Fig. 11A; B), which point to the compositional field of Fe-Mg rich S-type granitoids and the Puncoviscana Fm. This enrichment in FeO, MgO and K<sub>2</sub>O, and the dilution of CaO suggest the existence of assimilation processes that involve an important contribution of metasedimentary material in the geochemistry of intrusive magmas during the emplacement process.

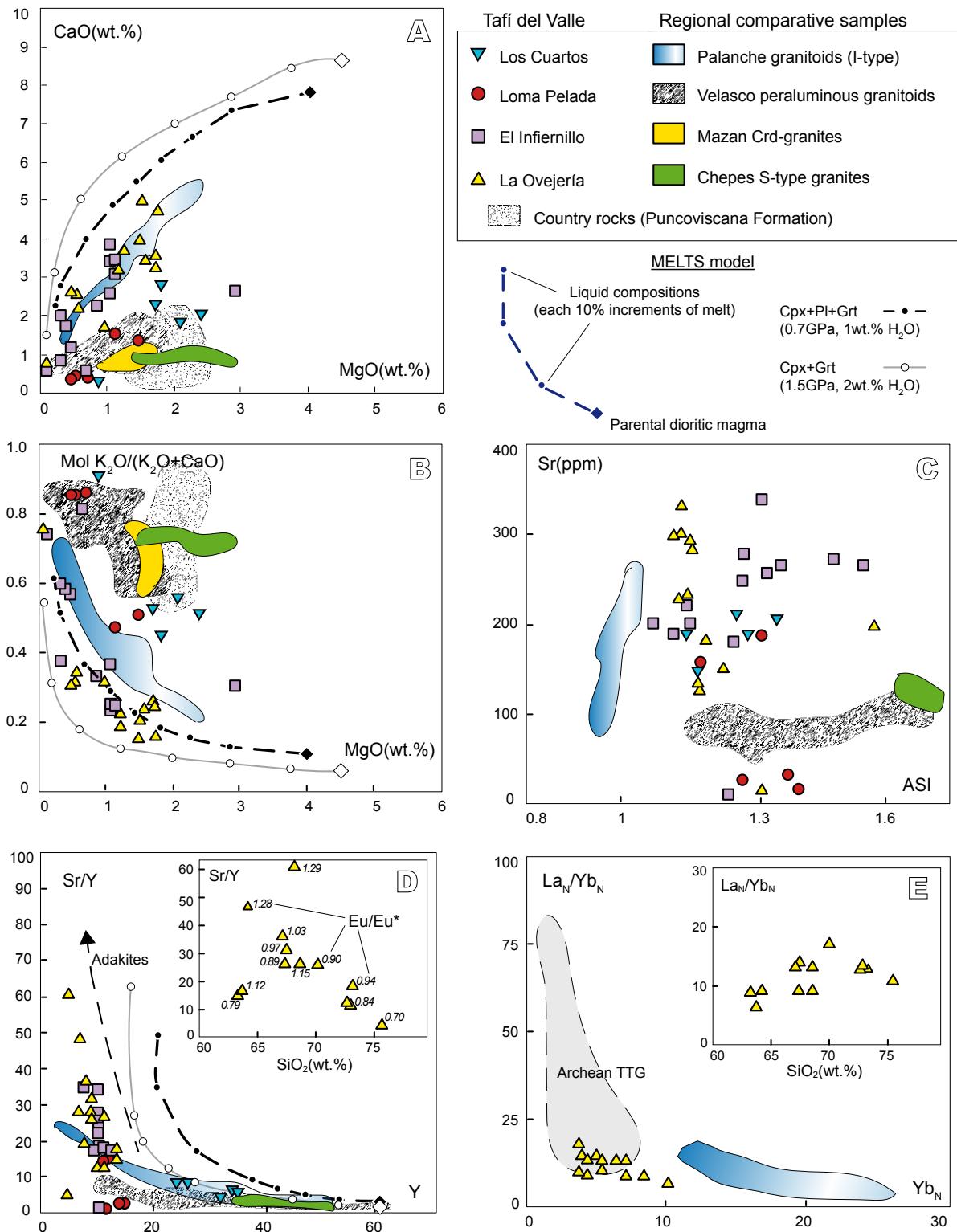
A group of the studied granites from Loma Pelada and Los Cuartos granitoids show highly evolved compositions (low CaO and MgO, and high K<sub>2</sub>O contents) (Fig. 11A; B), typical of granites segregated in the last stages of magmatic differentiation, or anatetic granites. They show an increasing peraluminosity and tend to approach to the host rocks location in the projected diagrams (increase in Fe and Mg content,

Fig. 12) that may be due to the greater Grt entrainment. These granitoids are located at the end of the compositional range of the regional S-type magmas, which are related to the anatetic melts generated in the Puncoviscana Fm. Besides, both the Loma Pelada and Los Cuartos granitoids include samples with intermediate geochemical characteristics that range between the samples of the El Infiernillo and La Ovejería and the regional metasedimentary rocks (Fig. 11A-E and 12). It could be explained by assimilation processes involving the I-type intrusive magmas and the metasedimentary host rocks or hybridization processes between trondhjemite I-type magmas as La Ovejería and El Infiernillo and anatetic S-type melts.

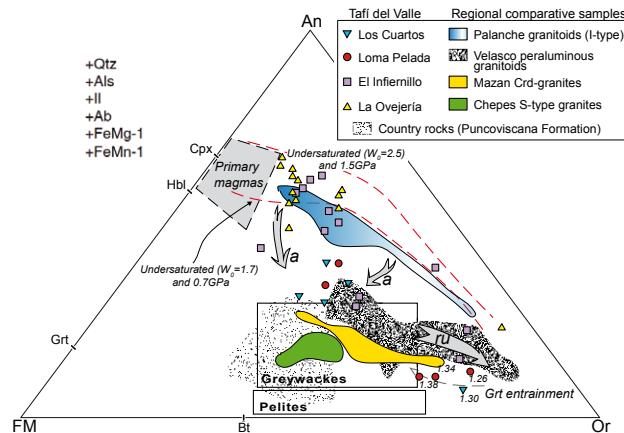
Based on the isotopic characteristics such as the initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio (0.7063–0.7069) and the  $\varepsilon_{\text{Nd}}$  (-1 to -3.8) of the Cumbres Calchaquíes granitoids, Toselli *et al.* (2002) indicate that a mixture between cortical and mantelic components were involved in the petrogenesis of these



**FIGURE 10.** Thompson normalization plot rock/MORB. La Ovejería pluton is compared with other S- and I-type regional granitoids. In general, La Ovejería shows lower trace element contents than the comparative I- and S-type granitoids.



**FIGURE 11.** Representation of geochemical variations of major and trace elements of the La Ovejería, El Infiernillo, Loma Pelada, Los Cuartos granitoids and main regional S and I-type intrusives. A) and B) CaO and molar relationship K<sub>2</sub>O/(K<sub>2</sub>O+CaO) vs. MgO. Black dashed and grey lines represent model liquid compositions calculated with Rhyolite-MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; Gualda *et al.*, 2012) modeling a solid residue composed by Cpx+Pl+Grt and Cpx+Grt, respectively. Major and trace element composition of the starting material are taken from Castro *et al.*, (2014). C) Sr vs. ASI of the selected samples and comparative granitoids. D) Sr/Y vs. Y (black arrow points to the adakites field by Defant and Drummond, (1990). In the inset, Sr/Y vs. SiO<sub>2</sub> and Eu/Eu\* ratios are plotted. E) La<sub>N</sub>/Yb<sub>N</sub> vs. Yb<sub>N</sub> and La<sub>N</sub>/Yb<sub>N</sub> vs. SiO<sub>2</sub> (inset). The field corresponding to the Archean TTG (Martin, 1986) is indicated.



**FIGURE 12.** Pseudoternary system defined for Opx (Fe-Mg-Mn), An (Ca), Or (K) phases. Location of compositional fields of primary magmas, pelites and graywackes and cotectic evolutions of examples were taken of Díaz-Alvarado *et al.* (2011) and Castro (2013).

magmas. Sales *et al.* (1998) obtained an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7063 for the Loma Pelada granite and achieved similar conclusions. Although these isotopic signatures could be primary in part due to a subcortical formation from a mixture of subducted sediments and basic rocks (Castro 2013, 2014), the addition of crustal material at the emplacement level by assimilation processes may achieve these ancient isotopic signatures.

## CONCLUSIONS

The geochemical characteristics of the intrusives recognized in the region of Tafí del Valle let us describe two main types of magmatism and a third group of granites that represents an hybridization processes between them. La Ovejería and El Infiernillo intrusive bodies represent the I-type magmatism with adakitic signature characteristic related with high-pressure conditions at the source, where the dehydration melting of basaltic rocks may be involved.

Loma Pelada and Los Cuartos granitoids show highly evolved compositions, typical of granites segregated in the last stages of magmatic differentiation, or anatetic granites. They show increasing peraluminosity and tend to approach to the host rocks location in the projected diagrams. These granitoids are located at the end of the compositional range of the regional S-type magmas, which are related to the anatetic melts generated in the Puncoviscana Fm.

In addition, the emplacement of I-type magmas in the middle crust, where anatexis and deformational processes were occurring simultaneously produce the interaction between intrusive magmas and the partially melted host rocks. This process is recognized in some intrusive

facies present in the Los Cuartos granite suite that show intermediate characteristics between purely calc-alkaline I-type and anatetic S-type magmas. This could be explained by assimilation processes involving the I-type intrusive magmas and the metasedimentary host rocks or hybridization processes between trondhjemite I-type magmas as La Ovejería and El Infiernillo and anatetic S-type melts.

The ongoing detailed structural studies in the region, combined with the geochronology of intrusive and metamorphic units, should provide some keys to understand the processes that conformed the region during the lower Paleozoic.

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## ELECTRONIC APPENDIX I

**TABLE I.** Major (wt. %) and trace element (ppm) composition of representative samples from the La Ovejería Tonalite

Sample	SV-101	SV-102	SV-103	SV-104	SV-105	SV-106	SV-107	SV-108	SV-109	SV-110	SV-111	SV-112	SV-113
Rock Type	Tn	Gr	Tn	Tn	Gr	Tn	Tn						
SiO <sub>2</sub>	63.22	68.49	67.45	72.90	68.56	72.65	67.12	73.21	64.12	70.06	75.57	67.35	63.66
TiO <sub>2</sub>	0.37	0.51	0.61	0.26	0.48	0.26	0.45	0.27	0.56	0.41	0.03	0.52	0.71
Al <sub>2</sub> O <sub>3</sub>	21.42	15.90	16.10	15.01	16.34	14.94	16.92	14.80	18.13	15.51	14.60	16.01	18.13
Fe <sub>2</sub> O <sub>3t</sub>	2.71	3.57	3.82	2.17	3.19	2.30	3.46	2.22	4.27	2.99	0.55	4.01	4.70
FeO <sub>t</sub>	2.44	3.22	3.44	1.95	2.87	2.07	3.12	2.00	3.85	2.69	0.50	3.61	4.23
MgO	0.96	1.58	1.73	0.50	1.25	0.55	1.50	0.57	1.76	1.19	0.06	1.72	1.51
MnO	0.19	0.06	0.09	0.06	0.05	0.06	0.05	0.05	0.09	0.06	0.04	0.07	0.07
CaO	1.70	3.47	3.25	2.56	3.67	2.54	3.94	2.17	4.74	3.20	0.68	3.56	5.01
Na <sub>2</sub> O	6.09	3.53	3.78	3.82	3.87	3.75	3.84	3.83	3.65	3.52	3.78	3.43	3.47
K <sub>2</sub> O	1.29	1.76	1.83	1.91	1.42	1.95	1.68	1.87	1.48	1.53	3.53	2.05	1.46
P <sub>2</sub> O <sub>5</sub>	0.48	0.12	0.12	0.09	0.15	0.09	0.10	0.09	0.19	0.12	0.08	0.14	0.21
Loi	1.06	0.32	0.43	0.43	0.46	0.41	0.37	0.52	0.51	0.52	0.67	0.41	0.46
Total	99.22	98.96	98.83	99.49	99.13	99.28	99.09	99.38	99.08	98.81	99.54	98.88	98.93
ASI (a)	1.48	1.13	1.14	1.15	1.12	1.16	1.11	1.21	1.12	1.17	1.29	1.12	1.11
Eu/Eu* (b)	0.79	1.29	0.97	0.84	1.15	0.86	1.03	0.95	1.28	0.90	0.70	0.89	1.12
La <sub>N</sub> /Yb <sub>N</sub> (b)	8.71	9.28	14.39	13.50	13.51	12.91	13.84	13.26	9.47	17.46	10.99	9.48	6.63
<i>Trace element</i>													
Li	18.05	26.16	57.77	38.91	13.87	36.98	17.56	20.38	16.54	22.19	10.81	32.94	17.88
Be	7.54	1.83	3.38	2.38	1.99	2.20	1.64	1.94	1.98	1.59	4.39	2.20	1.52
Sc	4.66	7.61	9.49	4.34	6.77	4.26	6.23	3.79	8.05	6.02	2.03	9.03	8.39
V	37.76	57.99	60.91	19.65	49.77	18.59	47.75	18.37	57.17	36.13	4.03	66.24	57.47
Cr	23.15	27.42	33.06	17.37	24.94	15.16	24.67	14.87	25.80	21.99	10.96	35.67	20.72
Co	22.43	27.43	28.81	30.90	22.49	20.95	27.27	24.62	25.69	28.62	28.80	28.41	30.69
Ni	10.99	15.06	18.69	10.62	13.52	7.71	13.80	8.23	14.22	13.13	8.47	17.43	9.73
Cu	18.59	6.41	18.06	7.55	22.59	7.15	9.16	8.27	10.79	11.99	3.12	10.99	31.41
Zn	76.75	53.12	61.17	40.83	48.14	39.60	44.85	35.55	48.06	42.95	14.50	61.90	64.14
Ga	26.69	16.73	18.87	16.15	17.84	15.29	16.13	13.84	15.81	14.86	12.00	18.87	20.66
Rb	64.80	57.83	120.27	68.86	47.31	64.77	45.68	53.40	38.04	42.79	89.87	66.05	57.07
Sr	197.99	295.34	283.15	138.61	235.50	128.39	299.90	154.44	333.74	184.84	20.05	302.76	230.85
Y	13.29	4.91	9.00	11.25	8.84	10.23	8.24	8.13	6.97	6.73	4.33	11.26	13.55
Zr	44.27	14.90	17.49	135.78	35.40	122.68	12.88	106.58	11.75	70.52	17.31	22.18	190.76
Nb	14.56	4.90	6.51	6.61	4.43	6.06	4.30	4.43	4.18	4.13	5.35	5.34	6.76
Cs	5.28	3.26	22.15	5.43	2.64	5.22	2.15	5.10	2.64	2.51	5.83	5.93	1.81
Ba	129.94	215.36	250.40	204.84	183.41	196.43	198.43	179.91	128.81	174.82	33.09	271.24	238.23
La	14.78	9.33	17.01	22.70	14.04	20.20	14.31	17.14	8.39	16.42	14.07	18.93	15.98
Ce	25.62	17.25	35.02	40.86	32.13	36.24	27.15	30.82	16.41	33.18	6.95	40.39	29.69
Pr	3.47	2.01	3.95	4.55	3.15	4.06	3.16	3.45	2.01	3.91	1.10	4.35	3.40
Nd	13.19	7.89	14.85	16.85	12.14	14.99	12.36	12.75	8.12	15.03	3.84	16.84	13.52
Sm	2.76	1.76	2.91	3.30	2.48	2.97	2.47	2.52	1.94	3.05	0.85	3.41	3.15
Eu	0.67	0.72	0.87	0.87	0.88	0.80	0.80	0.74	0.80	0.81	0.19	0.96	1.17
Gd	2.37	1.64	2.55	2.97	2.17	2.71	2.27	2.27	1.86	2.45	0.84	3.12	3.22
Tb	0.36	0.22	0.36	0.44	0.33	0.39	0.33	0.34	0.29	0.35	0.14	0.45	0.51
Dy	2.02	1.05	1.86	2.23	1.71	2.07	1.69	1.71	1.56	1.62	0.78	2.42	2.84
Ho	0.41	0.20	0.37	0.46	0.34	0.41	0.34	0.33	0.30	0.29	0.17	0.50	0.58
Er	1.20	0.59	1.05	1.28	0.93	1.17	0.96	0.91	0.84	0.76	0.53	1.38	1.54
Tm	0.17	0.10	0.15	0.20	0.13	0.16	0.13	0.14	0.12	0.11	0.12	0.21	0.26
Yb	1.15	0.68	0.80	1.14	0.71	1.06	0.70	0.88	0.60	0.64	0.87	1.36	1.64
Lu	0.18	0.11	0.13	0.19	0.11	0.18	0.11	0.13	0.09	0.11	0.14	0.20	0.28
Hf	0.95	-0.24	-0.09	2.68	0.34	2.70	-0.33	2.27	-0.34	1.22	-0.38	0.07	3.50

**TABLE I.** (Cont.)

Sample	SV-101	SV-102	SV-103	SV-104	SV-105	SV-106	SV-107	SV-108	SV-109	SV-110	SV-111	SV-112	SV-113
Rock Type	Tn	Gr	Tn	Tn	Gr	Tn	Tn						
Tm	0.17	0.10	0.15	0.20	0.13	0.16	0.13	0.14	0.12	0.11	0.12	0.21	0.26
Yb	1.15	0.68	0.80	1.14	0.71	1.06	0.70	0.88	0.60	0.64	0.87	1.36	1.64
Lu	0.18	0.11	0.13	0.19	0.11	0.18	0.11	0.13	0.09	0.11	0.14	0.20	0.28
Hf	0.95	-0.24	-0.09	2.68	0.34	2.70	-0.33	2.27	-0.34	1.22	-0.38	0.07	3.50
Ta	9.50	2.35	2.54	3.64	1.98	2.72	2.36	2.42	2.22	2.57	3.84	2.35	2.83
Pb	8.53	10.28	10.55	13.34	10.07	12.62	9.55	9.90	8.65	7.46	28.13	10.36	7.73
Th	6.13	1.57	4.40	7.95	5.44	7.25	3.28	6.71	1.03	4.75	1.02	5.59	5.50
U	2.99	0.35	0.48	1.36	0.39	1.21	0.29	1.10	0.37	0.55	1.33	0.53	1.18

Tn: tonalites, Gr: granodiorites

(a) ASI = Mol Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O+CaO)

(b) Chondrite - normalized (Nakamura, 1974)