



PEG 2011  
ARGENTINA

# 5<sup>th</sup> INTERNATIONAL SYMPOSIUM ON GRANITIC PEGMATITES

## ***Field Trip Guidebook***

**"GRANITIC PEGMATITES OF THE SAN LUIS RANGES"**



CONICET



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AGENCIA

NACIONAL DE PROMOCION  
CIENTÍFICA Y TECNOLÓGICA







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—GRANITIC PEGMATITES OF THE SAN LUIS RANGES”

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## **PROGRAM**

*Thursday, February 24<sup>th</sup>, 2011*

- Departure from Mendoza at 8 am.
- Arrival to the Hotel Amerian Park, San Luis. Lodging and lunch.
- Departure to Stop 1: Paso del Rey leucogranite.
- Stop 2: San Luis I & II pegmatites.
- Return to the hotel.

*Friday, February 25<sup>th</sup>, 2011*

- Departure to Stop 3: Cerro La Torre leucogranite.
- Stop 4: Santa Ana pegmatite.
- Box lunch in the field.
- Stop 5: Independencia Argentina pegmatite.
- Return to the hotel.

*Saturday, February 26<sup>th</sup>, 2011*

- Departure to La Toma. Visit stone stores and PG La Toma milling plant of pegmatite raw material.
- Lunch at La Toma.
- Stop 6: visit to Potrerillos granite and Rancul pegmatite.
- Stop 7: La Elsa pegmatite.
- Stop 8: Las Cuevas pegmatite.
- Return to the hotel.

*Sunday, February 27<sup>th</sup>, 2011*

- Departure to La Estanzuela pegmatite field.
- Stop 9: San Elías pegmatite.
- Box lunch in the field.
- Stop 10: La Viquita pegmatite.
- Farewell early dinner.
- Return to Mendoza.

## THE PAMPEAN PEGMATITE PROVINCE

The Pampean pegmatite province (PPP) was defined to include the economic fields of granitic pegmatites of central and northwestern Argentina (Galliski 1992, 1994a, 1994b, 2009). It contains more than 95% of the granitic pegmatites of the country, with mineral resources that had been mined during the past 80 years, producing the majority of the feldspar, quartz and mica plus Be-, Li-, Ta-, Bi- and Rb-bearing minerals. The PPP extends discontinuously for more than 800 km N-S and 200 km E-W, from 24°30' to 33°30'S, mostly in the Sierras Pampeanas of northwestern and central Argentina (Fig. 1), but the three northern districts are in the southern part of Cordillera Oriental and the adjacent mountain block of Puna. Its possible extension to the South could be even more than 400 km as indicated by discontinuous outcrops under recent cover that reach the province of La Pampa.

### The Tectonic Setting

The orogenic pegmatite fields of the Pampean pegmatite province developed mainly in the early Paleozoic, during the Pampean (~550-520 Ma) and especially Famatinian (~500-435 Ma) orogenic cycles, along a pericratonic mobile belt located in the western protomargin of Gondwana. The tectonic evolution of this mobile belt is complex and it includes the accretion of several terranes (*Cf.* Collo *et al.* 2009). Significant facts in the geological evolution of the pegmatite province include: (1) the ensialic deposition of several thousand meters thick psammopelitic succession of sediments, represented by the Puncoviscana Formation and equivalent protoliths, during the Late Proterozoic - Early Cambrian, and (2) the Upper Ordovician collision of the Precordillera terrane. The present tectonic setting that exposes the pegmatite province in faulted blocks eastward of the Andean Cordillera, results from the flat subduction geometry of the Nazca plate under this segment of the South America plate.

### The Distribution of the Pegmatite Fields

#### *The orogenic pegmatite fields*

The orogenic pegmatite fields encompass pegmatites of muscovite, muscovite-rare-element and rare-element classes using the classification of Černý & Ercit (2005). The distribution of the economic pegmatite fields is

plotted in Figure 1. The muscovite class pegmatites are dominant in three fields aligned in the western side of the province, and one in the eastern side.

The different fields from the rare-element pegmatite belt belong to the LCT (Li, Cs, Ta) petrogenetic family. They are aligned N-S and mostly hosted in medium-grade metamorphic rocks, preferentially in amphibolite facies from an Abukuma-type metamorphic belt, that suffered polyphase deformation during the Pampean and Famatinian orogenic cycles. Along the rare-element belt the lithium bearing pegmatites crystallized under increasing pressure conditions from the petalite-subtype pegmatites of the El Quemado district in the north, passing through the spodumene-subtype pegmatites of Ancasti district in the middle, and finishing in the economic pegmatite fields of the San Luis ranges.

The Conlara, Totoral and La Estanzuela pegmatite fields are located in the San Luis ranges and have an important past record of producing mica, beryl, spodumene, tantalite, and lastly, K-feldspar, albite and quartz. These districts are hosted in metamorphic complexes of medium grade, intruded by orogenic and postorogenic granites. The medium-sized pegmatites are representative of several types and subtypes as beryl-columbite-phosphate, spodumene, albite-spodumene and albite. The K-Ar ages of the pegmatites from this belt, except for the Córdoba districts, are grouped in the Lower Paleozoic, in good correlation with the granitic magmatic of the Famatinian orogenic cycle. They are genetically linked to a suite of two- mica, or muscovite-tourmaline leucogranite, which usually are small to medium size composite intrusive of variable fabric, within the aplite to pegmatite range. They are peraluminous, low-Ca calc-alkaline rocks that have high LILE and volatile contents, especially B and P. They have total REE depleted contents and high initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $\geq 0.71$ ). Most of these S-type leucogranite and associated pegmatites are syn- to late-kinematic and were slightly or strongly deformed during the late-stage phases of the Famatinian deformation. The most favored model for the origin of this suite comprises episodic crustal anatexis, produced by muscovite  $\pm$  biotite dehydration melting, of dominant Puncoviscana protoliths by shear-heating during a collisional orogeny, as proposed by Nabelek & Liu (2004) for other regions (Galliski 2009).



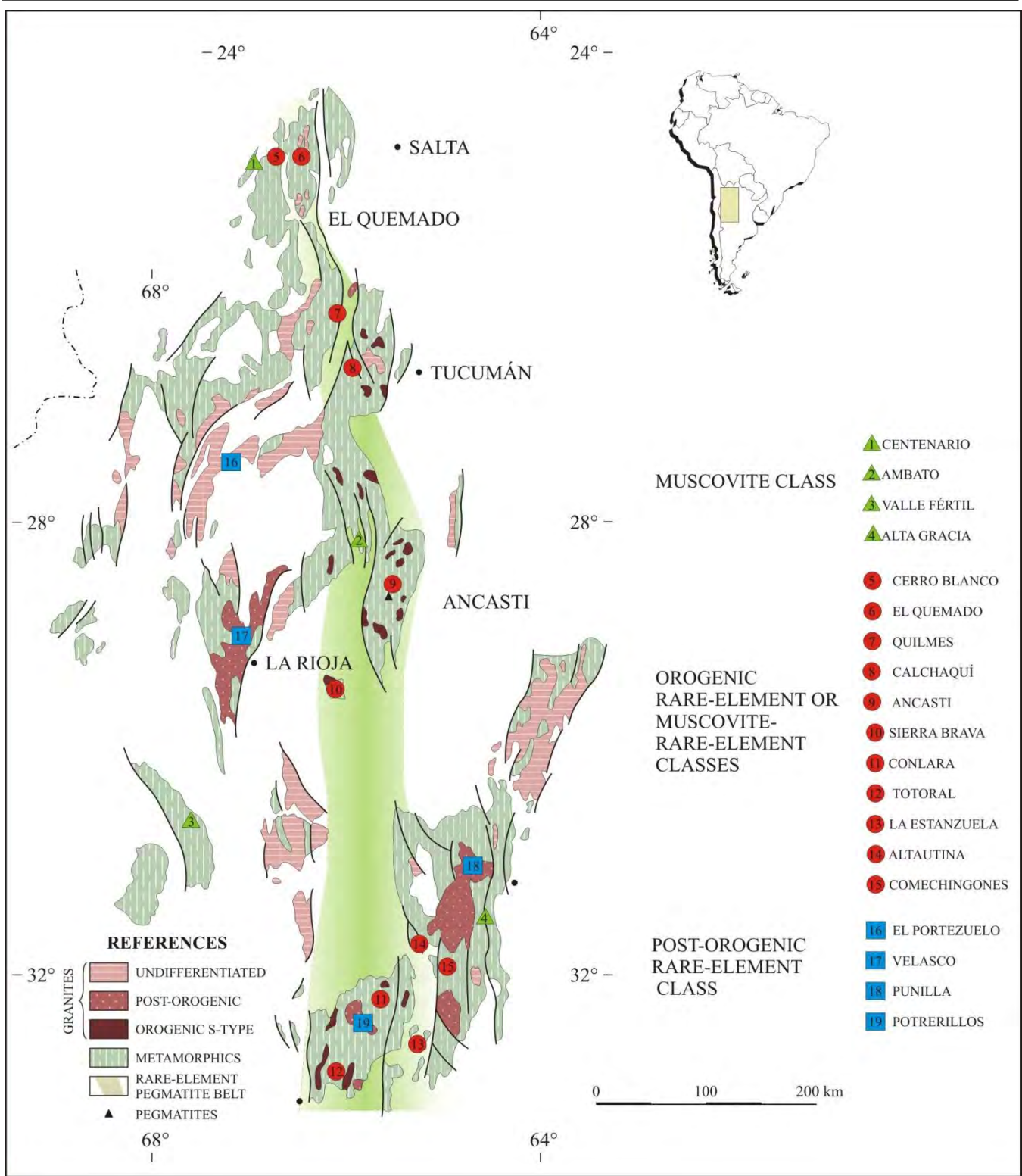


Figure 1: Schematic geological map of the Pampean pegmatite province showing the main lithological units and the distribution and classes of the pegmatite economic fields (modified from Galliski & Černý 2006)

This collisional leucogranite suite is space-related to another suite of TTG dominant lithology, which includes some more basic intrusives; it is also calc-alkaline, peraluminous, and has lower  $^{87}\text{Sr}/^{86}\text{Sr}_i$  ratios ( $\sim 0.706$ ). This last suite has been considered of I-type and related to a subduction setting, with variable lower crust component and possible assimilation of supra-crustal protoliths (Pankhurst *et al.* 2000).

#### *The post-orogenic pegmatite fields*

The granitic pegmatites of this kind form distinctive units in the El Portezuelo (Papachacra) and Potrerillos groups, and Velasco and Punilla districts. The pegmatites of the El Portezuelo group belong to the miarolitic class, miarolitic-rare-element subclass, possibly of gadolinite-fergusonite type and NYF (Nb, Y, F) petrogenetic family (Colombo 2006). The pegmatites from the Velasco district are units of beryl-columbite-phosphate subtype contained in the Huaco sieno- to monzogranite, dated at 350-358 Ma (Grosse *et al.* 2008). The pegmatites of the Punilla field are rounded bodies, similar to the Velasco ones, but generally larger, with more varied mineralogy, and contained in porphyritic granites of the Achala batholith, dated at  $368 \pm 2$  Ma (Dorais *et al.* 1997). Except for the El Portezuelo miarolitic pegmatites that have a diagnostic NYF mineralogy, and the Potrerillos pegmatites that locally have primary fluorite, monazite-(Ce) and ilmenorutile suggesting the same signature, the pegmatites of the other districts are difficult to classify because they lack typical diagnostic paragenesis.

In general, the parental granites of these pegmatites form composite batholiths or stocks lacking post-emplacement deformation, that were intruded in upper- to medium upper crust levels (P 150-250 MPa), mostly during the Lower Carboniferous. Petro-graphically, they are generally biotite porphyritic granites to monzo- or sienogranites,

locally showing K-feldspars with incipient rapakivi-like textures. They are usually high silica, meta- to mildly peraluminous, high-K calc-alkaline granites, with Fe-, Mg-, and Ca-contents higher than the orogenic leucogranites. Commonly, these granites are moderately LIL and HFSE enriched. The initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, if not disturbed, are generally low to medium (0.703-0.706); the contents and normalized REE patterns, and  $\delta^{18}\text{O}$  values are most likely comparable to those of the NYF petrogenetic family. These attributes suggest that this is a post-orogenic suite probably of aluminous A-type granites, intruded in an intraplate tectonic setting. In the El Portezuelo and Huaco granites the genetic interpretation favor a mixed source with melting of crustal I-type granite protoliths, previously metasomatized by a mantle fluid component (Colombo 2006, Grosse *et al.* 2008).

#### **Concluding Remarks**

The framework for the geological evolution of at least the Famatinian representatives of the Pampean pegmatite province comprises basically three major episodes: (1) intrusion of muscovite class pegmatites, poorly or non-connected with parental granites, in a MP-MT metamorphic environment generally westward of, (2) a LCT rare-element pegmatite belt and the parental collisional leucogranites placed at the axis of a LP-MT metamorphic belt developed in the Upper Ordovician during the Famatinian tectonic cycle, and (3) occurrence of a suite of rare-element pegmatites, locally with definite NYF signature, mostly contained in post-orogenic granites that form major composite batholiths or minor plutons, possibly of aluminous A-type granites intruded during the Lower Carboniferous in an intraplate tectonic setting. Comparing with the Eastern Pegmatite Province of Brazil, the PPP has a pericratonic tectonic setting and its radiometric ages are slightly younger.

## THE PEGMATITE FIELDS OF SAN LUIS RANGES

The three pegmatite fields of the San Luis province are located in different mountain blocks. El Totoral and

Conlara are placed in the Sierra Grande de San Luis and La Estanzuela is situated in the La Estanzuela, El Portezuelo, and Tilisarao ranges (Fig. 2).

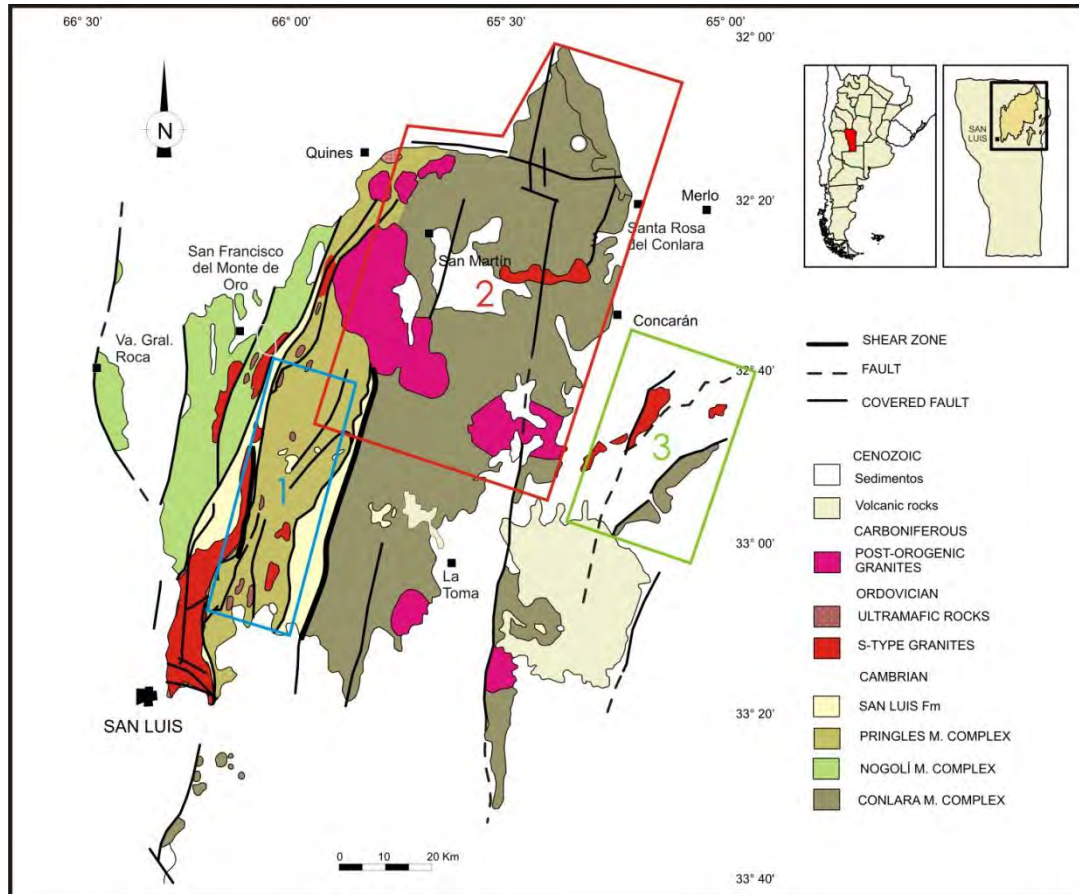


Figure 2: Schematic geological map of the San Luis ranges showing the location of the 1: El Totoral, 2: Conlara and 3: La Estanzuela pegmatite fields.

## THE TOTORAL PEGMATITIC FIELD

The Totoral pegmatite field (TPF) is the southernmost of the Pampean pegmatite province (Galliski 1994a, b) and it is located at  $32^{\circ} 53' 33'' 01' S$  and  $65^{\circ} 55' 66'' 00' W$ , in the Pampean Ranges of San Luis Province, Argentina (Fig. 3). The granitic rocks of the TPF intrude the Pringles Metamorphic Complex (PMC), formed mainly by a thick psammopelitic sequence that undergoes mostly high-T low-P metamorphism in the lower Paleozoic during the Pampean and Famatinian cycles (Sims *et al.* 1997).

Stenken *et al.* (2006) discussed the previous works and based in new SHRIMP U-Pb data concluded that the protoliths of the unit was deposited in the Pacific margin of the nearby Pampean orogen in the early to mid-Cambrian, and that the metamorphism took place between  $498 \pm 10$  and  $456 \pm 19$  Ma. The metamorphic host-rocks of the TPF are fine-grained gneisses and, predominantly, Mu-Qtz-Bt-Grt-Chl-Pl-Mc-Sil-Crd $\pm$ Tur $\pm$ Ap $\pm$ Zrn $\pm$ Ep $\pm$  Hem (symbols according to Kretz 1983) schists that eastward grade to phyllites and were formed at  $\sim 450$ - $500^{\circ}C$  and 2-4 kbars.



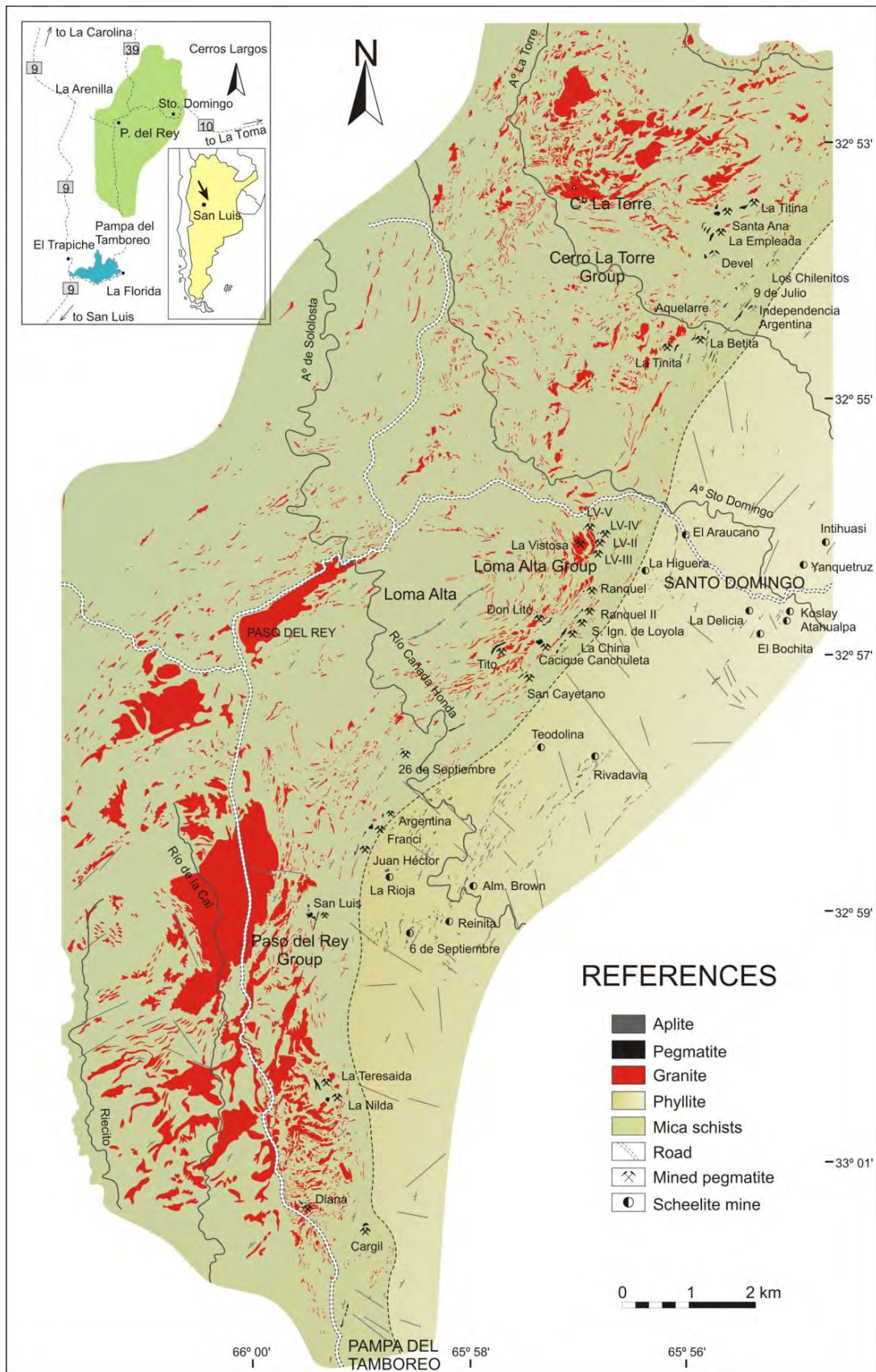


Figure 3: Geological map of the El Totoral pegmatite field showing the distribution of the different pegmatites and their parental leucogranites (modified from Oyarzábal *et al.* 2009).

The TPF (Oyarzábal *et al.* 2009) comprises a swarm of rare-element pegmatites of LCT (Li-Cs-Ta) petrogenetic family that forms a 17 Km long NNE-SSW trending belt outcropping on the eastern flank of Cerro La Torre and Loma Alta - Paso del Rey granitic intrusives. The pegmatites belong to different kinds: (1) barren-transitional to beryl type, (2) beryl type of beryl-columbite-phosphate subtype, (3) complex type of spodumene subtype, (4) albite-spodumene type and (5) albite type. The pegmatites carried a rare-element mineralization mined in the middle of the last century by beryl, tantalite and spodumene (Herrera 1963, Angelelli & Rinaldi 1963), and more recently by industrial minerals.

### THE GRANITES – PASO DEL REY LEUCOGRANITE

The representative magmatic units comprise Cerro La Torre and Loma Alta - Paso del Rey pegmatitic leucogranites. These granites have heterogeneous fabrics that include potassic pegmatitic pods with a high content of common accessory minerals, and extensive sodic replacements.

TABLE 1: AGES OF GRANITIC IGNEOUS ROCKS FROM THE TOTORAL PEGMATITE FIELD

Rock	Age	Method	Mineral	Ref.
Paso del Rey leucogranite	454±21	Rb-Sr	whole rock	1
	608±26	U-Pb SHRIMP	zircon	2
	456±30	U-Pb SHRIMP	zircon	3
	597±54 to 491±19	<sup>207</sup> Pb/ <sup>206</sup> Pb evaporation	zircon	4
Pegmatites				
Victor Hugo	503±24	K-Ar	muscovite	5
C.Canchuleta	433±33	K-Ar	muscovite	5
San Luis I	317±11	K-Ar	muscovite	5
	450±10-12	U-Pb	tant-(Mn)	6
Pegmatite	444±9	K-Ar	muscovite	7
	398±9.2	K-Ar	muscovite	7
Santa Ana	455±25	U-Pb	uraninite	8
	465±15	U-Pb	uraninite	8
<sup>1</sup> Llambías <i>et al.</i> (1991)		<sup>5</sup> Galliski & Linares (1999)		
<sup>2</sup> von Gosen <i>et al.</i> (2002)		<sup>6</sup> von Quadt & Galliski (2011)		
<sup>3</sup> Steenken <i>et al.</i> (2006)		<sup>7</sup> López de Luchi <i>et al.</i> (2002)		
<sup>4</sup> Steenken <i>et al.</i> (2008)		<sup>8</sup> Linares (1959)		

The modal composition (Fig. 4a) grades from granodiorite to granite, nevertheless strong fractionation gradients are observed from granodioritic to garnet-, tourmaline- and muscovite- alkali-feldspar granitic dominant facies (Fig. 4b). According to discriminant plots of tectonic setting, both stocks can be considered like syn-collisional; however, some evidences allow proposing that the emplacement mechanism predates the main deformation event. The granites are silicic, peraluminous S-type, low in Ca, Mg, Fe, Sr, Ba, Ti and Sr. Their REE pattern (Fig. 4c) are similar to the tourmaline-muscovite granites of the Black Hills (Nabelek & Liu 2004). The Paso del Rey leucogranite gave an <sup>87</sup>Sr/<sup>86</sup>Sr initial ratio of 0.7118 (Llambías *et al.* 1991). López de Luchi *et al.* (2007) grouped them in an Ordovician granodiorite-granite suite (OGGS), comprising two different subgroups based in Zr thermometry, both showing some evidence of solid-state deformation, and considering them the result of orogenic partial melting of graywacke protolith during the Famatinian (Lower Paleozoic) orogeny. Different ages for these granites have been published in many studies and they are quoted in Table 1.

### Geology and types of pegmatites

The pegmatites of the TPF have been classified in the following types and subtypes into the rare-element class, after the systematic of Černý & Ercit (2005): (1) barren-transitional to beryl type pegmatites: La Vistosa (and their nearby deposits La Vistosa II, III, IV and V), (2), beryl type, beryl-columbite-phosphate subtype pegmatites: **Santa Ana, La Empleada**, Los Chilenitos, Ranquel and Cacique Canchuleta, (3) complex type, spodumene subtype: **San Luis II** and La Teresaida, (4) albite-spodumene type: **San Luis I** and Diana, and (5) albite type: **Independencia Argentina** and Aquelarre (**bold** occurrences will be visited).

The barren-transitional to beryl type pegmatites belong to the Loma Alta pegmatite group and they are hosted into mica-schists or minor leucogranitic lenses. The emplacement has been permissive, with strong structural control, along to a sub-parallel joint pattern. The pegmatite occurrences consist on five dyke-like deposits, the greater one is 12 m wide and 105 m long; they are slightly zoned, with border (Qtz-Ms±Grt), wall (Mc-Qtz-Ms>Bt±Tur-Grt-Ap), intermediate (Mc-Qtz-Ms±Tur) and core (Qtz±Brl) zones (Oyarzábal *et al.* 2009).

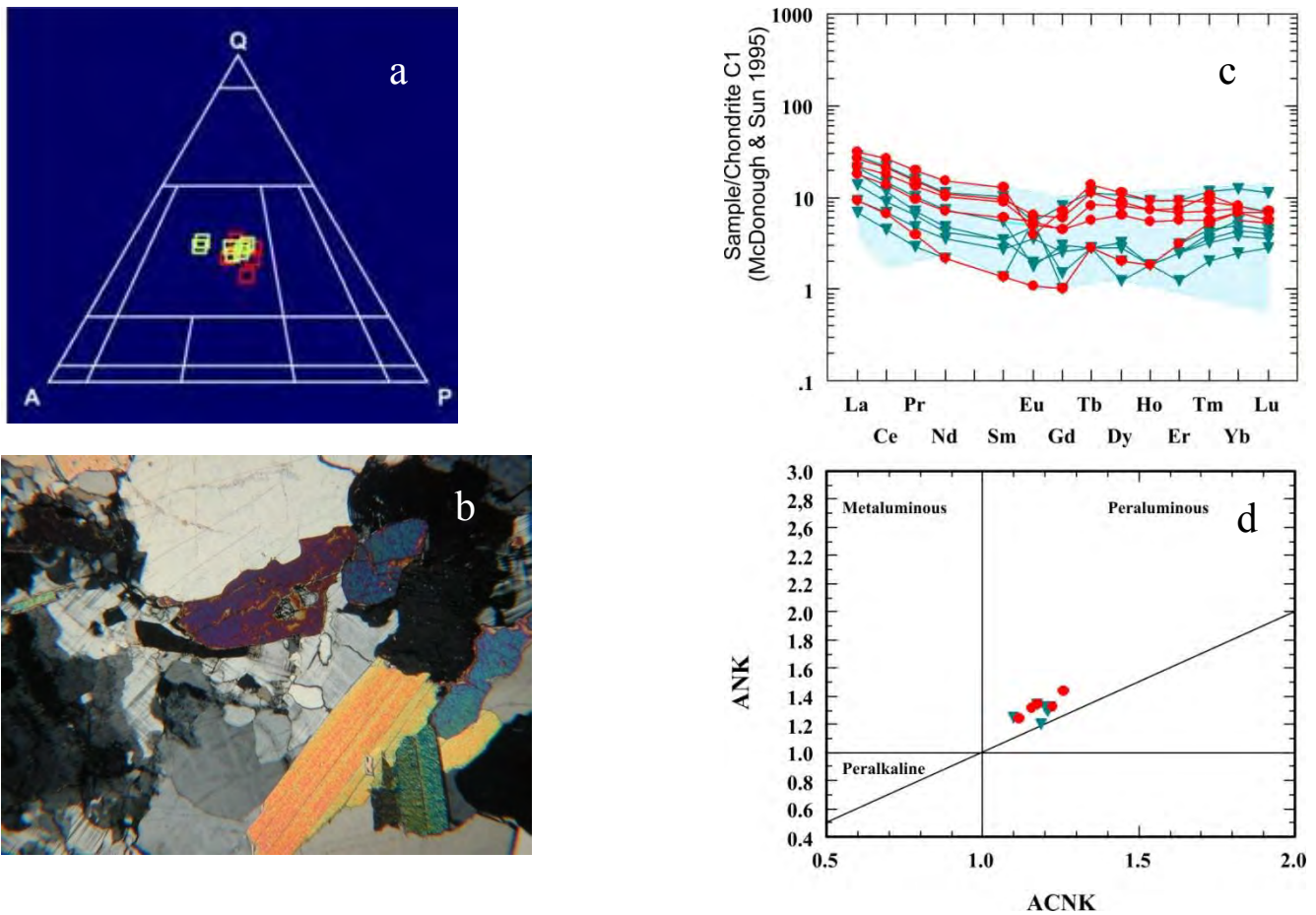


Figure 4a: Modal composition of the Paso del Rey leucogranite plotted in the QAPF triangular diagram, yellow squares correspond to medium-grained samples, red squares to pegmatitic facies; 4b: photomicrograph of a tourmaline-muscovite leucogranite of Paso del Rey; 4c: REE diagram with the samples of Paso del Rey and Cerro La Torre leucogranites (red and bluish respectively) with the domain of Harney Peak granites after Nabelek & Liu (2004); 4d: ASI index in the diagram for the considered leucogranites.

The beryl-columbite-phosphate subtype of beryl type pegmatites is located in two different places: at the southeastern part of the Cerro La Torre granite and at the southeastern area of the Loma Alta group. In general, the pegmatite outcrops are 60-90 m long and less than 30 m wide, and occur as single tabular to lenticular-like bodies intruded with sharp contacts in mica-schist host rocks. Their internal structure ranges from moderately to well zoned, showing the following units: border, wall, intermediate and core (Qtz±Brl) zones. The primary mineral association comprises Qtz-Mc-Ab-Ms-Brl-Col-Tur-Ap-Grt; primary phosphate minerals of the triphylite-lithiophilite and beusite-grafonite series occur in the most internal units and originate, by a late-stage hydrothermal overprint, a myriad of secondary Mn-Fe-(Al-Ca-Li) phosphates.

The complex type, spodumene subtype pegmatites are located in the southernmost part of the TPF, emplaced in

mica-schists and close to the Paso del Rey granite. The pegmatites show tabular morphology and evidences of deformation during and after their emplacement. San Luis II is located inside some of the anticlinal crests of a folded albite-spodumene type pegmatite, named San Luis I. The internal structure is complex, consisting of border (Ms-Qtz ± Bt-Grt-Ap), wall (Mc-Qtz-Ms-Spd), intermediate (Mc-Qtz-Spd± Ms-Ab) and core (Qtz) zones; spodumene forms giant prismatic crystals (~ 2 m long) hosted in massive quartz. This last unit contains some reworked triphylite-lithiophilite nodules. The Ms-Ab replacement units contain columbite-(Mn), tantalite-(Fe) and tantalite-(Mn) as accessory minerals (Galliski & Černý 2006).

The albite-spodumene type pegmatites have tabular shape with high axial ratio. They have albite and quartz dominant over spodumene and K-feldspar in composition, and a homogeneous and symmetric



internal structure, with a predominant internal zone of elongated microcline and spodumene crystals enclosed in a medium-sized Ab-Qtz-Spd±Ms-Ap-Grt matrix. The prismatic microcline and spodumene crystals display parallel orientation forming comb-structure across the pegmatite. San Luis I pegmatite has been synkinematically intruded and folded during a strong compressional event.

The albite type pegmatites have been recognized in a restricted area located in the southeastern area of the Cerro La Torre group. The most conspicuous exponents are Independencia Argentina, studied in detail by Galliski *et al.*, (1994) and Aquelarre pegmatites; both of them are tabular bodies, with approximately 200 m long and 5-20 m wide, with N35°-40°E strike and 45°-70°W dip. They are asymmetrically zoned, with border (Ab-Qtz±Ms-Ap), wall (Qtz-Ab), outer intermediate (Ab-Qtz±Ms), middle intermediate (Ab-Qtz-Spd±Ms), inner intermediate (Ms-Qtz±Ab) and core (Qtz±Ms) zones, and a fine-grained Ab-bearing replacement unit (Ab±Qtz-Ms-Ap-Col).

### Geochemistry

The chemistry of the K-feldspar and muscovite from coarse-grained facies of granites and pegmatites reflects that: (1) all pegmatites show a progressive trend of geochemical evolution from barren-transitional to beryl type to albite type pegmatites, the evolutionary level reached by each one of them is similar to the reported in other fields for pegmatites of identical types; (2) K-feldspar from granites show, in their more evolved facies, concentrations in trace elements according with their fractionation trends, and (3) it is possible to relate genetically the granites with the pegmatites in terms of a tendency of continuous variation, extended from less evolved granitic facies to more geochemically specialized pegmatites.

The K/Rb-Cs (Fig. 5), K/Cs-Rb, K/Rb-Rb/Sr and K/Rb-Ba diagrams for K-feldspar from granitic facies and intermediate zones of pegmatites allow to establish a specific domain for fertile granites in rare-element pegmatites and a clear fractionation trend that defines four successive fields assigned at pegmatite groupings of identical types: I) barren to poorly beryl- mineralized pegmatites (La Vistosa), II) beryl type, beryl-columbite-phosphate subtype pegmatites (Los Chilenitos, La Empleada, Santa Ana, Ranquel and Cacique Canchuleta), III) complex type, spodumene subtype (San Luis II and La Teresaida) and albite-spodumene type pegmatites (San Luis I and Diana), and IV) albite type pegmatites

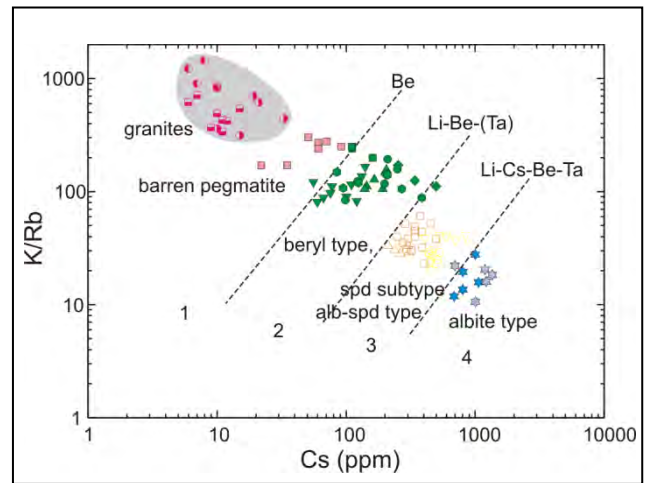


Figure 5: K/Rb vs Cs diagram for K-feldspar from the granites and intermediate zones of different kind of pegmatites of the TPD. The symbols are:  $\blacksquare$  C° La Torre,  $\bullet$  Loma Alta,  $\blacklozenge$  Paso de Rey,  $\blacktriangle$  La Vistosa,  $\blacktriangle$  Los Chilenitos,  $\blacktriangledown$  La Empleada,  $\bullet$  Santa Ana,  $\blacklozenge$  Ranquel,  $\blacklozenge$  Cacique Canchuleta,  $\blacktriangle$  San Luis II,  $\blacklozenge$  La Teresaida,  $\blacktriangledown$  San Luis I,  $\bullet$  Diana,  $\blackstar$  Independencia Argentina,  $\blackstar$  Aquelarre.

(Aquelarre and Independencia Argentina). It was not possible to recognize between pegmatites of the complex type, spodumene subtype, and albite-spodumene type, since these two kind of pegmatites differ more in their internal structure than in their composition otherwise equivalent (Černý 1991). These domains attributed to different types of pegmatites could be named in terms of their economic mineralization as barren, beryl-bearing, lithium-bearing and albite-bearing pegmatites. The boundaries that define these domains are similar to the specified ones by Galliski *et al.* (1997) for pegmatites from the Pampean pegmatite province.

The cesium concentration in early muscovite from pegmatites is similar to the concentration in K-feldspar in all studied deposits, and constitutes an excellent indicator of evolved trends in pegmatites of the TPF. Except in beryl type pegmatites, the content of this trace element in muscovite allows to identify very specific domains for different pegmatite types.

The K/Rb-Ba diagram for K-feldspar discriminates the Cerro La Torre from Paso del Rey and Loma Alta granites because the former one is depleted in barium content. In addition, if the great dispersion of data is diminished and only the average values are considered, a similar tendency can be observed in other variation

diagrams. This means that Cerro La Torre is the more fractionated granite, and this statement is in agreement with the modal and normative compositions, bulk chemical analysis composition and petrological characteristics of the TPF granites (Oyarzábal, 2004).

In muscovite from pegmatites, barium exhibits a good correlation respect to the pegmatite evolution and allows identifying two compositional extremes assigned to barren-transitional to beryl type and albite type pegmatites. The values corresponding to beryl- and spodumene-bearing pegmatites show a considerable dispersion.

In the K/Rb-P<sub>2</sub>O<sub>5</sub> diagram (Fig. 6), the 0.1 wt. % P<sub>2</sub>O<sub>5</sub>

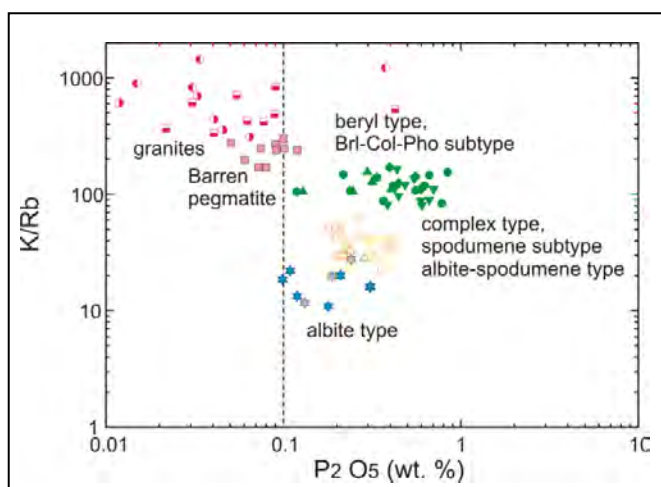


Figure 6: K/Rb vs. P<sub>2</sub>O<sub>5</sub> diagram for K-feldspar from the granites and intermediate zones of different kind of pegmatites of the TPD. Symbols are the same that in Figure 5.

border line separates granites and barren deposits of mineralized pegmatites. However, the phosphorous content in K-feldspar does not vary according to the geochemical evolution of the pegmatites; instead, higher contents indicate high levels of concentration of this element in the melt from the earliest stages of pegmatite consolidation. In some beryl-rich pegmatites such as Santa Ana, La Empleada, Ranquel and Cacique

Canchuleta, the primary phosphate minerals are volumetrically very important, and consequently their K-feldspar exhibits a relatively high concentration of phosphorous.

P<sub>2</sub>O<sub>5</sub> exhibits a greater affinity for K-feldspar than for muscovite, because generally in micas their concentration is very small and there is no direct relation between the content of this element and the type of pegmatite or the concentration of phosphate minerals. This different behavior of phosphorous in both silicates is explained by the “beryllite substitution” in the structure of K-feldspar (London 1992).

### Concluding remarks

The close-space associations of granites and pegmatites, the variation in the mineralogy and distribution of different types of pegmatites and, especially, the geochemistry in some major and trace elements of the K-feldspar and muscovite from the coarse-grained facies of granites and pegmatites of the TPF show that:

- 1) The granites and pegmatites form a rare-element pegmatitic field in which different magmatic units are petrogenetically linked forming a fractionation trend extended from the less evolved granitic facies to the most geochemically differentiated pegmatites.
- 2) The pegmatites show a progressive trend of geochemical evolution from barren-transitional, beryl type, complex type of spodumene subtype ending with albite type pegmatites. The evolutionary level reached by each one of them is similar to the reported one in other fields for pegmatites of identical types.
- 3) In agreement with the paragenetic associations, the contents of K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Ba, Sr, Rb and Cs that plot in the variation diagrams forming an almost continuous fractionation trend show the parental affinities of this suite of S-type granites and its swarm of rare-elements pegmatites.

SAN LUIS I AND II PEGMATITES

*Geological Setting and Internal Structure*

The San Luis mine is located at lat. 32°59'20" S and long. 65°59'30W in the El Totoral pegmatite field. The host rock of the pegmatite is a Mu-Bt-Qtz-Pl-St-Sill-Chl-schist of the Pringles Metamorphic Complex (Sims *et al.* 1997)

intruded by the Paso del Rey S-type leucocratic granite of possible Ordovician age. The San Luis pegmatites are located approximately 300 m to the east of the border of the leucogranite. To the east of the pegmatites, the metamorphic grade diminishes slowly to phyllites first and then to slates. Westward of the Paso del Rey granite, the metamorphic grade increases slowly along several km up to gneisses.

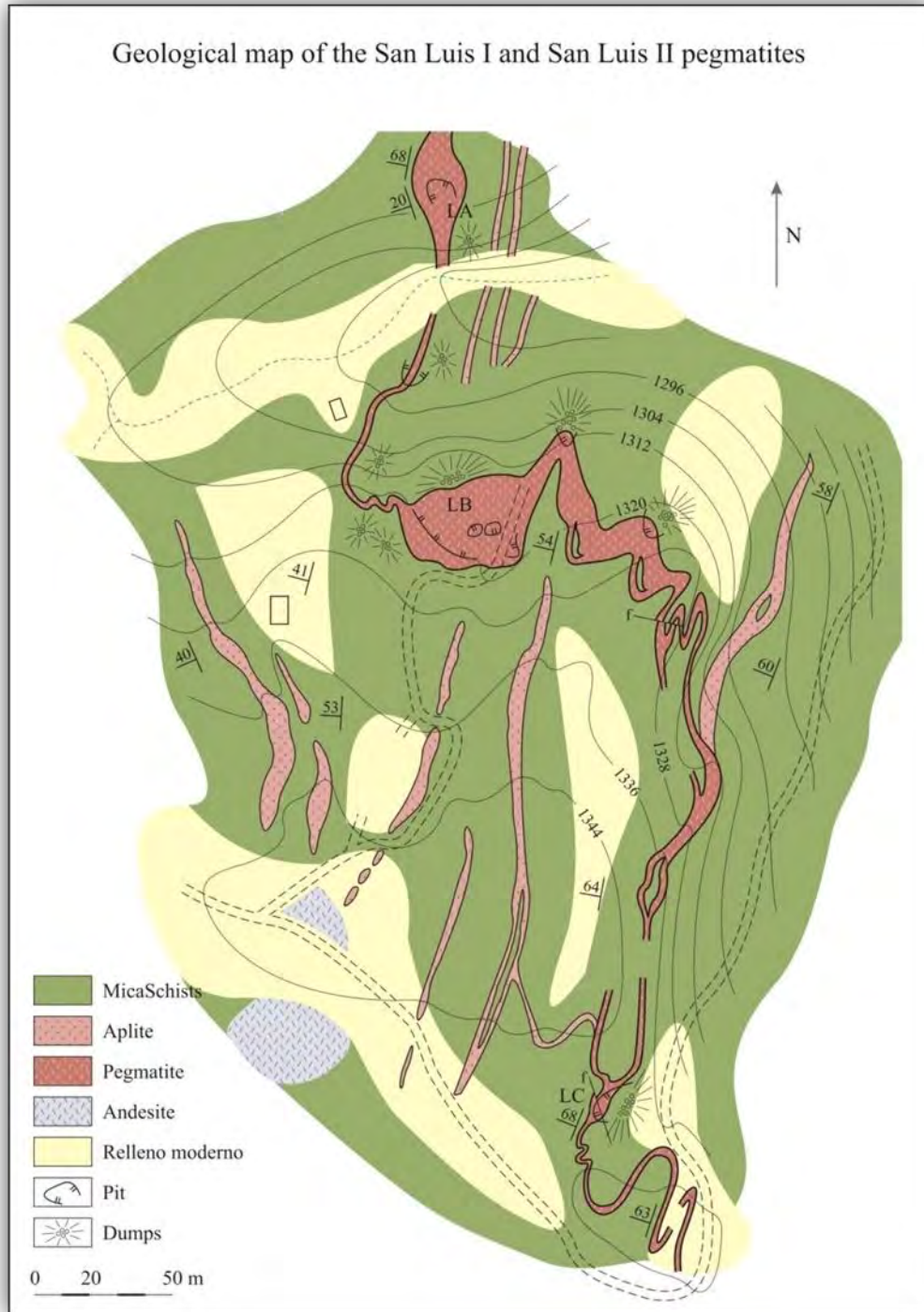


Figure 7: Schematic geological map of the San Luis pegmatites.



The San Luis deposits comprise two rare-element pegmatites placed together called San Luis I (SLI) and San Luis II (SLII) which description is mainly based in Oyarzábal & Galliski (1993). The San Luis I (SLI) is an albite-spodumene type of pegmatite with a variable thickness between 2 and 12 m and more than 1000 m long (Fig. 7 and 8). It is a zoned pegmatite with border-wall and internal zone. The border-wall zone reaches a maximum of 0.40 cm; it is fine-grained and is formed by oriented prismatic crystals of spodumene totally replaced by muscovite,

contained in a groundmass of Qtz (40%), Ab (30%) and Kfs (25%), with Grt, Ap and Tur as accessories. The contact with the host-rock is silicified and tourmalinized. Some dm-sized prismatic crystals of Kfs pass from the wall to the internal zone. The internal zone is homogeneous with very well developed Unidirectional Solidification Texture, with prismatic megacrystals of Kfs of 50-60 cm or up to 1.2 m long. The groundmass of this zone is greenish gray, fine-grained and with variable composition from outside inward:

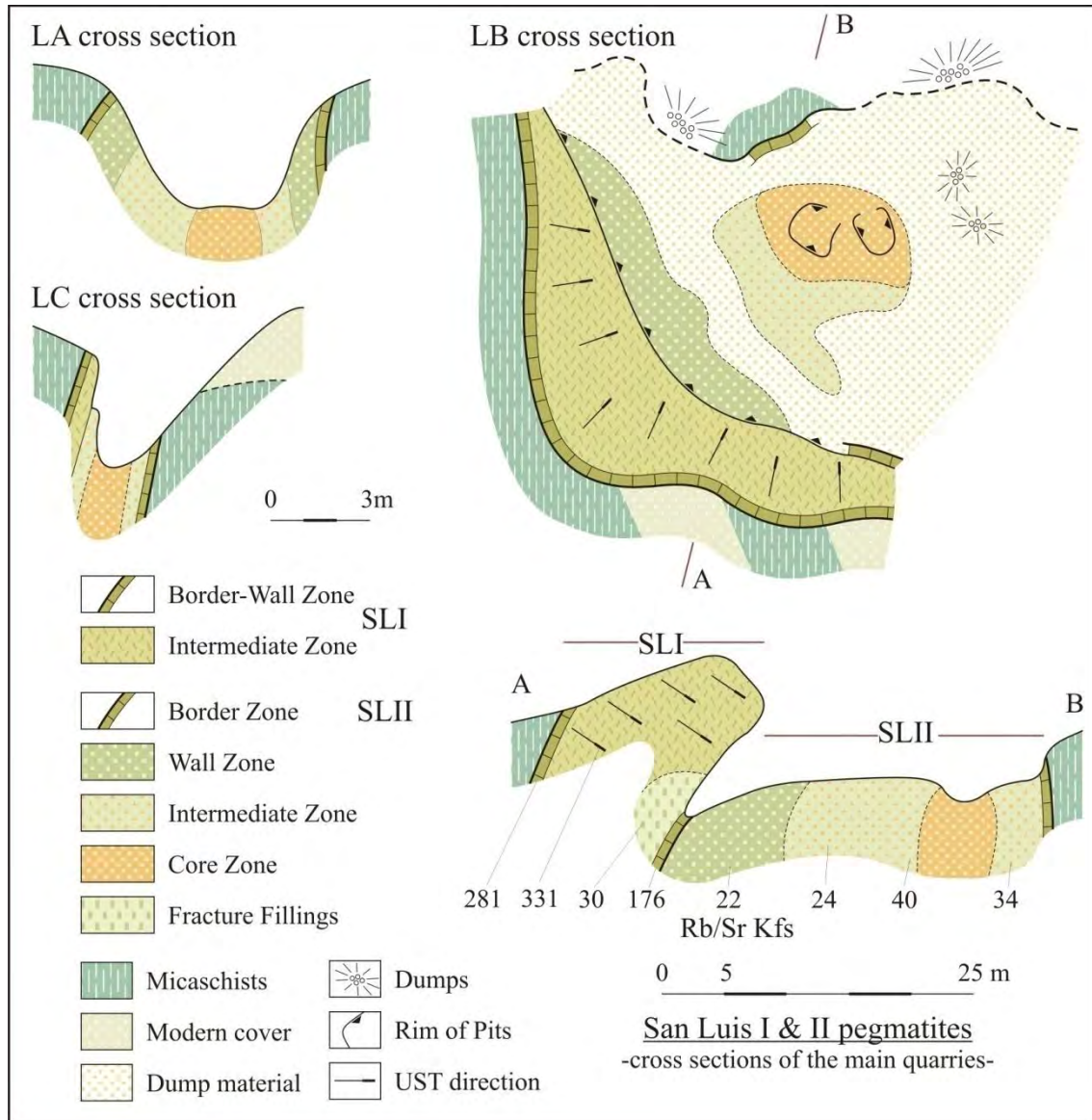


Figure 8: Schematic cross-section of the San Luis pegmatites.

Qtz 50-25%, Ab 25-35%, Spd 25-35, Ms <5-2 %. Minor accessory minerals are garnet, greenish apatite, and scarce schorl. In the footwall of this unit, in the main quarry, the spodumene prismatic crystals reach up to 30 cm long and

are tipped with the tip up. These crystals are associated with muscovite and gray quartz. This assemblage is intruded by fracture filling units of coarse-grained microcline, quartz, spodumene and muscovite.

The main outcrop of the San Luis II pegmatite is visible in the core of a fold of SLI located in the main quarry. The exposed surface is partially covered by dumps but a careful inspection can recognize zoning and the presence of border, wall, intermediate, and core zones. The border zone only occurs in the West side of the quarry and grades to Mc + Qtz from the wall zone. Increasing grain size and the first occurrence of spodumene mark the passage to the intermediate zone composed by microcline in 2 m crystals, silicified 1.5 m long spodumene crystals, interstitial quartz, albite and muscovite. This zone increases inward the grain size and the modal proportion of quartz and spodumene and grades to the core zone formed by these two minerals. In the core margin association occasionally occur nodules of phosphates, beryl, and replacement units composed by fine-grained muscovite and albite with columbite-group minerals. The quartz core and the intermediate zone have fracture fillings of opal.

### Mineralogy

The combined mineralogy of both pegmatites comprises: plagioclase, K-feldspar, quartz, spodumene, muscovite, garnet, beryl, tourmaline, zircon, columbite-group minerals, apatite, triphylite, ferrisicklerite, mitridatite, dufrenite, pyrite, calcite, opal, and Mn-oxides.

Plagioclase: it is usually of fine grain and anhedral and its composition goes from An<sub>18</sub> in the wall zone to An<sub>8</sub> in the internal zone. Cleavelandite (An<sub>2.5</sub>) is frequent in SLII in radial aggregates or broken transparent crystals.

K-feldspar: it is normally microcline with high degree of (Al:Si) order usually fresh but sometimes replaced by muscovite or is slightly caolinized. It includes grains of smoky quartz, muscovite or spodumene. Late-stage, partially lixiviated, microcline of this occurrence was investigated by Černý *et al.* (2003), who found that the cavity-lining K-feldspar shows considerable alteration and overgrowth by low-temperature phases, indicative of substantial hydrothermal activity, which promoted (Al:Si)-ordering to give low microcline in both the primary perthitic crystals and the nonperthitic overgrowths.

Spodumene: occurs in three different assemblages: (i) as 3 to 12 cm long prismatic crystals embedded in Ab+Qtz+Mu matrix in SLI, (ii) as 30 cm long tipped crystals in filling units of SLII that cut SLI and (iii) as giant meter-long prismatic crystals sometimes silicified in the intermediate and core zones of SLII.

TABLE 2: CHEMICAL ANALYSES OF CGM FROM SLII

Sample	LU4AA	LU4B	LU4C	LU6A	LU7FB	LU7FC
WO <sub>3</sub>	0.00	0.25	0.00	0.25	0.14	0.00
Nb <sub>2</sub> O <sub>5</sub>	28.90	31.38	28.48	22.20	54.30	43.70
Ta <sub>2</sub> O <sub>5</sub>	52.70	49.48	53.95	60.00	25.10	36.00
TiO <sub>2</sub>	0.47	0.52	0.39	0.59	0.59	0.85
ZrO <sub>2</sub>	0.04	0.33	0.15	0.00	0.00	0.18
SnO <sub>2</sub>	0.29	0.26	0.00	0.00	0.01	0.03
UO <sub>2</sub>	0.40	0.33	0.13	0.04	0.23	0.15
As <sub>2</sub> O <sub>3</sub>	0.04	0.03	0.01	0.04	0.01	0.02
Y <sub>2</sub> O <sub>3</sub>	0.00	0.01	0.00	0.00	0.01	0.01
MgO	0.00	0.00	0.02	0.03	0.02	0.01
CaO	0.02	0.01	0.03	0.00	0.01	0.03
MnO	11.40	10.92	10.90	7.04	10.90	10.50
FeO	4.51	5.71	5.71	8.62	7.06	6.18
ZnO	0.00	0.02	0.04	0.00	0.06	0.00
Fe <sub>2</sub> O <sub>3</sub>	0.61	0.00	0.00	0.00	1.33	1.75
Total	99.40	99.25	99.81	98.81	99.78	99.41
W	0.000	0.018	0.000	0.019	0.009	0.000
Nb	3.741	4.013	3.689	3.002	6.120	5.181
Ta	4.103	3.807	4.204	4.881	1.702	2.567
Ti	0.101	0.111	0.084	0.133	0.111	0.168
Zr	0.006	0.046	0.021	0.000	0.000	0.023
Sn	0.033	0.029	0.000	0.001	0.001	0.003
U	0.025	0.021	0.008	0.003	0.013	0.009
As	0.007	0.005	0.002	0.007	0.002	0.003
Y	0.000	0.002	0.000	0.000	0.001	0.001
Mg	0.000	0.000	0.009	0.013	0.007	0.004
Ca	0.006	0.003	0.009	0.000	0.003	0.008
Mn	2.765	2.616	2.645	1.784	2.302	2.332
Fe <sup>2+</sup>	1.081	1.351	1.368	2.156	1.471	1.355
Zn	0.000	0.004	0.008	0.000	0.011	0.000
Fe <sup>3+</sup>	0.131	0.000	0.000	0.000	0.249	0.345
CTotal	12.001	12.026	12.047	11.999	12.002	11.999

Muscovite: it occurs in several generations but it is modally important only in the border zone of SLII and in its replacement units. Garnet: it occurs as 1 to 3 mm rounded red crystals dispersed in SLI and sometimes slightly altered. Beryl: it is a minor accessory phase identified as small crystals in thin sections in the wall and internal zones of SLI. Tourmaline: dark, supposed schorl crystals occur in the exocontact of SLI and in some xenoliths of the schist englobed in this pegmatite. Zircon: it occurs as 0.1 mm accessory crystals in SLI.

Columbite-group minerals: tabular crystals up to 3x2x0.2 cm included in plagioclase, Kfs or cleavelandite or quartz are fairly common in SLII pegmatite. Their chemical composition (Table 2) plotted in the CGM quadrilateral (Fig.9) shows that the members present correspond to columbite-(Mn), tantalite-(Fe) and tantalite-(Mn) showing an evolutionary trend to increasing #Ta (Galliski & Černý 2006).

Apatite: green to bluish, up to 5 cm crystals of fluorapatite are a relatively common accessory phase. This apatite-group member is, according to IR spectroscopy, very different to the white, secondary acicular crystals of carbonate apatite produced by alteration of the primary nodules of triphylite.

Triphylite: dark nodules 10 to 20 cm in diameter of primary phosphates are present in the core-margin assemblage of SLII pegmatite. Most of them are altered but some remnants of the primary phase show XRD patterns of triphylite, which in turn englobed grains of pyrite also frequently altered. The secondary phosphate phases identified comprise: mitridatite (Galliski *et al.* 1998), dufrenite and ferrisicklerite. Some calcite is present in the late-stage alteration sequence of the phosphates.

Opal and Chalcedony: they occur as yellowish brown veinlets up to 4 cm thick, filling some late-stage fractures. Mn-oxides occur in three generations, (i) covering the nodules of phosphates, (ii) in mm-sized acicular sprays of cryptomelane in druses of phosphates, (iii) as mats of 0.5 mm long fibers of chalcophanite? growing inside cavities contained euhedral crystals from the intermediate zone of SLII (Oyarzábal 2004).

#### *Composition of the pegmatite melt. Emplacement and Discussion*

The extraordinary coarse grain size of the pegmatites and especially their textural heterogeneity prevent normal chemical analysis of them. Because of this fact, global compositions of granitic pegmatites are scarce (Černý 1991, London 2008). The chemical composition of the volumetrically dominant internal zone of the SLI pegmatite was approached in three steps: 1) obtaining the modal composition of the groundmass and the megacrystals of Kfs, 2) sampling and analyzing the groundmass of this zone of the pegmatite and 3) integrating the modal proportion in SLI and the chemical composition of the Kfs to the chemical composition of the groundmass. The result of this exercise is quoted in Table 3.

The intrusion of the SLI pegmatite happens close to the transition brittle-ductile zone of the metasedimentary sequence, after the regional metamorphic peak and the thermal overprint produced by the intrusion of the Paso del Rey granite on the mica-schist of the PMC. In the main segment of the SLI, the pegmatite possibly had a W-E strike that suggest, according to Brisbin (1986),

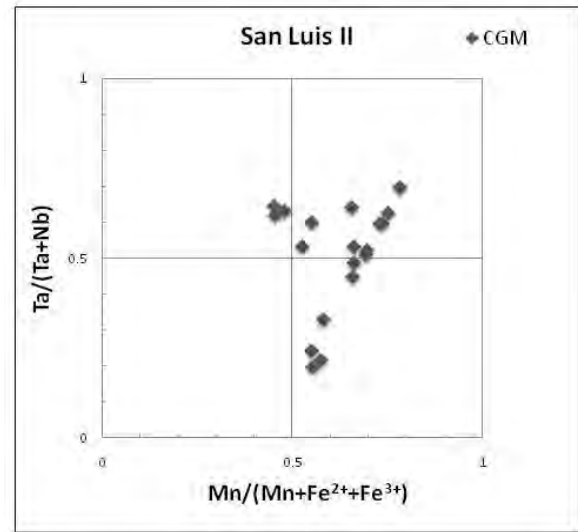


Figure 9: CGM chemical composition of SLII

TABLE 3: CHEMICAL COMPOSITION OF THE SAN LUIS I PEGMATITE

% wt.	Groundmass <sup>1</sup>	K-feldspar	Pegmatite
SiO <sub>2</sub>	76.7	64.46	74.42
TiO <sub>2</sub>	<0.01	---	0.01
Al <sub>2</sub> O <sub>3</sub>	16.9	18.55	17.21
Fe <sub>2</sub> O <sub>3</sub>	0.63	0.1	0.53
MgO	0.07	---	0.06
MnO	0.19	---	0.15
CaO	0.12	0.17	0.13
Na <sub>2</sub> O	3.56	0.5	2.99
K <sub>2</sub> O	0.63	15.04	3.31
P <sub>2</sub> O <sub>5</sub>	0.08	0.02	0.07
LOI	0.55		
ppm			
Li	10,000		10,000
Nb	70		57
Ba	<50	28	<45
Rb	200	3226	763
Sr	30	47	34
Y	<10		
Zr	20		16

<sup>1</sup> Analysis by X-Ral Act. Serv.

that deviatoric stress was operating in the same direction. The crystallization proceeds synkinematically and the pegmatite was disharmonically folded in ~20m folds that produced approximately 40% shortening.



Some of the many evidences supporting this explanation are the UST, the horses of schist in some hinges, the radial fracturing of the pegmatite, the chevron style of folding of the schists between successive flanks of the folded pegmatite, and the folded and faulted unit of SLI before emplacement of SLII in section D.

The origin of the juxtaposition of both SLI and SLII was discussed by several authors but it is not clearly resolved yet (Angelelli & Rinaldi 1963, Herrera 1963, Oyarzábal & Galliski 1993, Galliski & Oyarzábal 1997).

According to Oyarzábal & Galliski (1993), the structural relationships between both pegmatites show that chronologically SLI was intruded first and afterwards SLII. What remains more confuse is if: 1) SLII was formed by a deferred parental pegmatite melt, 2) by a laterally displaced self intrusion of a remnant of SLI pegmatite melt, or 3) SLII crystallized from a different batch of melt, non-parental with SLI pegmatite melt. The Rb/Sr ratios of the Kfs from both pegmatites (they are quoted in Fig. 8, AB section) show that the Kfs from SLI seems more evolved than the ones of SLII what confused the previous interpretation. However, the presence of several batches of melts that crystallized systematically coarse-grained spodumene subtype pegmatite in almost every fold axis, suggest that the hypothesis 2 is more possible.

#### Age and Concluding remarks

The age relationship of San Luis I and II pegmatites is relatively easy to establish because the cutting relationship are fairly clear and show that the order of formation was: first SLI that crystallized synkinematically and, after its folding, it was emplaced SLII. The absolute age is more difficult to know. A K-Ar age on muscovite from San Luis I was obtained by Galliski & Linares (1999) with a value of  $317 \pm 11$  Ma that was considered too young for the geological setting and, possibly, it represent a cooling age. If it is accepted that the pegmatites are coeval with the Paso del Rey leucogranite based on geological grounds, the question is translated to the age of the granite which, in turn, is variable according to the different methods used and the different authors (Table 1). The problem seems to be close to resolution because the new U-Pb age on tantalite-(Mn) obtained by Von Quadt & Galliski (2011) is in excellent agreement with the Rb-Sr errorchron of Llambías *et al.* (1991) (Table 1) and probably the granite and the pegmatites are parental and they have the same age of  $\sim 455$  Ma.

#### CERRO LA TORRE PEGMATITE GROUP

The Cerro La Torre pegmatite group comprises the parental leucogranite which is the northernmost of the TPD, and the associated pegmatites located to the southeast of the granite and called Santa Ana, La Titina, La Empleada, Devel, Los Chilenitos, Independencia Argentina, Nueve de Julio, Aquelarre La Betita and La Tinita (Fig. 10).

The Cerro La Torre is a small irregular stock of alkali feldspatic leucogranite. The pluton is formed by a swarm of folded lenses, texturally heterogeneous, medium to coarse, to pegmatitic in grain size. K-feldspar, sodic plagioclase and quartz are usually accompanied by abundant accessory muscovite, garnet, tourmaline and fluorapatite. The granite is silicic (avg. 75 wt. %  $\text{SiO}_2$ ) and peraluminous (ASI  $\sim 1.25$ ), with low Mg, Fe and Ca contents (Galliski *et al.* 2009). The Rb/Sr values of the K-feldspar from this granite vary from 190 to 844 with an average of 388, and  $\text{P}_2\text{O}_5$  is variable between 0.02 and 0.43 wt. % (Oyarzábal 2004). The host-rock of the granite and pegmatites is a mica-schist belonging to the Pringles Metamorphic Complex, considered Cambrian to Ordovician in age (Sims *et al.* 1997, Steenken *et al.* 2006). The metamorphism of the mica-schist slowly

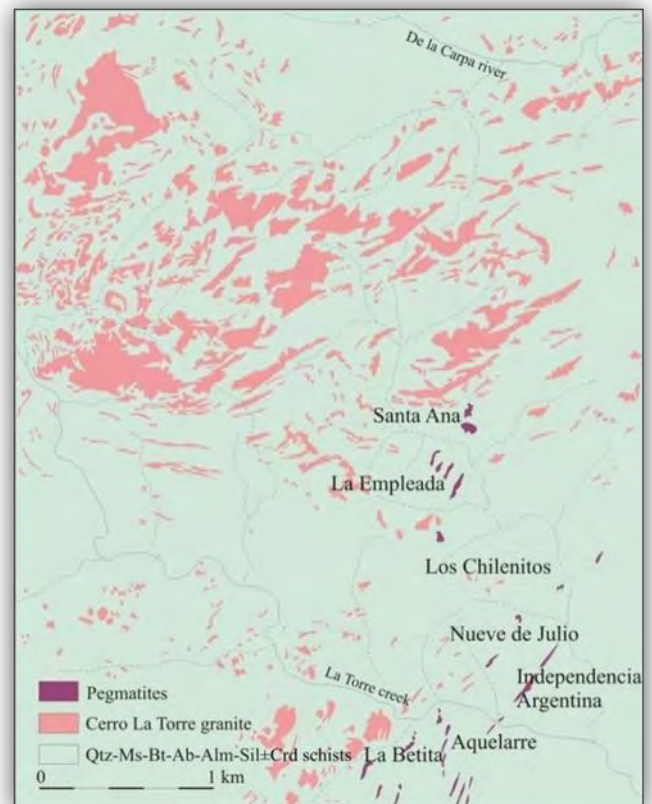


Figure 10: Map of the Cerro la Torre pegmatitic group.

diminishes toward the East, grading to phyllites and then slates in approximately 3 km. The petrographical and chemical attributes of the Cerro La Torre granite are similar and typical of the so called fertile granites from rare-element pegmatite fields (Černý & Meintzer 1988). We consider that since this granite is the single pluton in the area of this pegmatitic group, it is the parental intrusive of the pegmatites (Galliski *et al.* 2009).

## SANTA ANA PEGMATITE

### Geological Setting and Internal Structure

The Santa Ana pegmatite is located at 32° 53' 32" S, 65° 55' 43" W (1340 m above sea level), San Luis province,

Argentina, approximately 1000 m east of the highest point of Cerro La Torre. The host-rock of the Santa Ana pegmatite is a medium-grade dark-grey mica-schist with a quartz + muscovite + biotite + plagioclase + almandine + cordierite ± (sillimanite) assemblage that carries dispersed centimeter-sized nodules of altered cordierite. Santa Ana is a beryl type, beryl-columbite-phosphate subtype of a rare-element pegmatite. Its main features were recently mentioned when an interesting association of qingheite - beusite - lithiophilite was described (Galliski *et al.* 2009).

The pegmatite is exposed over ~1250 m<sup>2</sup>, and at the surface it has an elliptical outline with a length of 62 m and a width of 32 m (Fig. 11). The pegmatite was forcefully emplaced in the host mica-schist, which is locally deformed and subconcordant with the attitude of

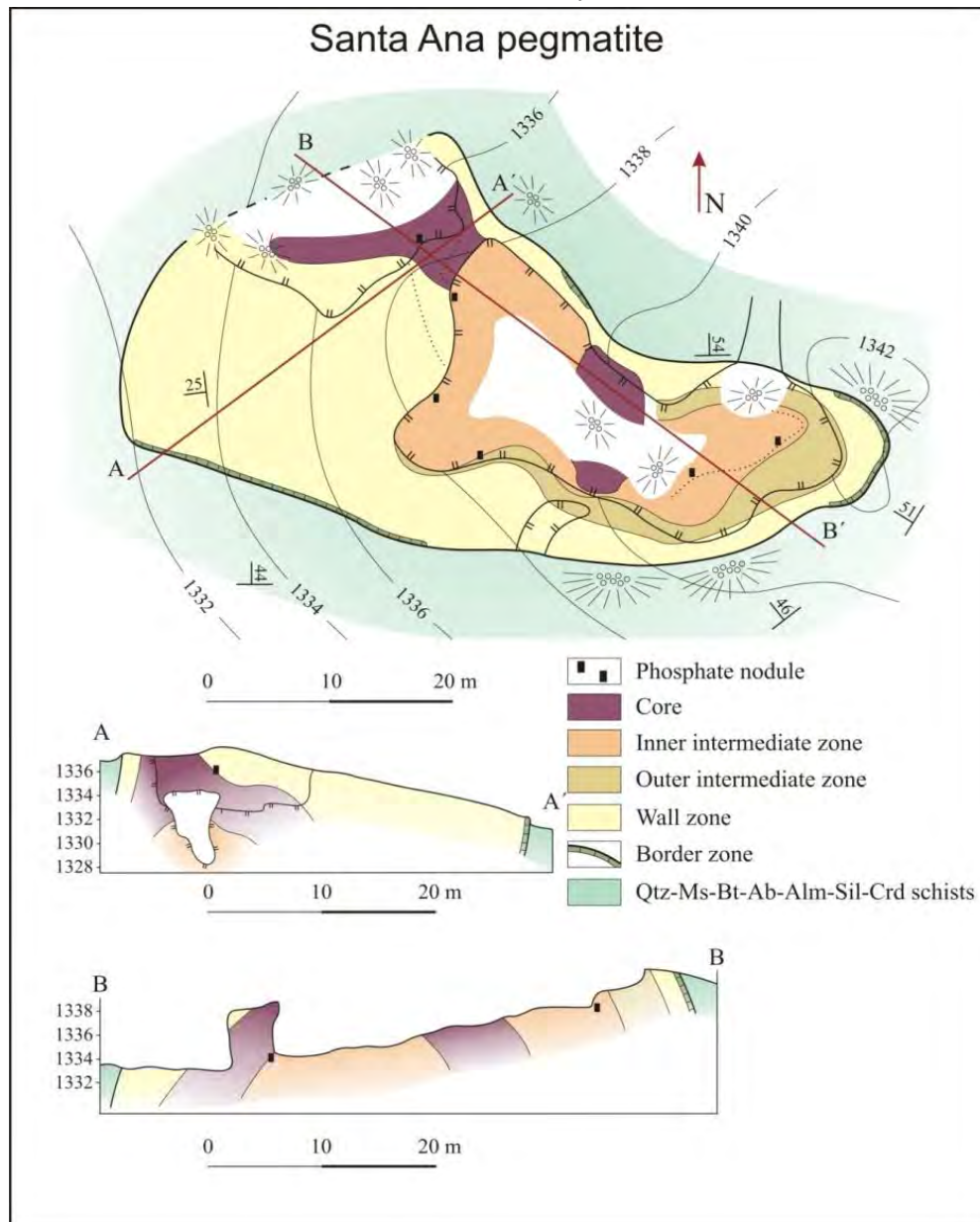


Figure 11: Schematic geological map of the Santa Ana pegmatite.

the pegmatite. The pegmatite itself underwent mild post-emplacement deformation that affected the original attitude and shape of the body. The pegmatite was mined mainly for beryl in the 1950s, later for K-feldspar, and nowadays some muscovite scrap is sporadically recovered from the dumps. Two old quarries opened mainly in the intermediate zones show the internal structure formed by border, wall, outer and inner intermediate, and core zones.

The border zone is discontinuous, 3 to 10 cm wide and it has 0.5 to 3 cm grain size and a granitic composition, plus small crystals of garnet included in quartz and scarce short prismatic schorl. The wall zone is separated by a sharp contact from the border zone. It shows medium to coarse grain size and is composed of Ab (50%), Qtz (40%), Ms and Kfs, with minor Tur in cm- to dm-sized black crystals and fluorapatite. In the western part of the pegmatite, veins of quartz cut across this unit. The outer intermediate zone is formed by blocky Kfs (60%) and interstitial Qtz (25%), Ab (10%) and Mu (5%). Increasing grain-size marks the transition into the inner intermediate zone, which consists mainly of Kfs and Qtz in meter-sized blocks. Albite and muscovite are subordinate; they seem to represent an interstitial late-stage association, locally replacing microcline. Close to the milky quartz of the core zone, bluish green beryl crystals 5 to 10 cm long, dark nodules of phosphates, and very scarce small crystals of a columbite-group mineral are found. In the central part of the pegmatite, a massive milky quartz core zone is in direct contact with the wall zone. The quartz has some sporadic, dark, radioactive nodules up to 10 cm in size, formed in central parts by altered primary uraninite crystals replaced by *gummite* and *himonite*. Small irregular fractures in quartz are filled by cm-sized, partially altered, radial bursts of brown fibrous crystals of eosphorite.

The K/Rb value of the Kfs for the outer intermediate zone varies from 193 to 84 with an average of 135, and P<sub>2</sub>O<sub>5</sub> varies from 0.39 to 0.61 with an average of 0.52 wt. %. In the Kfs of the inner intermediate zone the K/Rb ratio ranges from 155 to 84 with an average of 122, and P<sub>2</sub>O<sub>5</sub> contents are 0.56 to 0.85 with an average of 0.70 wt. %. The geochemistry of Kfs of Santa Ana pegmatite is consistent with a beryl-columbite-phosphate subtype of rare-element class of pegmatites of the LCT (Li, Cs, Ta) petrogenetic family according to the Černý (1991) and Černý & Ercit (2005) classifications. U-Pb isotopic data

obtained on uraninite gave ages between 455 ± 25 and 465 ± 15 Ma (Linares 1959).

### Mineralogy

The minerals recognized in Santa Ana pegmatite are: microcline, quartz, albite, muscovite, schorl, garnet, beryl, uraninite, CGM, pyrite, fluorapatite, beusite, lithiophilite, qingheiite, sicklerite, huréaulite, eosphorite and Mn-oxides.

Microcline: it forms 55 to 65 % of the pegmatite usually in blocky crystals with perthitic exsolutions and with high degree of triclinicity. Milky quartz is the second more abundant mineral in anhedral masses except some tiny late-stage crystals associated with oxidized pyrite in some filling units. Albite is also an abundant, usually interstitial phase, associated with some beryl crystals. Muscovite, primary in dm-sized flakes, or secondary in some units is spreaded in almost any zone. Garnet is present in the border zone in 1 mm euhedral red crystals of possibly almandine composition included in quartz. Schorl occurs in the border and wall zone, and is fairly abundant in the tourmalinized schist of the host-rock. In the border zone is a minor accessory but in the wall zone is abundant in dm-sized crystals. Beryl was an abundant accessory phase in the early mining times of Santa Ana pegmatite and it was intensively mined. Nowadays, it is a scarce mineral that usually is found in fragments in the dumps. The pieces are blue or green and the imprint of the crystals in the quartz indicate that they are coarse grained. Uraninite occurs in the core margin association in scarce cubic crystals of ~1 cm normally altered. Columbite-group minerals are quite rare in this pegmatite.

### The phosphate nodules

The nodules of phosphates are restricted to the intermediate zone of the Santa Ana pegmatite (Fig. 11). Their size varies from 0.3 to 1 m, and the shape is roughly ellipsoidal. The primary minerals are usually highly oxidized to a very dark grey to black mass of manganese and iron oxides. In the less altered portions, dark brown sicklerite is fairly common, as well as huréaulite. However, the upper part of one of the nodules is partially exposed at the edge of the floor of the main quarry, and the phosphates are largely fresh. In hand specimen, the phosphate minerals consist of pale brown to flesh-colored cleavable masses of beusite, which hosts parallel lamellae of lithiophilite,



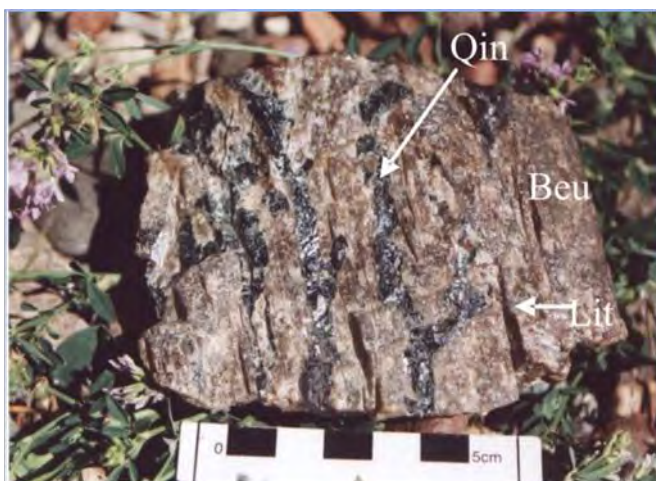


Figure 12: Sample of a nodule of beusite with exsolutions of lithiophilite, crosscut by veinlets of green qingheite.

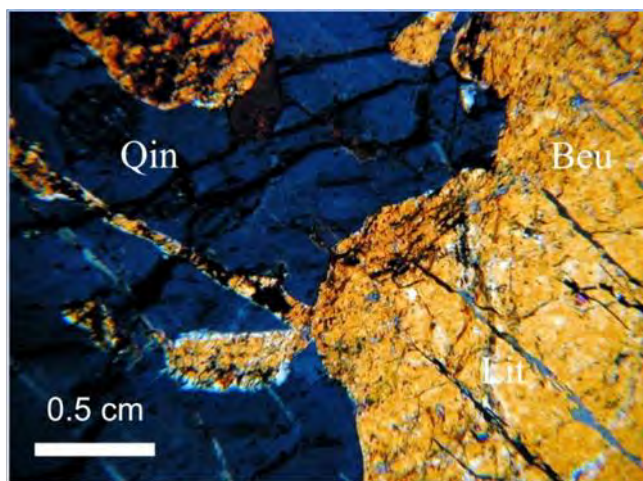


Figure 13: Photomicrograph of beusite with lithiophilite exsolutions replaced by qingheite.

several cm long and less than 1 mm wide. Darker, deep green, 0.5 cm wide, irregular veinlets of qingheite cross-cut the beusite - lithiophilite aggregate (Fig. 12). The border of the beusite - lithiophilite nodule is overgrown by a shell of qingheite, which in turn is covered by quartz. The outer part of the qingheite shell also includes cm-sized flakes of muscovite, and it is oxidized to a black material. Locally, the internal veinlets of qingheite are parallel to the lithiophilite lamellae, but cross-cutting relationships are by far more common, with textural patterns (Fig. 13) indicative of partial replacement of the beusite - lithiophilite aggregate by qingheite.

This occurrence of qingheite was the second one found and it has deep jade-green color, with a vitreous luster, and its streak is white greenish. It has a good {010} cleavage and a conchoidal fracture. Its hardness is 5 on the Mohs scale; its density measured with a pycnometer is 3.637 (0.006) g/cm<sup>3</sup>; the calculated density is 3.626 g/cm<sup>3</sup>.

The chemical composition of the main phases is shown in the Tables 4 and 5. The plotting of these compositions is represented in the triangular diagrams of Figure 14 in both cases taken from Galliski *et al.* (2009). The origin of this assemblage of beusite+lithiophilite was attributed by Hurlbut & Aristarain (1968) to the exsolution of an unstable primary phase that crystallized in nodules. The qingheite is obviously a late phase which origin was ascribed to replacement by Galliski *et al.* (2009).

TABLE 4: CHEMICAL COMPOSITIONS OF QINGHEITE								
	SANTA ANA				LA EMPLEADA QINGHE			
	Main phase		Oxidized phase		Main phase			
<i>n</i>	6	σ	3	σ	3	σ	**	
P <sub>2</sub> O <sub>5</sub> , wt	45.11	0.21	44.92	0.55	44.36	0.23	45.75	
TiO <sub>2</sub>	—	—	—	—	—	—	0.05	
Cr <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	—	0.04	
Al <sub>2</sub> O <sub>3</sub>	5.07	0.22	6.07	0.05	5.13	0.04	4.54	
Fe <sub>2</sub> O <sub>3</sub>	4.04	0.04	5.22	0.11	4.24	0.25	2.25	
MgO	6.21	0.26	4.08	0.04	8.07	0.08	9.78	
MnO	24.21	0.29	25.21	0.06	21.48	0.24	23.66	
FeO	6.38	0.07	6.25	0.26	6.24	0.24	3.95	
ZnO	0.12	0.1	0	0	0	0	0.23	
CaO	0.5	0.04	0.9	0.1	0.58	0.03	0.94	
SiO <sub>2</sub>	0.01	0.02	0	0	0	0	—	
BaO	0.01	0.02	0.01	0.02	0	0	—	
Na <sub>2</sub> O	9.24	0.07	7.03	0.06	9.57	0.08	8.75	
K <sub>2</sub> O	0.02	0.02	0.01	0.01	0.01	0.01	0.04	
Li <sub>2</sub> O	—	—	—	—	—	—	0.02	
F	0.04	0.03	0.08	0.08	0.1	0.04	—	
Cl	0.01	0.01	0.01	0.01	0.01	0	—	
TOTAL	101	0.59	99.78	0.55	99.79	0.17	100	
<sup>†</sup> T	P	11.92	0.020	1.987	0.053	11.759	0.018	11.981
4M2(b)	Al	1.870	0.080	2.260	0.010	1.890	0.010	1.656
	Ti	—	—	—	—	—	0.012	
	Cr	—	—	—	—	—	0.010	
	Fe <sup>3+</sup>	0.950	0.010	1.240	0.020	1.030	0.060	0.524
	Zn	0.030	0.020	0.000	0.000	0.000	0.000	0.052
	Fe <sup>2+</sup>	1.150	0.010	0.500	0.025	1.080	0.046	1.020
	Mg	—	—	—	—	—	0.700	
	Li	—	—	—	—	—	0.026	
	Σ	4.000	—	4.000	—	4.000	4.000	
4M2(a)	Mg	2.890	0.120	1.920	0.030	3.770	0.030	3.800
	Fe <sup>2+</sup>	0.515	0.005	1.149	0.056	0.230	0.010	
	Mn	0.595	0.005	0.931	0.005	0.000	0.200	
	Σ	4.000	—	4.000	—	4.000	4.000	
4M1	Mn	4.000	0.036	4.000	0.023	4.000	0.058	4.000
2X1b	Fe <sup>2+</sup>	0.000	—	0.000	—	0.289	0.012	
	Mn	1.806	0.016	1.800	0.010	1.696	0.025	2.000
	Ca	0.167	0.013	0.200	0.020	0.015	0.001	
	Na	0.027	0.001	0.000	—	0.000	—	
	Σ	2.000	—	2.000	—	2.000	—	
2X1a	Ca	0.000	—	0.103	0.010	0.180	0.007	
	Na	2.000	0.021	1.897	0.014	1.820	0.010	2.000
	Σ	2.000	—	2.000	—	2.000	—	
4X2	Na	3.567	0.038	2.400	0.017	3.987	0.021	3.250
	K	0.010	0.010	0.010	0.000	0.000	0.000	0.015
	Li	—	—	—	—	—	0.310	
	Sr	—	—	—	—	—	—	
	Ba	0.002	0.003	0.002	0.003	0.000	0.000	
	□	0.421	—	1.588	—	0.013	0.430	
	Σ	4.000	—	4.000	—	4.000	—	

\* Analyzed for V, As, Si, Th, U, Y, Ce, La, Nd, Bi, Pb and S but not detected.  
 \*\* Taken from chemical data and allocation of cations of Ma *et al.* (1983)  
<sup>†</sup> Number of cations on the basis of 48 oxygens.

TABLE 5. CHEMICAL COMPOSITIONS OF BEUSITE AND LITHIOPHILITE								
n	BEUSITE				LITHIOPHILITE			
	SANTA ANA**		LOS ALEROS†		SANTA ANA††		LOS ALEROS‡	
	5	σ	1	recalc.	7	σ	1	recalc.
P <sub>2</sub> O <sub>5</sub>	41.12	0.82	40.20	41.40	46.61	0.84	47.00	47.88
SiO <sub>2</sub>	—		1.50		—		0.78	
Al <sub>2</sub> O <sub>3</sub>	0.08	0.14			0.02	0.01	0.50	
MgO	1.71	0.39	2.56	2.64	5.57	1.05	6.33	6.45
MnO	35.45	0.22	35.50	36.60	23.46	1.00	22.60	23.02
FeO	13.81	0.47	14.20	14.62	14.89	0.82	12.80	13.04
ZnO	0.31	0.43			0.02	0.03		
CaO	6.37	0.60	4.64	4.78	0.31	0.39		
SrO	0.01	0.01			0.01	0.02		
BaO	0.02	0.03			0.02	0.04		
Na <sub>2</sub> O	0.04	0.05			0.03	0.03	0.03	0.03
K <sub>2</sub> O	0.03	0.05			0.06	0.05		
Li <sub>2</sub> O	0.00	0.00	0.14		9.94	0.09	9.40	9.58
F	0.07	0.04			0.08	0.07		
Cl	0.02	0.02			0.01	0.02		
TOTAL	99.03	1.11	99.71	100.0	101.0	1.26	99.69	100.0
P	2.010	0.018	2.000		0.988	0.018	1.000	
Al	0.010	0.010			0.000	0.000		
Mg	0.150	0.030	0.225		0.210	0.040	0.224	
Mn	1.734	0.027	1.767		0.497	0.020	0.481	
Fe	0.666	0.022	0.698		0.312	0.017	0.269	
Zn	0.010	0.020			0.000	0.000		
Ca	0.394	0.035	0.292		0.008	0.010		
Sr	0.000	0.000			0.000	0.000		
Ba	0.000	0.001			0.000	0.000		
Na	0.005	0.005			0.002	0.002	0.002	0.002
K	0.000	0.000			0.000	0.000		
Li	0.000	0.000			1.000	0.000	0.951	
F	0.012	0.008			0.006	0.005		
Cl	0.000	0.000			0.000	0.000		
Σ <sub>Cations</sub>	4.98	0.021			3.017	0.026		

\* Analyzed for V, As, Si, Th, U, Y, Ce, La, Nd, Bi, Pb and S but not detected.  
 \*\* Number of cations based on 8 atoms of oxygen.  
 † Data from Hurlbut & Aris tarain (1968), analyst J. Ito, atomic prop. based on 2P.  
 †† Li content assumed from stoichiometry. Number of cations based on 4 oxygens.  
 § Data from Hurlbut & Aris tarain (1968), analyst J. Ito, atomic prop. based on 1P.

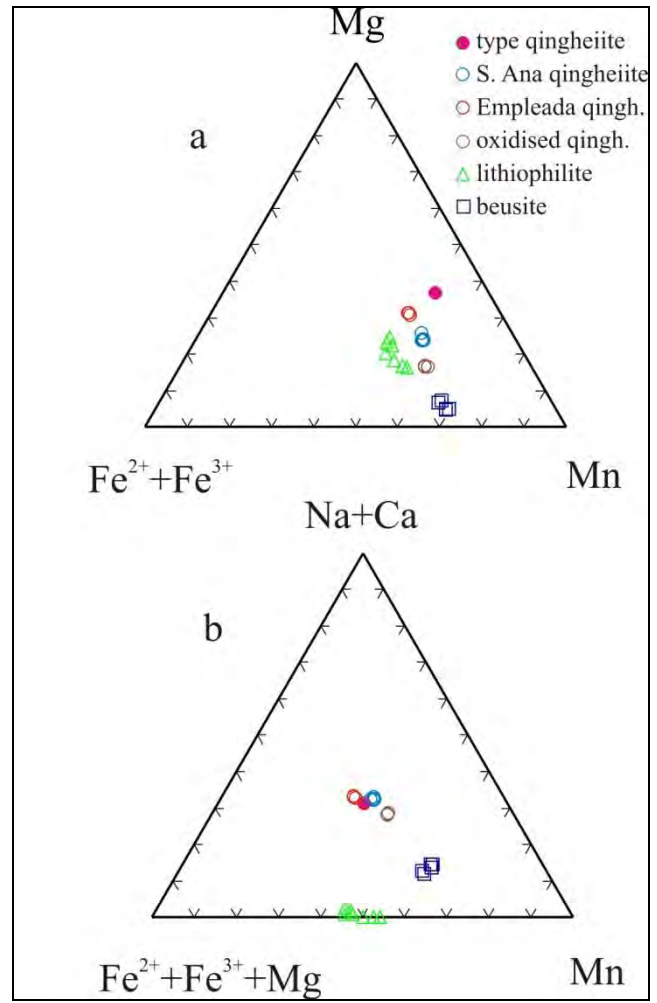


Figure 14: Triangular plots showing the compositions of qingheite, beusite and lithiophilite from Santa Ana, La Empleada, Los Aleros and Qinghe. A) Mg – Fe<sub>tot</sub> – Mn, B) (Na + Ca) – (Fe<sub>tot</sub> + Mg) – Mn and C) Na – Ca – Mg.

INDEPENDENCIA ARGENTINA PEGMATITE

*Geological Setting and Internal Structure*

The Independencia Argentina mine is an albite type, rare element class pegmatite, located in the San Luis range at

65° 55' 28" W and 32° 54' 20" S. The pegmatite crops out in the SE border of a pegmatite population linked with the small stock of C° La Torre. This intrusive is a leucogranite fertile in rare element pegmatites of LCT petrogenetic family of probably Ordovician age that intrudes micaschists of medium grade.

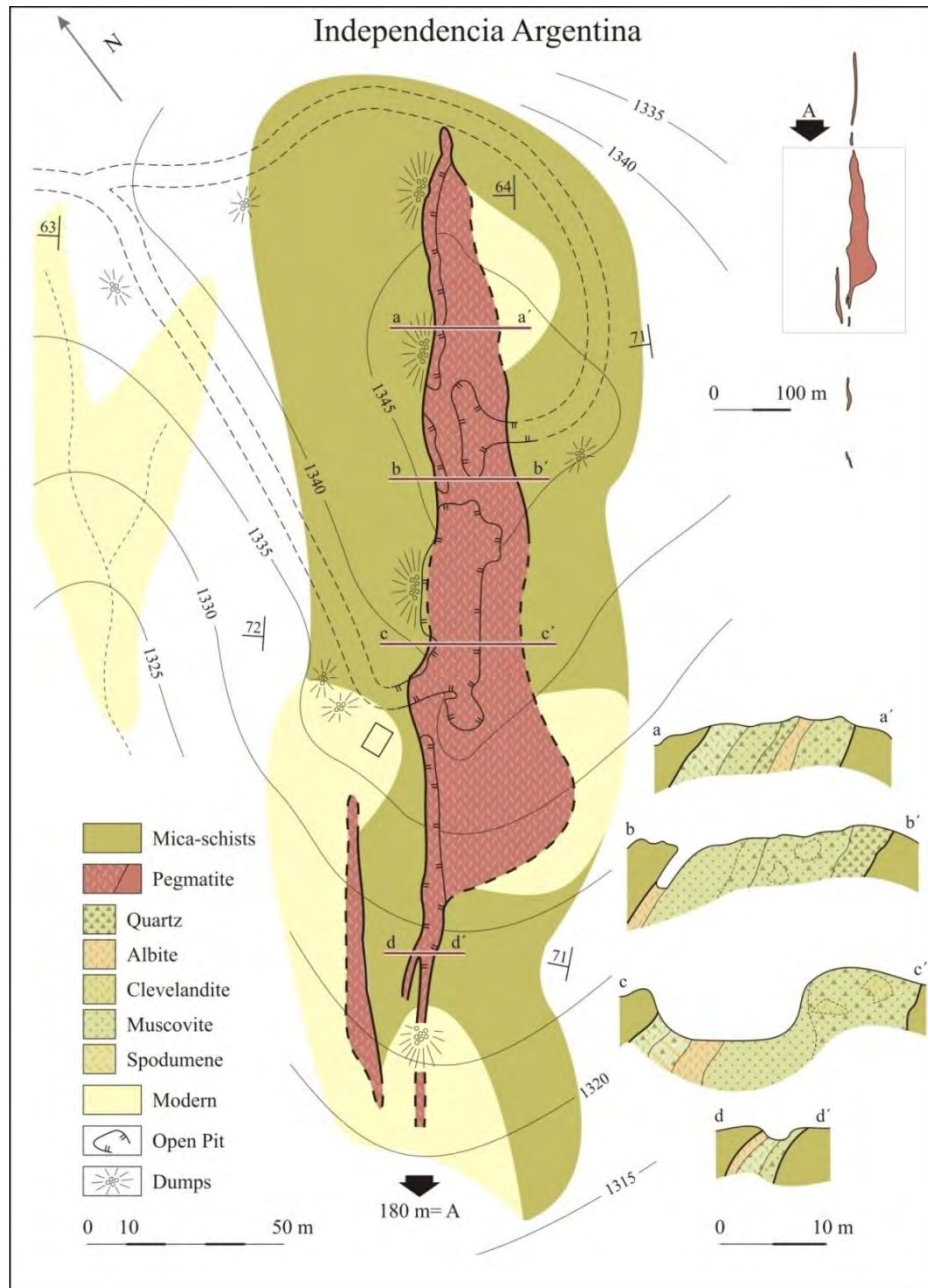


Figure 15: Geological map of the Independencia Argentina pegmatite.

The pegmatite has N35°-40°E strike and 45°-70°W dip, it is tabular, with 200 m long and 5 m wide average size in the main segment, but in the central part it reaches 30 m wide. The internal zoning is asymmetric, the wall and intermediate zones are in the west portion and they are

principally composed by albite and quartz±muscovite; scarce K-feldspar and spodumene are partially replaced. The quartz core is in the E side, and has pods of muscovite or albite in the transition to the inner intermediate zone. A tabular replacement unit of saccharoidal albite that



reaches 3 m wide in some parts is located in the hanging wall portion. The pegmatite was emplaced early synkinematically during the Famatinian orogenic cycle and later was boudinaged especially in the southern part. Its most probable origin is by synkinematic fractional crystallization of one of the latest batches of pegmatitic magma derived from the Cerro La Torre granite differentiation (Galliski *et al.* 1994).

### Mineralogy

Besides de rock-forming minerals, the accessory ones are columbite-group minerals, microlite, bismuth, fluorapatite, beryl, garnet and hematite. The albite is present as cleavelandite in the different units or saccharoidal albite in the replacement unit. The cleavelandite occurs in 2-3 mm tabular crystals, usually fractured, associated with Qtz ± Mu ± CGM. The saccharoidal albite has An<sub>00</sub> composition and a high grade of Al:Si order.

TABLE 6 : CHEMICAL ANALYSES OF CGM FROM IND. ARG.						
Sample	IA9B2	IA9B3	IA9B4	IA9B5	IA9B6	IA9C3
Nb <sub>2</sub> O <sub>5</sub>	45.88	31.86	25.86	47.65	30.48	28.32
Ta <sub>2</sub> O <sub>5</sub>	34.12	49.55	55.85	33.51	53.35	52.94
TiO <sub>2</sub>	0.08	0.32	0.70	0.12	0.57	0.85
SnO <sub>2</sub>	0.00	0.00	0.13	0.00	0.04	0.13
MnO	9.72	8.47	7.24	9.71	7.49	8.06
FeO	7.72	7.12	7.44	7.20	5.99	7.25
Fe <sub>2</sub> O <sub>3</sub>	0.23	0.60	0.87	0.74	1.96	0.65
Total	97.75	97.92	98.09	98.93	99.88	98.22
Nb	5.512	4.092	3.404	5.588	3.809	3.678
Ta	2.466	3.828	4.423	2.364	4.011	4.135
Ti	0.016	0.068	0.153	0.023	0.118	0.184
Sn	0.000	0.000	0.015	0.000	0.004	0.015
Mn	2.188	2.038	1.786	2.134	1.754	1.961
Fe <sub>2</sub>	1.767	1.834	2.024	1.723	1.838	1.898
Fe <sub>3</sub>	0.045	0.128	0.191	0.144	0.408	0.141
CTotal	11.994	11.988	11.996	11.976	11.942	12.012

The CGM occur as mm-sized laths associated with cleavelandite or included in quartz veinlets, and as tiny crystals included in saccharoidal albite. The crystals have oscillatory zoning and fast transitions between the different members of the group that built up the laths: columbite-(Fe), columbite-(Mn) and tantalite-(Fe) (Fig. 16) (Galliski & Černý 2006). Yellow crystals of some member of the

microlite subgroup minerals in <1 mm rounded grains are dispersed in the saccharoidal albite and usually surrounded by a pink halo. Fluorapatite is frequent in blue crystals dispersed in saccharoidal albite, sometimes associated with CGM. Bismuth is a rare inclusion in CGM only visible under the microscope. Rutile in acicular crystals occurs included in euhedral quartz from veins cutting the intermediate zone.

### Concluding remarks

The Independencia Argentina is considered a pegmatite of albite type that is the farthest emplaced related to the Cerro La Torre pegmatite group. Its origin was ascribed by Galliski *et al.* (1994) to the intrusion of a Na-rich pegmatite melt that synkinematically crystallized inward border, wall intermediate and core zones with asymmetric development of the successive shells. The re-opening of the former crystallized system, with the intrusion of a second batch of Na-rich melt, that suddenly crystallized by loss of volatiles, has formed the unit of saccharoidal albite. Late-stage boudinaged of the entire pegmatite produce the present segmentation and tilted counter clockwise the entire block of country rock-pegmatite.

The pegmatite was emplaced synkinematically and later, during the Ocoyic diastrophism, it was boudinaged especially in the southern part. Its most probable origin is by synkinematic fractional crystallization of one of the latest batches of pegmatitic magma derived from the Cerro La Torre granite differentiation.

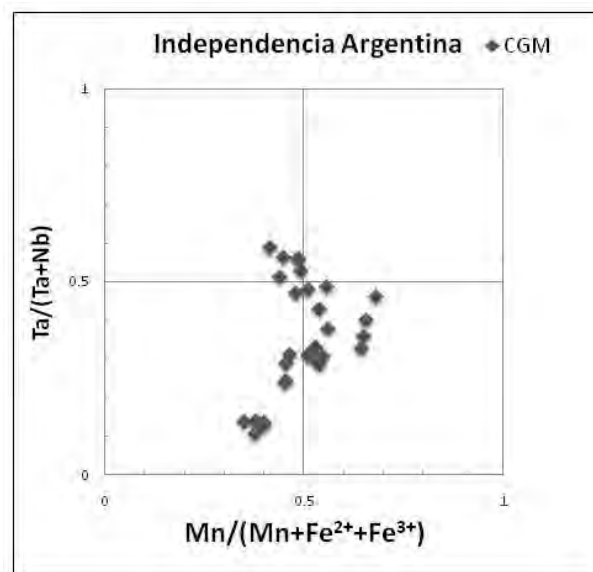


Figure 16: CGM chemical composition of the Independencia Argentina pegmatite.

## THE CONLARA PEGMATITE FIELD

This field comprises the granitic pegmatites that outcrop in the northern and eastern part of the Sierra Grande de San Luis (Fig. 2) (Galliski 1994a), basically intruding rocks of the Conlara Metamorphic Complex (Sims *et al.* 1997) or equivalents. The pegmatites can be grouped in two different kinds: 1) the orogenic -basically Famatinian and, eventually, some of them Pampean-LCT pegmatites and 2) the post-orogenic -in relation to the Famatinian orogenic cycle - NYF pegmatites.

The LCT pegmatites are distributed in geographically well defined pegmatitic groups, in between them: Paso Grande-La Toma, Villa Praga-Las Lagunas, and San Martín-Cautana. The mineralogy and the geochemistry of K-feldspars and muscovite of these pegmatites are typical of the LCT petrogenetic family. Most of the units are of rare-element class (*REL*), *REL-Li* subclass, with barren, beryl and complex types. These pegmatites were intensively mined in the last 60 years by mica, beryl, tantalum ore minerals, spodumene, feldspar and quartz. They comprise mostly barren to beryl type pegmatites, in less proportion complex type spodumene subtype pegmatites. The minerals of these pegmatites are: quartz, albite, microcline, muscovite, biotite, beryl, spodumene, schorl, garnet, ixiolite, columbite-group minerals, and pyrochlore-super group minerals (Galliski *et al.* 2009). Primary phosphate nodules in the geochemically more primitive pegmatites are bobfergusonite (Tait *et al.* 2004) or triplite; in the more evolved bodies they belong to the triphylite-lithiophilite or beusite-lithiophilite series (Hurlbut & Aristarain 1968; Galliski 1994b), which by successive alteration stages can produce complex assemblages of: sicklerite, varulite, huréaulite, jhansite-group minerals, triploidite, qingheiite, apatite, dickinsonite and joosteite (Roda-Robles *et al.* 2009). The parental granites of this pegmatites form a suite of small S-type granites synkinematic intruded and heterogeneously sheared, in an arrangement generally harmonious with the structure of the country rock. The ages of this suite is usually Ordovician belonging to the Famatinian orogenic cycle.

The NYF pegmatites form a well delimited subgroup in the Potrerillos granite. In other parts of the field they are more difficult to identify. The Potrerillos subgroup of intraintrusive pegmatites is considered as an example of rare-elements class (*REL*), *REL-REE* subclass, allanite-monazite type. The mineralogy of these pegmatites comprise: quartz, albite, microcline, biotite, muscovite, schorl, bismutite, columbite-(Fe), fluorite, rutile, hematite, beryl, fluorapatite, pyrite, bismuthinite, clinovisbanite, scheelite, monazite-(Ce), molybdenite, -*imonites*” and opal. The parental granites form a post-orogenic, A-type, dominantly monzogranitic suite of Lower Carboniferous age.

## POTRERILLOS PEGMATITE SUBGROUP

### *Geological Setting*

After the completion of the evolution of the Famatinian tectonic cycle which S-type magmatism produced most of the LCT granitic pegmatites of the San Luis ranges, the next important granitic plutonism corresponds to a suite of alkaline granites that intrude the previous exhumed and eroded orogenic belt. These granites form composite batholiths or isolated plutons, some of which have parental pegmatites. The volumetrically most important occurrence of this magmatic activity build the Las Chacras-Potrerillos batholith (Fig. 17, 18) which geological setting, petrology and geochemistry was addressed by several researchers, particularly by Brogioni (1993, 1997), and more recently by Siegesmund *et al.* (2004) and López de Lucchi *et al.* (2007).

The Potrerillos pluton is the southernmost intrusive of the Las Chacras-Potrerillos (LCPC) batholith. It is composed of three predominant facies that according to Siegesmund *et al.* (2004) are biotite porphyritic granite (BPG), biotite-bearing equigranular red granite (BRG) and muscovite-bearing equigranular red granite (MRG). The BPG has been dated by the same authors yielding a U-Pb zircon age of 382±5 Ma and cooling ages in biotite of 362±8 and 352±7 Ma. Studied pegmatites are hosted by two main lithologic units, one of them being a coarse-grained porphyritic monzogranite equivalent to the BRG, and the other a coarse grained equigranular monzogranite equivalent to the MRG.

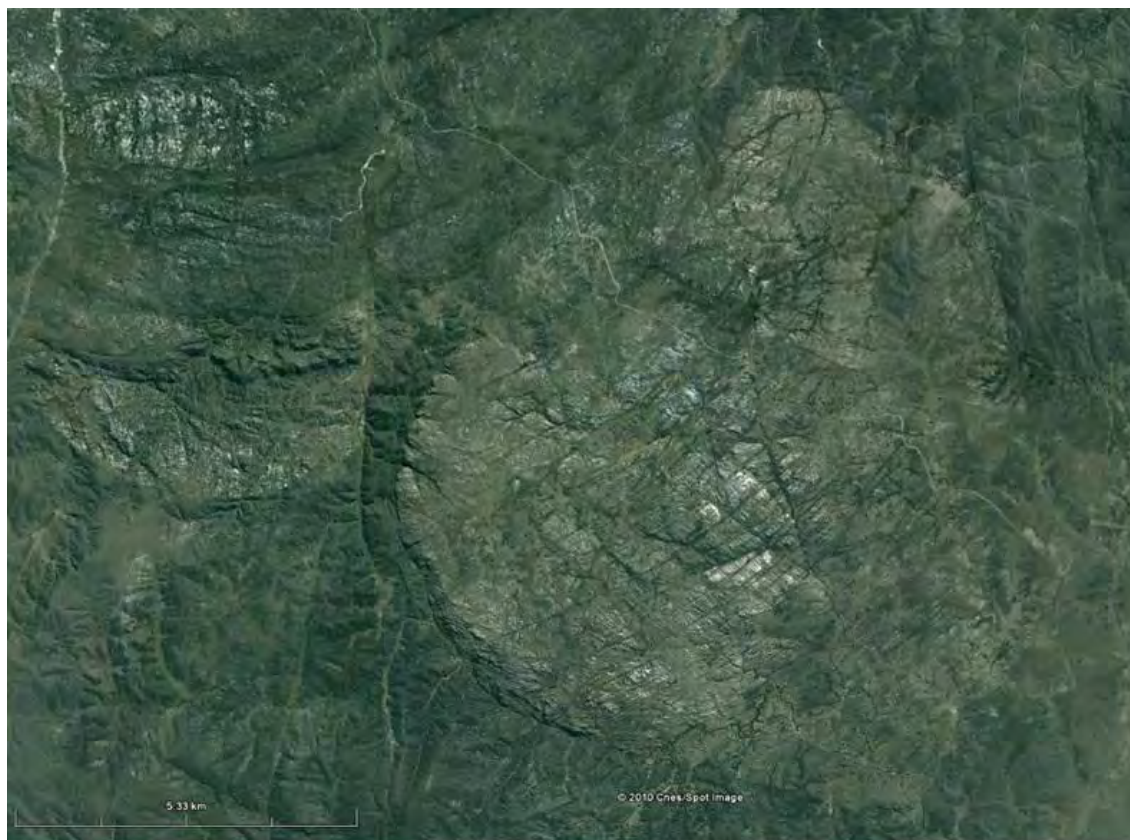


Figure 17: Google Earth image showing the strong contrast between the Potrerillos granite with the Conlara Metamorphic Complex.

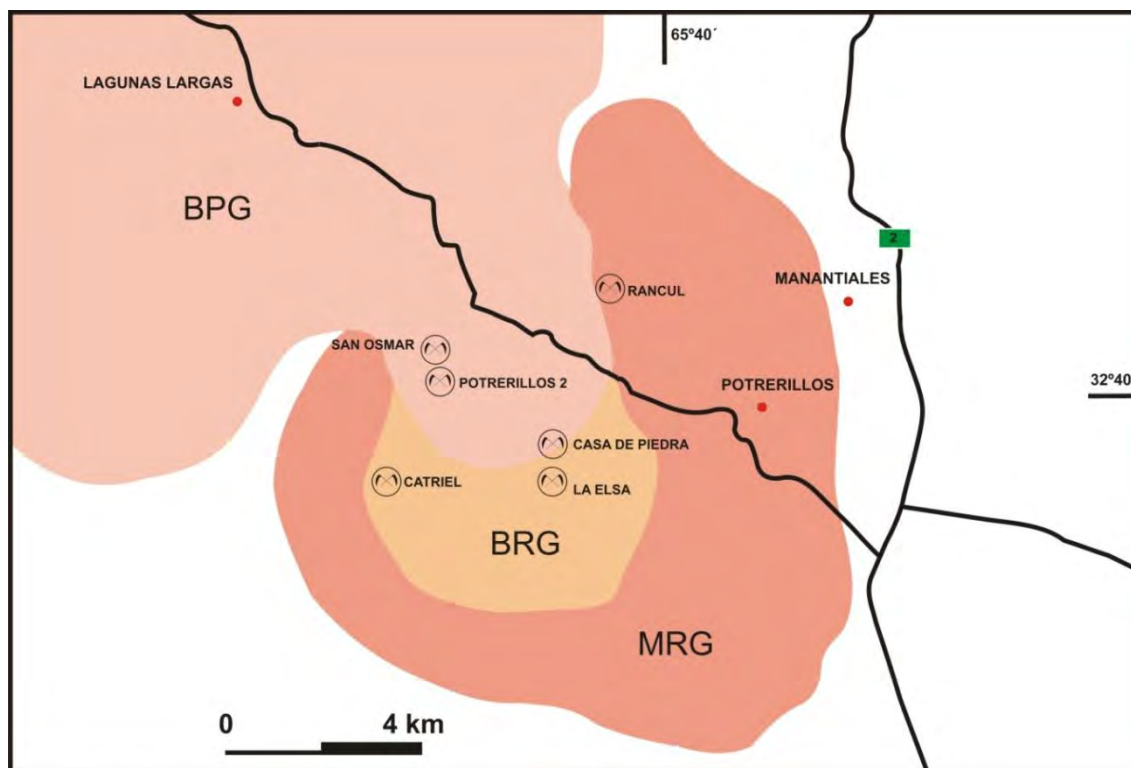


Figure 18: Schematic geological map showing the main facies of the Potrerillos granite with the location of the pegmatites.



## Geology of the Pegmatites

The pegmatites of the Potrerillos subgroup belong to the Conlara pegmatitic field, which is hosted in a granite suite of the post-orogenic Devonian to Carboniferous LCPC batholith. They were initially considered as possible examples of NYF or Hybrid pegmatites by Galliski (1994a, b). Additional information obtained by preliminary trace element geochemistry of K-feldspar and muscovite, shows primitive patterns typical of barren or poorly evolved granitic pegmatites (Galliski *et al.* 1997). After the works of Bernard (2009) and Roquet (2010), they are considered as rare-element pegmatites of the *REL-REE* subclass and allanite-

monazite type. The pegmatites are located in the surroundings of the Potrerillos village, in the Libertador General San Martín department, San Luis province, Argentina. The subgroup has six bodies called: Rancul, La Elsa, Casa de Piedra, San Osmar, Potrerillos 2 and Catriel. Pegmatite body shapes are usually rounded or elliptical, less commonly irregular, with discrete sizes averaging from 10 to 50 m in diameter. The pegmatites show a vertical development, that possibly look like the turnip-shaped bodies described by other authors or are similar to thick lenses. They were mined for K-feldspar and quartz and minor beryl as a by-product, and all of them have open quarries with good exposures.

TABLE 7: MINERALOGY OF THE POTRERILLOS PEGMATITES						
	Rancul	La Elsa	Piedra	Osmar	Potr 2	Catriel
Quartz	▲	▲	▲	▲	▲	▲
K-feldspar	▲	▲	▲	▲	▲	▲
Albite	▲	▲	▲	▲	▲	▲
Biotite	■		■	■	■	■
Muscovite	■	■	■	■	■	■
Tourmaline	■	■	■	■	■	■
Beryl	●	●				●
Allanite				●	●	*
Fluorite		●				
Fluorapatite	●		●	●	●	
Monazite-(Ce)		*				*
Ilmenite	●					
Ilmenorutile	●				●	●
Rutile	●			●		●
Pyrochlore	*					
Scheelite			*			
Hematite	●	●		●	●	
Pyrite	●	●				●
Bismuthinite			*			
Molibdenite			*			
Bismutite	*					
Clinovisbanite	*					
Goethite	●		●	●		
Mn-oxides	●					
Opal			*			

Minerals: ▲ major, ■ accessory, ● subordinate, \* rare

### Mineralogy

The mineralogy and fabric of the pegmatites are simple and were summarized by Roquet *et al.* (2011). The Table 7 taken from that contribution shows the minerals found. The zoning is ill-defined and uniform with a border-wall zone where the granite transitionally grades to a coarse-grained intermediate zone composed of K-feldspar and quartz, with minor albite, normally interstitial, or forming spherical aggregates in some bodies. The core zone is irregular and discontinuous, poorly defined, normally made of milky to pink or gray quartz with inclusions of large, isolated crystals of K-feldspar. Biotite is a common accessory mineral occurring as 5 to 10 cm wide black booklets, irregularly concentrated in the intermediate zone. Muscovite is more widespread, associated with K-feldspar or quartz. Black tourmaline, in radiating crystals or in broken prisms, is a common minor accessory mineral in all the studied pegmatites. Beryl in blue, sometimes gemmy crystals, or more commonly in yellowish green prisms up to 5-7 cm

long, is abundant and is associated with albite, tourmaline or included in quartz. Fluorapatite is also abundant, in anhedral gray to green crystals or in thin prisms. Prismatic allanite-(Ce) up to 2 cm long occurs included in quartz but is not found in all the pegmatites; scarce monazite-(Ce) occurs in small, cm-sized crystals, though it is more common in microscopic sizes. Ilmenorutile is a quite common accessory and contains inclusions of U-bearing pyrochlore. Hematite is a common oxide in masses of 5 to 10 cm. A couple of pegmatites contain aggregates of rutile crystals sized 0.5 to 3 cm, often with profuse hematite exsolutions. Scheelite is very rare and only occurs in one pegmatite. Pyrite in 2 to 10 cm anhedral masses, variably replaced by goethite, is present in most pegmatites normally included in core quartz. Bismuthinite is occasionally present but it is more commonly altered to bismutite or, more rarely, to clinobisvanite. Goethite, Mn-oxides and opal occur in some of the pegmatites. Muscovite of the San Osmar pegmatite was dated in  $359 \pm 12$  Ma by Galliski and Linares (1999).

## THE RANCUL PEGMATITE

### Internal Structure

The Rancul pegmatite is located at  $32^{\circ}38'54''$ S y  $65^{\circ}40'42''$ W and to 1130 MASL. The host-rock is red, fine grained granite formed by Kfs-Pl-Qtz-Ms. The Rancul mine has three different pegmatite bodies and some minor pegmatitic pods (Fig. 19). The contact pegmatite-host-rock is usually transitional with increasing grain size in the border wall zone ill-defined. The biggest body is the East one that presents a well developed intermediate zone and a core zone. The intermediate zone is coarse-grained and composed by Kfs (60%) and Qtz (40%). The Kfs is light pink microcline in euhedral crystals with high (Al:Si) order included in gray to milky interstitial quartz. The core zone is formed by Qtz (95%)  $\pm$  Py-Ilm-Ap-Srl (5%). The pegmatite has replacement units of biotite, muscovite and tourmaline. The replacement units of biotite are irregular and composed by 2-10-30 cm subhedral crystals of biotite with some frequency altered to vermiculite. The replacement units with tourmaline are distributed normally in the intermediate zones and formed by radial or divergent prism of schorl. The replacements

of muscovite are scarce and developed on microcline crystals.

### Mineralogy

The minerals found in the Rancul pegmatite are: quartz, microcline, albite, biotite, muscovite, beryl, apatite, schorl, rutile, pyrite, columbite, bismutite, clinobisvanite, hematite and *-imonite*". Quartz is usually anhedral, grey to milky and does not present vugs. K-feldspar occurs as subhedral to euhedral prismatic crystals of coarse to very coarse grain-size. Albite is scarce in the pegmatite; it occurs in tabular pink to white aggregates associated to the replacement units with biotite. Biotite is the main accessory mineral, it occurs in partially altered booklets. Muscovite is the 2M<sub>1</sub> polytype, fine-grained and possibly growth at a late-stage at expenses of microcline. Beryl occurs associated with quartz in light blue crystals found in the dumps. Fluorapatite was found as 20 cm grayish green crystal associated with quartz, muscovite and schorl in a sample of the dumps. Schorl always is present in prismatic or acicular black euhedral to subhedral crystals associated to quartz or microcline.

Rutile occurs included or associated with quartz or albite in dark grey cm-sized grains. It has up to 17% of Nb<sub>2</sub>O<sub>5</sub> +

Ta<sub>2</sub>O<sub>5</sub> (Nb >> Ta) and contains microscopic exsolutions of a U-bearing member of the pyrochlore supergroup.

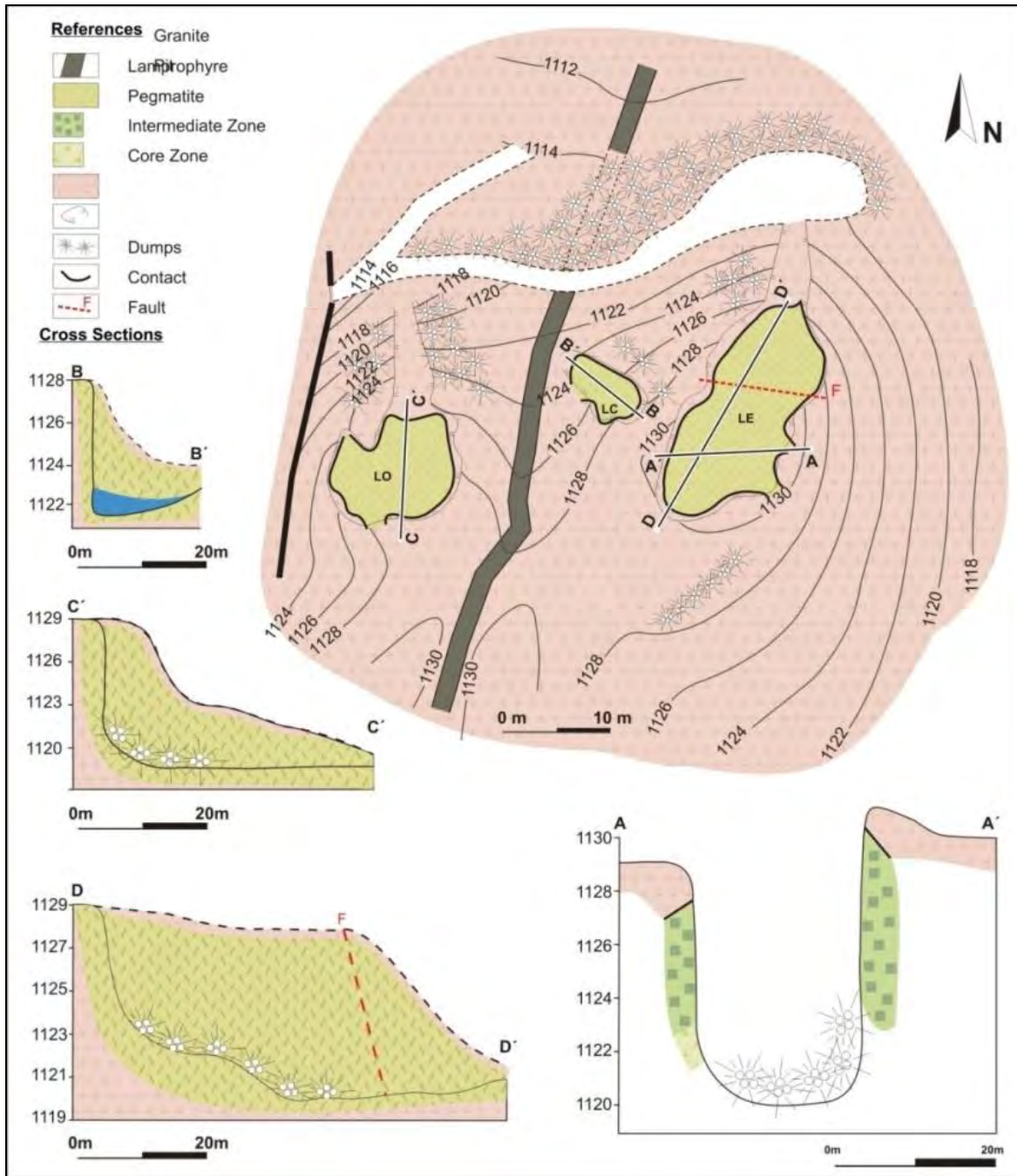


Figure 19: Schematic map showing pegmatite bodies and some minor pegmatitic pods of the Rancul mine.

## THE LA ELSA PEGMATITE

### *Geological Setting and Internal Structure*

This pegmatite is located in the same geological environment that Rancul at 32°40'44"S and 65°41'24"W approximately at 1193 MASL. The host-rock is a

holocrystalline, medium-grained white to pink granite formed by Kfs-Pl-Qtz-Bt-Ms. The contact of the pegmatite with the granite is transitional and the border zone is missing. The shape in plant of the pegmatite is subcircular with 30 m long, 18 m wide and 7 m of visible depth. The



zoning is simple and is represented by wall, intermediate and core zones, with replacement units of tourmaline and muscovite and fracture filling of albite + beryl. The wall zone has a discontinuous development, is medium-grained and is composed by Ab (50%) - Qtz (30%) - Ms (13%) ± Srl-Grt-Bis (7%). The intermediate zone has coarser grain size and a change in modal composition with Qtz (60%) - Mc (30%) ± Srl-Fl. The core zone is volumetrically

significant and is composed by Qtz(80%)±Fl-Srl-Hem-Brnt-Mnz. There are also minor replacement units of muscovite and schorl, and a fracture filling of albite with accessory beryl.

The most remarkable mineralogical aspect of this pegmatite is the occurrence of primary Y-bearing fluorite associated with K-feldspar and quartz, and the presence of monazite-(Ce).

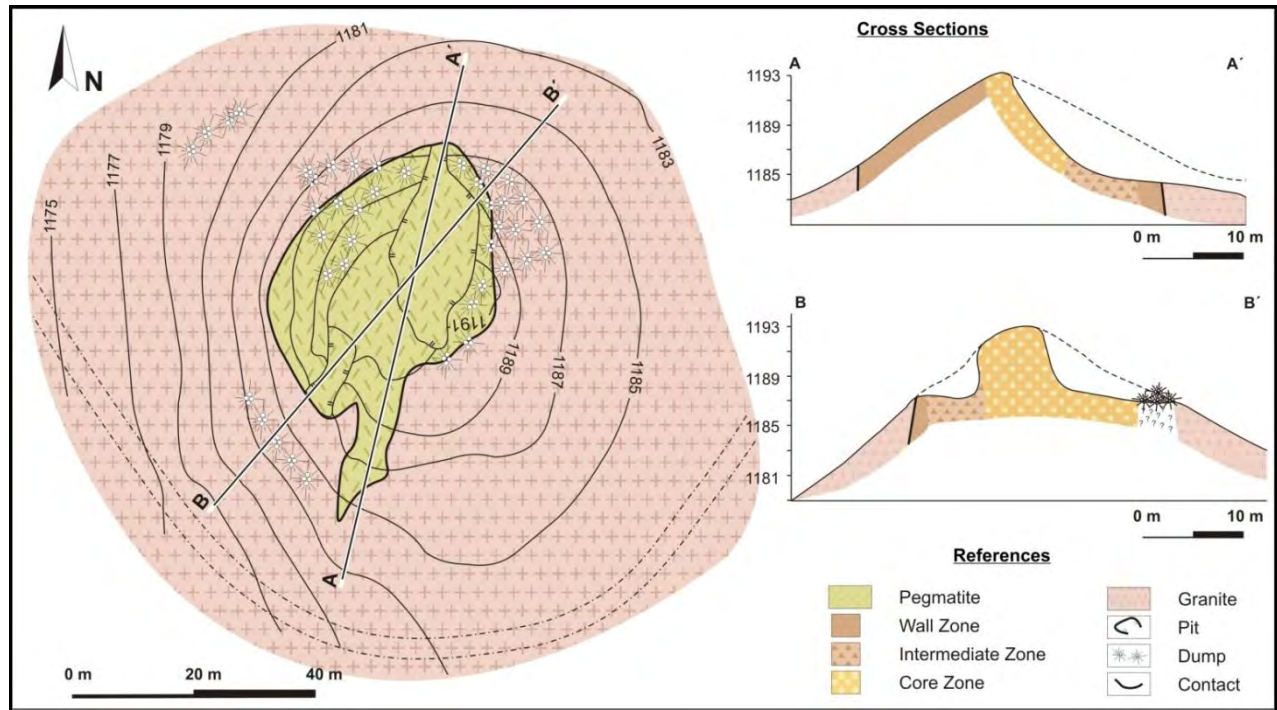


Figure 20: Geological map and cross section of the La Elsa pegmatite.

### Concluding Remarks

There are several facts that strongly suggest classifying the pegmatites of the Potrerillos subgroup as representatives of the NYF petrogenetic family. Among them, we considered: the intragranitic occurrence, the simple zoning, the particular mineralogy especially with monazite-(Ce), allanite (in other pegmatites), and particularly with magmatic fluorite.

The parental granites have post-orogenic emplacement in relation to the Famatinian orogenic cycle and petrological and geochemical affinities with A-type intrusives (Roquet *et al.* 2011). Considered together, the evidences support the classification of the pegmatites as Rare-Element (*REL-REE* subclass) representatives of the allanite-monazite type according to the classification of Černý & Ercit (2005).

## LAS CUEVAS PEGMATITE

### *Geological Setting & Internal Structure*

The Las Cuevas pegmatite is located at 32°23'10"S and 65°42'25"W in the San Martín department, San Luis province. There are several previous works that describe the internal structure or some mineral occurrences but the last one resume the old information and complete several aspects (Martínez & Galliski 2010). The pegmatite is emplaced in Early Paleozoic gneisses and mica-schists of the Conlara Metamorphic Complex (Sims *et al.* 1997). The main body of Las Cuevas pegmatite has a tabular shape and is folded, outcropping in an extension of 400 m with an average thickness of 10 m in the southern part. In the northern end the pegmatite dips 31° W, to the south, it strikes N10°W with a variable dip between 82° and 44° W (Fig. 25).

The pegmatite was differentially mined in seven open pits, and some underground workings concentrated in the northern end and, nowadays, it is inactive. Mining operation was discontinuous and directed first to beryl, later on to spodumene, tantalum-bearing ores and lately to albite, K-feldspar and quartz. The zoning is well developed and comprises 8 units.

The **border zone** is present in the foot wall of the pit A with a variable thickness between 3 and 10 cm, fine grain and formed by Qtz (70%) - Ms (25%) ± Pl-Grt-Ap-Tur. In the hanging wall diminishes the grain size and increases the Qtz and Ab proportion.

The **wall zone** in the pit A has a thickness between 5 and 30 cm and grain size from fine to medium. The composition is Ab (80%), Ms (15%) and Qtz (3%). The accessory minerals are: Ap-CGM and Fe-oxides.

The **saccharoidal albite zone** is present in the footwall of the pit A. The maximum thickness is 25 cm and is composed by Ab (90%) – Qtz (10%) with subordinate Ms and Grt-Ap and ore minerals as accessories phases.

The aplitic texture has some planes of garnet accumulation resembling line-rock.

The **albite-quartz zone** occurs in the pit A with a thickness of up to 40 cm and medium to coarse grain size. The composition varies from Ab (90-60%) and Qtz (10-40%). The accessory minerals are tourmaline, beryl, garnet, apatite, muscovite and ore minerals.

The **muscovite zone** is present in the roof of the pit A. The thickness is 70 cm and the grain size coarse to very coarse. It is dominantly composed by muscovite (90%), albite (5-10%) and quartz (<5%) with tourmaline, apatite, garnet and ore minerals as accessories.

The **outer intermediate zone** is present in most of the quarries and it is composed by Qtz (60%), Mc (40%), Ab, Ms, and subordinate Sp; the grain size is very coarse. The accessory phases comprise beryl, apatite, elbaite, amblygonite-montebrazite, triphylite-lithiophilite, mitridatite, and Mn- and Fe-oxides.

The **inner intermediate zone** is formed by Mc (50%), Qtz (40%) and Sp (10%) with minor muscovite. The accessory minerals are apatite, garnet, transition metal phosphates nodules, mitridatite and secondary Mn- Fe-oxides. The grain size is coarse to very coarse and fine-grained muscovite replacement units and Ms-Qtz-Ab-Tur replacement units are common. Inside this zone, there are some local modal variations that reach, in an ill-defined subzone, compositions of Qtz (60-70%), Sp (40-30%) with subordinate Ms and Ab as replacement minerals. Another variation was observed in the D quarry and it is formed by Mc (40%), Sp (30%), Qtz (20%), Ab (10%) and subordinate muscovite. In this work appear some fine-grained, pink lithian muscovite (lepidolite *s.l.*) locally replacing spodumene crystals.

The **core zone** was observed in the pits A and C. In A, this zone is composed by Qtz (99%) with some albite replacements. In C the modal composition vary Qtz (90-85%) - Sp (10-15%).

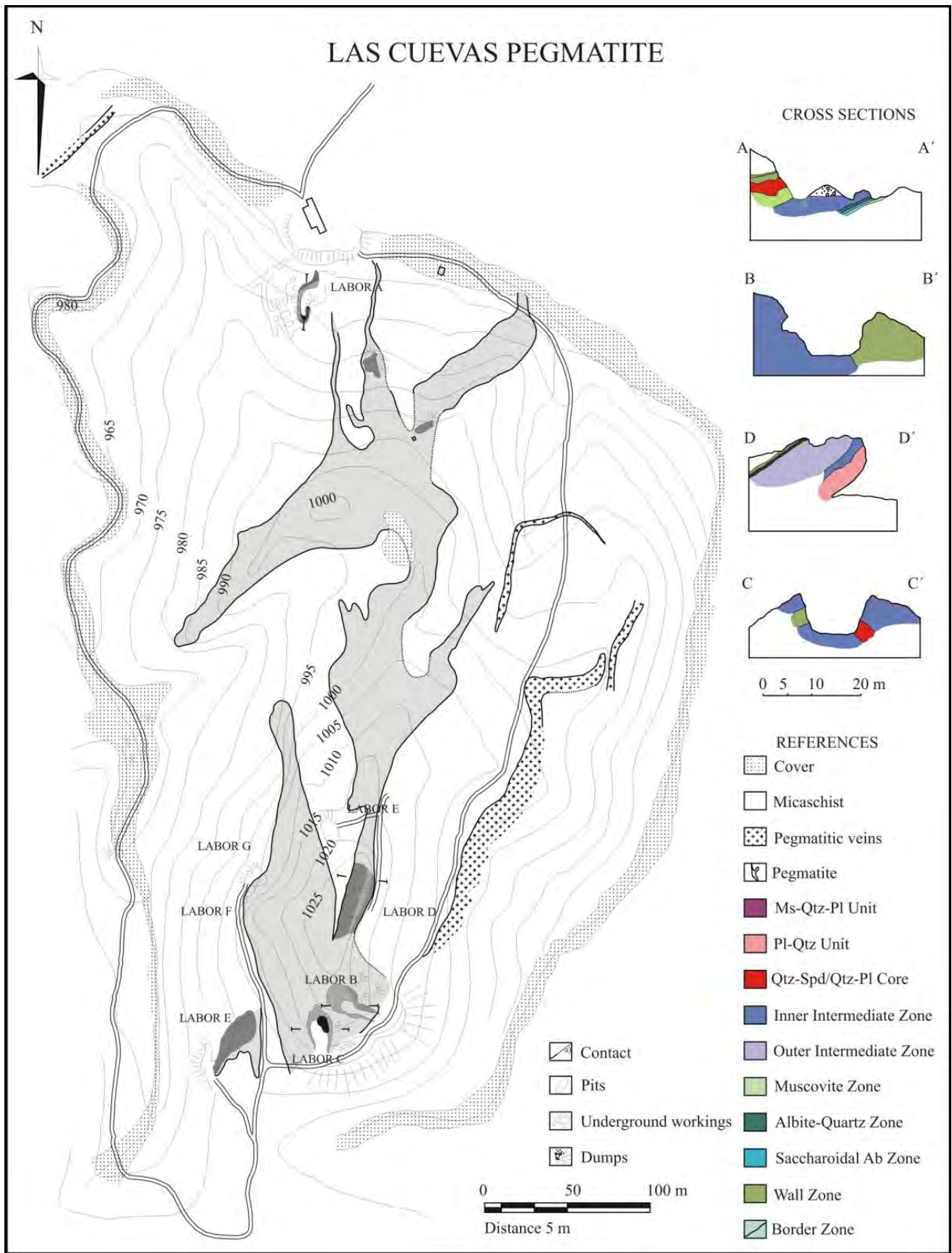


Figure 21: Geological map of Las Cuevas pegmatite showing the zoning in the main quarries.



## Mineralogy

The minerals identified in Las Cuevas pegmatite are: quartz, microcline, spodumene, albite, muscovite, apatite, beryl, schorl, zircon, garnet, columbite-(Mn), tantalite-(Mn), pyrochlore and microlite subgroup minerals, rutile, amblygonite-montebrazite, triphylite-litiophilite, elbaite, eucryptite, lepidolite, bismuthinite, pyrite, huréaulite, phosphosiderite, beraunite, rockbridgeite, stewartite, bismutite, dickinsonite, mitridatite and Fe- Mn-oxides.

**Quartz:** it is the most abundant mineral, usually in milky masses, very seldom presents some simple crystallographic forms. It normally has abundant trends of fluid inclusions and inclusions of acicular rutile. In the pit D some of the quartz is replaced by cleavelandite (Fig. 22).



Figure 22: Replacement of quartz from the core zone of Las Cuevas pegmatite by late-stage cleavelandite.

**Microcline:** it is very abundant in the intermediate zones in grey to pink crystals of metric sizes. With relative frequency, it is replaced by an assemblage of Ms-Qtz-Ab-Tur-Brl-Ap, by saccharoidal Ab with or without Brl or by an association of Ms-Qtz-Ab. The degree of (Al:Si) order is maximum. Occasionally it presents alteration to sericite or caolinite.

**Plagioclase:** it is present in all the units in different grain size and colors, with compositions generally in the range of albite and sometimes stained with a greenish hue of possible mitridatite. The late-stage replacement of cleavelandite is very conspicuous, occasionally associated with schorl and or garnet.

**Spodumene:** it is present in several zones and different generation in prismatic crystals that reach up to 3-5 m long. The color is variable between white, greenish white and grayish green. Usually the crystals are elongated and striated after [001] and present  $a \{100\}$  and  $m \{110\}$  with frequent (100) twins. Alteration is frequent and of two types: a) to veinlets of cymatolite (Ab + Ms) and b) to veinlets of Ab + Eu (eucryptite). This sequence was explained by London & Burt (1982) as: spodumene → eucryptite + albite → muscovite + albite → muscovite, which means a first stage of alkali metasomatism, followed for a second stage of acid replacement. In the F quarry, long prismatic spodumene crystals are associated with cleavelandite, "lepidolite" and occasionally decimetric crystals of pink elbaite (Fig. 23, 24) in a late-stage replacement of primary units.



Figure 23: Late-stage association of long prismatic spodumene crystals in a mass of *lepidolite* + quartz.

**Schorl:** it is widespread associated with Ab or Ms or Ab-Qtz-Ms in grain-size variable between fine to coarse. It produce also strong tourmalinization of the mica-schist in the host-rock or especially in the enclaves of the mica-schist frequents in the hanging wall of the pegmatite.

**Elbaite:** it occurs in the F quarry in seldom prismatic crystals than can reach 25-30 cm in length. The color vary from green in the border to pink inward. The crystals are usually very fractured.





Figure 24: A 25 cm long, prismatic elbaite crystal from the core-margin assemblage of the Las Cuevas pegmatite.

Beryl: it is normally present in the Ab+Qtz zone in prismatic euhedral crystals up to 20 cm with yellowish, greenish, pinkish white, pink and light or dark green. Very seldom is replaced by muscovite.



Figure 25: prismatic hexagonal crystals of white beryl.

CGM: the columbite group minerals occur concentrated especially in the northern end of the pegmatite where it tends to be with a low angle of dipping. They were mined by underground works and most of the analyzed crystals were available by courtesy of the owner of the mine. The usual occurrence was in massive pockets of several hundred of kilograms made by crystals of several cm with rough crystallographic forms. The analyzed crystals show compositions corresponding to columbite-(Mn) that evolved to tantalite-(Mn) (Table 8 and Fig. 26). The inclusion of the pyrochlore

supergroup minerals are not so frequent as in other pegmatites.

TABLE 8: SELECTED CHEMICAL ANALYSES OF CGM

Sample	CUE1A	CUE2A	CUE3B	CUE5A	CUE6B	CUE6C
WO <sub>3</sub>	0.23	0.00	0.09	0.92	0.07	0.26
Nb <sub>2</sub> O <sub>5</sub>	41.80	42.80	27.30	53.40	31.20	54.20
Ta <sub>2</sub> O <sub>5</sub>	38.50	36.70	54.80	25.00	50.90	24.50
TiO <sub>2</sub>	0.08	0.87	0.12	0.84	0.14	0.87
UO <sub>2</sub>	0.08	0.44	0.00	0.02	0.00	0.49
As <sub>2</sub> O <sub>3</sub>	0.03	0.00	0.02	0.00	0.03	0.00
Y <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.18	0.00	0.04
Sb <sub>2</sub> O <sub>3</sub>	0.05	0.00	0.00	0.01	0.01	0.00
Bi <sub>2</sub> O <sub>3</sub>	0.00	0.05	0.02	0.00	0.00	0.00
MgO	0.00	0.00	0.00	0.03	0.00	0.01
CaO	0.01	0.02	0.00	0.02	0.01	0.14
MnO	17.30	17.40	15.30	12.30	15.60	17.50
FeO	0.00	0.00	0.61	6.11	0.56	0.58
ZnO	0.01	0.16	0.08	0.00	0.00	0.12
Fe <sub>2</sub> O <sub>3</sub>	1.06	0.96	0.29	0.18	0.77	0.24
Total	99.15	99.40	98.66	99.01	99.29	98.95
W	0.016	0.000	0.007	0.060	0.005	0.017
Nb	5.058	5.114	3.601	6.081	3.996	6.158
Ta	2.802	2.638	4.348	1.713	3.921	1.674
Ti	0.016	0.173	0.026	0.159	0.030	0.164
U	0.005	0.026	0.000	0.001	0.000	0.027
As	0.005	0.000	0.004	0.000	0.005	0.002
Y	0.000	0.000	0.000	0.024	0.000	0.005
Sb	0.006	0.000	0.000	0.001	0.001	0.000
Bi	0.000	0.003	0.002	0.000	0.000	0.000
Mg	0.000	0.000	0.000	0.011	0.000	0.000
Ca	0.003	0.006	0.000	0.005	0.003	0.038
Mn	3.922	3.895	3.781	2.624	3.743	3.725
Fe <sup>2+</sup>	0.000	0.190	0.149	1.287	0.132	0.123
Zn	0.002	0.031	0.017	0.000	0.000	0.022
Fe <sup>3+</sup>	0.213	0.190	0.064	0.034	0.164	0.046
CTotal	12.048	12.266	12.002	12.000	12.000	12.001

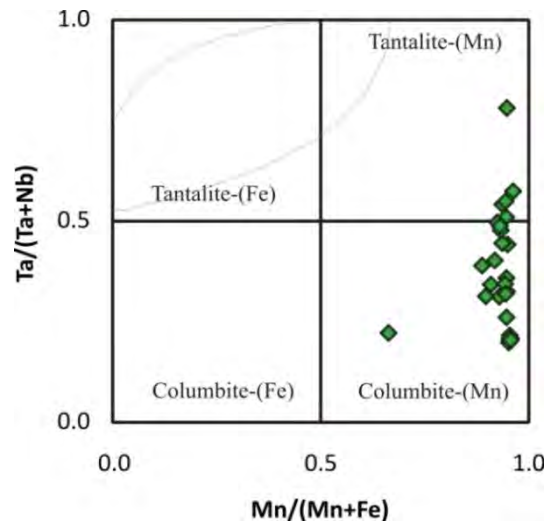


Figure 26: Columbite-group minerals from Las Cuevas pegmatite plotted in the CGM quadrilateral.

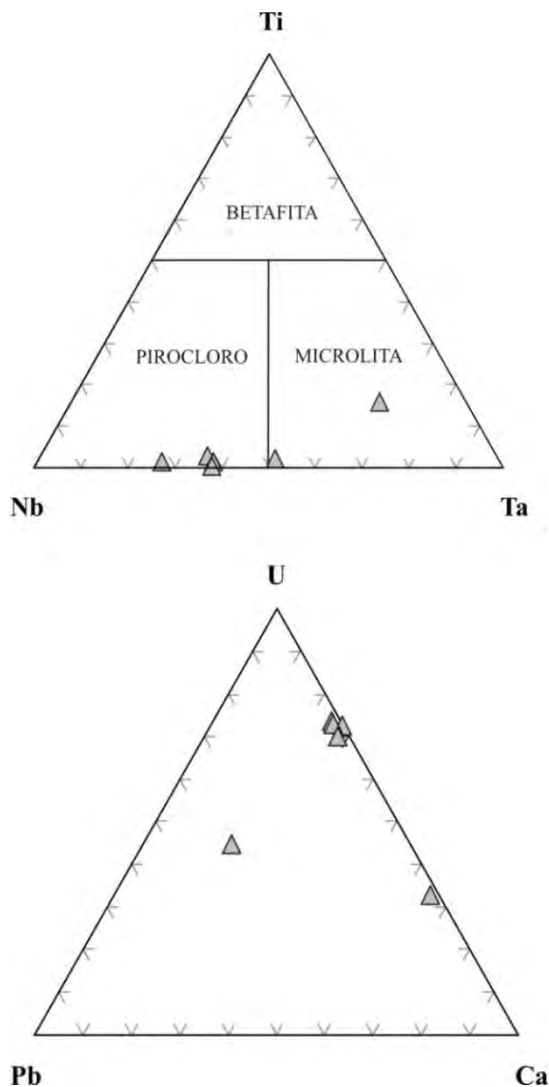


Figure 27: Pyrochlore supergroup minerals from Las Cuevas pegmatite plotted in the triangular Nb-Ta-Ti and U-Pb-Ca.

Pyrochlore supergroup minerals: they form microscopic inclusions in CGM. Some of them were analyzed but the totals are low, the partial data allow classifying them as belonging to the pyrochlore and microlite groups (Fig. 27). Some of the analyzed points are U-rich but the quality of the data preclude intending classify the phases to the species level in the schema of the IMA (Atencio *et al.* 2010).

Zircon: it is commonly present as millimetric inclusions in petrographic minerals of the pegmatite.

Bismuthinite and bismutite: the sulphide occurs as prismatic crystals and masses contained in the intermediates zones, close to the core. Occasionally it is

associated with tantalite-(Mn). The carbonate is a frequent product of alteration of the former mineral.

Pyrite: it is a fairly common accessory in cubic crystals up to 8 mm replaced by hematite.

Amblygonite-Montebasite: rounded white to grayish white nodules of members of this series, sometimes with rough presence of crystallographic forms, are present in the internal zones of the pegmatite, frequently with some degree of alteration.

Triphylite-Lithiophilite: the nodules of the Li and transition metals phosphates are common accessories in Las Cuevas pegmatite not in big masses but preferently in small nodules with variable grade of alteration. One sample analyzed corresponds to an almost pure lithiophilite end member. Alterations of the primary phases give several secondary phosphates still under study, among them were preliminarily identified: huréaulite, frondelite, phosphosiderite, beraunite and stewardtite.

#### Concluding Remarks

The Las Cuevas is one of the biggest units of the Conlara pegmatite field and belongs to the Rare-Element class, *REL-Li* subclass, complex type, spodumene-subtype of granitic pegmatites. It is a tabular body trending to the northwest, with dips ranging from vertical to subhorizontal. The host-rocks of the pegmatite are usually quartz-mica-schists. The depth of emplacement was in the ductile to brittle transition domain, possibly ranging between 7 and 12 km. The intrusion of the pegmatite was forced, producing secondary folding in the host rock and enclosing metric-sized xenoliths. The emplacement took place during the Eopaleozoic, shortly after the regional metamorphic peak, but it was prekinematic related to the late tectonism belonging to the Ocolytic phase, at the end of the Famatinian orogenic cycle. Eight zones of different mineral association, texture and setting have been identified in this pegmatite.

The processes of pegmatitic differentiation, indicated by the chemical composition of trace elements in K-feldspar and muscovite, are comparable and do not differ from the known paths of similar world and national pegmatites of this type showing lineal fractionation trends. Besides, the individual analysis shows a lineal differentiation, in some cases with an overprint between the samples of different zones, resulting from changes in the physico-chemical conditions of crystallization.

## THE LA ESTANZUELA PEGMATITE FIELD

This pegmatite field was defined by Galliski (1994a) as comprising the pegmatites of the Tilisarao, La Estanzuela and El Portezuelo ranges. These ranges are minor orographic units located to the east of the Sierra Grande de San Luis (Fig. 2). The geology of the basement of these ranges is formed by rocks of the Conlara Metamorphic Complex according to Sims *et al.* (1997), represented mainly by mica-schists, phyllites and gneisses, with some banks of marbles, amphibolites and quartzites. This metamorphic basement is intruded by usually small subconcordant lenses of granites synkinematically emplaced, and by swarms of pegmatites and aplites, except in the Tilisarao range where the granite form a major pluton.

Most of the pegmatites of this district do not differ substantially from the ones that occur in the Conlara pegmatite field, and they include representatives of the LCT petrogenetic family, rare-element class (*REL*), *REL-Li* subclass, with complex types of spodumene- and lepidolite-subtypes, and of albite-spodumene type. Barren or beryl type pegmatites are scarcer and tend to occur in the southern part of the district in the El Portezuelo range. In general, the pegmatites are irregular lens-shaped bodies, tens to hundreds meters long, emplaced after the metamorphic peak but that suffered post-emplacement deformation. Besides the usual rock-forming minerals, the pegmatites carry spodumene, beryl, tourmaline, *lepidolite*, CGM, WGM in one pegmatite, amblygonite-montebrazite, triphylite-lithiophilite and the array of secondary phosphate species.

### SAN ELÍAS PEGMATITE

The San Elías pegmatite is located approximately at 32° 51' 28" S and 65° 07' 06" W a few hundred meters to the west of La Viquita pegmatite (Fig. 28). San Elías is a rare-element class pegmatite of LCT petrogenetic family, which internal structure and mineralogy were initially described in general by Angelelli and Rinaldi (1963) and Herrera (1963), meanwhile Galliski *et al.* (1999) mentioned its principal features. The pegmatite is a tabular body that has 140 m long, a N-S strike, and dip with a high angle to the east. It is partially exposed because the eastern side is covered by Quaternary loess and the outcropping wide varies in between 27 and 15 m. The pegmatite is zoned with border, wall, intermediate and core zones. The border and wall zones are fine and medium grained rocks respectively, that are principally composed by Pl (An ~15), Qtz and Ms. The



Figure 28: Google Earth image of the San Elías (left) and La Viquita (right) pegmatites.

intermediate zone has a medium to coarse sized grain association of Kfs, Qtz, and Ab as main minerals. In the southern part of the pegmatite, there is a non-well defined subzone composed by cleavelandite and small crystal and nodules of amblygonite-montebrazite, with blue, green, colorless and pink tourmaline as principal accessory minerals. Nb-Ta minerals and yellow beryl are scarcely present in this zone. In the internal part, this subzone shows a widespread developing of gray, pink or purple, fine-grained, massive lepidolite. The core is irregular and is composed by quartz that includes a few big-sized idiomorphic crystals of K-feldspar. In the core margin assemblage there are abundant vugs in the cleavelandite, with late-stage growth of quartz, cookeite, hydroxylherderite and fluorapatite. Mostly in the northern half portion of the pegmatite, there are also some relicts of Mn-Fe-Li phosphates and nodules of an interesting assemblage of secondary Al-Li-Be-Ca-Sr phosphates including montebrazite, augelite, hydroxylherderite, fluorapatite, goyazite and crandallite (Galliski *et al.* 2011).

According to the described mineralogy the pegmatite is geochemically evolved with Na-Li rich phases and shows high  $\mu PFO_2$  and  $\mu HF$ . It was provisionally classified as a lepidolite-subtype pegmatite (Galliski *et al.* 1999), but montebrazite is also an important component. In the last years, with the discovery that the Al-Li phosphates widely disseminated in the feldspars lowered considerably the melt point of the powdered raw minerals, the pegmatite was intensively mined by this high quality ceramic material and the quartz by-product, with severe consequences for the excellent exposition of the phosphatic assemblage.



## LA VIQUITA

### Geological Setting & Internal Structure

The La Viquita granitic pegmatite is located at 65°06'30"W and 31°51'00"S, in the department of Chacabuco, San Luis province, Argentina. Together

with San Elías and La Viquita Sur, it forms a cluster of Li-bearing granitic pegmatites located in the western side of the northern end of La Estanzuela range (Fig.28). This range belongs to the Eastern Pampean Ranges and consists of a thick sequence of graywackes and shales with minor banks of limestone and scarce mafic rocks, metamorphosed to a medium grade during the Lower Paleozoic (Sims *et al.* 1997).

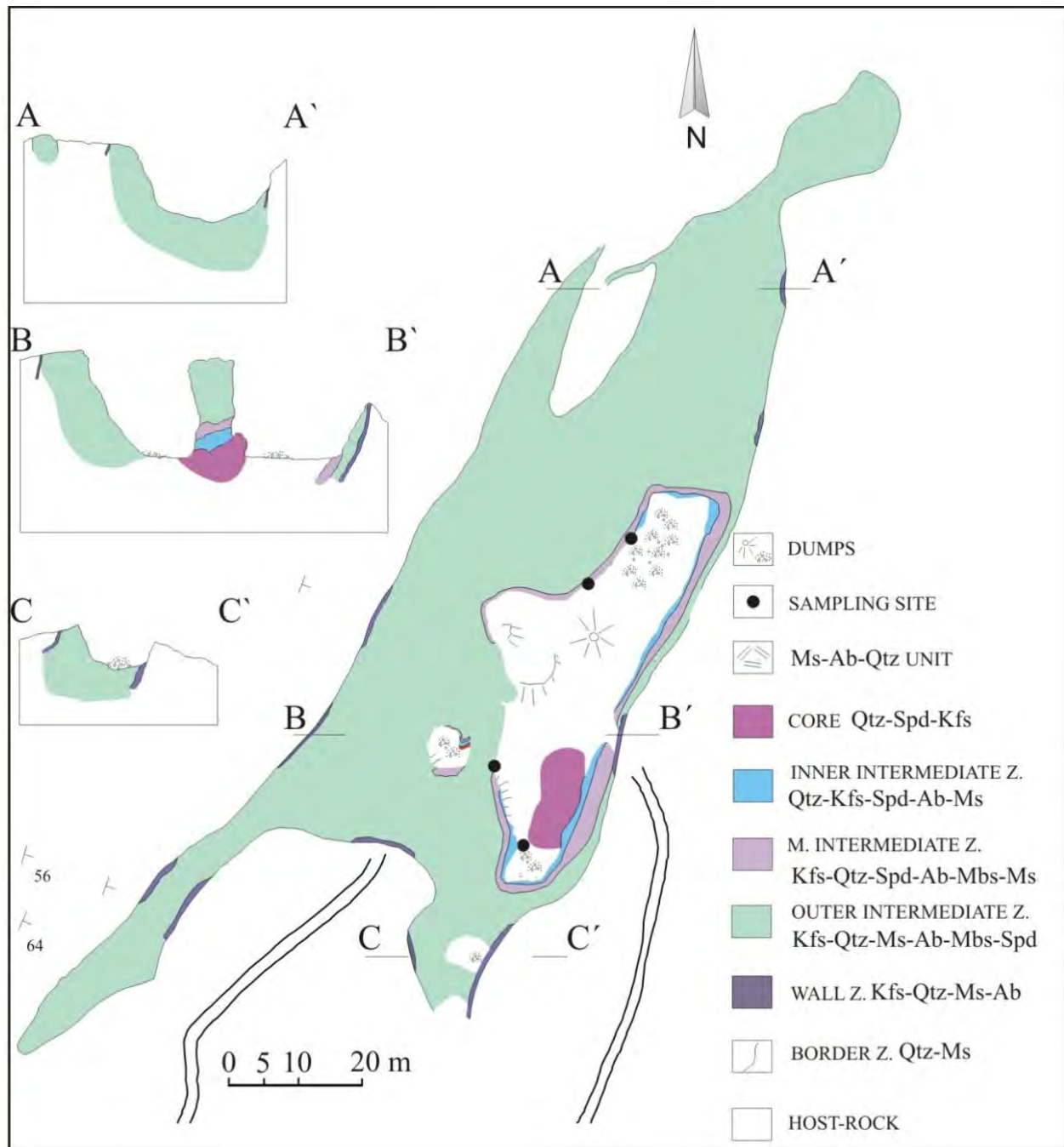


Figure 29: Geological map of the La Viquita pegmatite



The La Viquita pegmatite is discordantly emplaced in a dark-grey, NNE-striking and moderately to steeply ESE-dipping quartz-biotite-muscovite-plagioclase schists with sporadic porphyroblasts of staurolite and garnet. In the exocontact, the schist recrystallized to tourmaline- and muscovite-bearing assemblages to a distance of ~20 cm from the pegmatite. The pegmatite has an approximately lenticular shape, with 40 by 190 m in the surface exposure (Fig. 29); the strike is N42°E and the dips 31°NW and 60°NW in the hanging and footwall respectively.

The internal structure displays a symmetrical zoning (Martínez & Galliski 2000, Galliski *et al.* 2008). The fine-grained Qtz + Mu border zone is less than 7 cm wide. The wall zone is  $\leq 1$  m wide, medium- to fine-grained (5 mm in apatite to 20 cm in muscovite), and it consists of Kfs (40%), Qtz (40%), Ab (10%) and Mu (10%), with accessory garnet, tourmaline, beryl, columbite-group minerals, apatite, and secondary Fe-oxides. The intermediate zone is subdivided into three different units: outer, middle and inner, all of them coarse-grained. The outer unit is composed of Kfs (70-80%), Qtz (25-20%), some muscovite and albite  $\pm$  tourmaline, the middle unit contains Kfs (50%), Qtz (30%), Spd (~20%) and minor Ab, whereas the inner unit is formed by Qtz (50%), Kfs (30%), Spd (~20%) and Ab. These three units have in common accessory beryl, cm-sized nodules of montebrasite, triphylite-lithiophilite and some of their alteration products, and some minor phases such as eosphorite, ernstite, columbite-group minerals and wodginite-group minerals. The core of the pegmatite is composed of Qtz (80%), Spd (~15%) and Kfs (5%), with traces of pyrite. In general, the cm-sized spodumene crystals are moderately to strongly altered.

There are two assemblages located in the core-margin that are distinctly different from the coarse grained, massive zones described: 0.5-1 m-sized aggregates of yellow muscovite + pink albite that carry tapiolite-(Fe), wodginite-group minerals and cassiterite, and vuggy quartz with cm-sized cavities, associated with Kfs (adularia), Ab, Mu, cassiterite, occasionally hydroxyl-herderite and apatite (Černý *et al.* 2011). The first assemblage is interpreted as a late magmatic feature, in analogy with similar occurrences at other localities and experimental work (*cf.*, *e.g.* London 1992, Černý 2005, and the recent discussion by Kontak 2006), but the second one is clearly of hydrothermal origin.

The K/Rb values of K-feldspar from wall to intermediate zones range from 90 to 20, and Cs contents

from 100 to 1000 ppm. These data are in agreement with the mineralogy, both indicative of a geochemically evolved rare-element pegmatite of LCT petrogenetic family enriched in Ta over Nb, Sn and Ti, and with Fe enriched over Mn. A K-Ar date on muscovite gives a dubious preliminary age of  $320 \pm 12$  Ma (Galliski & Linares 1999). Mining of La Viquita pegmatite produced approximately 30 t of beryl, 55 t of spodumene, 80 t of amblygonite-montebrasite, 600 t of K-feldspar and 1 t of tantalum ore previous to 1962 (Angelelli 1984). Later on, the pegmatite was worked only sporadically and the underground workings (11 m deep) used to mine Ta-bearing minerals became completely buried under dumped waste.

### Mineralogy

The mineralogy of the La Viquita pegmatite in terms of Ta-Nb-Sn-Ti elements is, up to date, the most interesting of the southern Pampean ranges (Galliski *et al.* 2008). The mineralogy of Li- and transition metals phosphate minerals is also attractive and some research is under way. The oxide phases are restricted to the columbite-group minerals (CGM), wodginite-group minerals (WGM), tapiolite-(Fe), and cassiterite. Most of these phases are considered of magmatic origin because of their textural relationships among themselves and to the adjacent silicates. Early CGM are randomly distributed among the rock forming minerals of the border, wall and outer intermediate zones. Later phases are associated with minerals of inner zones or with the assemblage of fine-grained Ab+Mu  $\pm$  Qtz, considered a primary part of the core-margin.

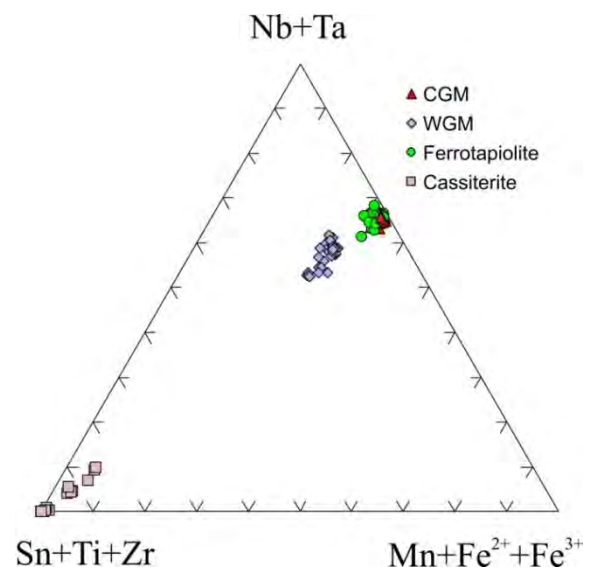


Figure 30: Triangular diagram showing the composition of the Nb-Ta-Sn-Ti ore minerals

The cassiterite hosted by the vuggy quartz is the only phase of hydrothermal origin. Typical secondary minerals of tantalum, such as microlite as a replacement of the columbite-group minerals in other pegmatites of the Pampean Ranges, were not found. The chemical compositions of the above phases, plotted in the Nb+Ta - Sn+Ti+Zr - Mn+Fe<sup>2+</sup>+Fe<sup>3+</sup> triangle (Fig. 30) and in the columbite quadrilateral (Fig. 31), show distinct clusters of data for each mineral group or species.

Columbite-Group Minerals

The columbite-group minerals occur in tabular to prismatic subhedral crystals up to 4 by 2 by 0.5 cm in size, but are usually smaller, black to very dark brown and striated parallel to their elongation. The crystals are dispersed mainly in the wall and intermediate zones, associated with albite, quartz, K-feldspar and muscovite. Three of the five members of the columbite-group minerals *sensu stricto* are represented in La Viquita: chemical compositions (Table 9) plot dominantly in the columbite-(Fe) quadrant of the columbite quadrilateral (Fig. 31), with a slight incursion into the tantalite-(Fe) field and a single columbite-(Mn) outlier. Some of the individual grains are almost homogeneous, as in the case of columbite-(Mn), but with distinct differences among the grains. However, columbite-(Fe) commonly shows fine-scale oscillatory zoning. The Ta# [Ta/(Ta+Nb) at.] shows sharp changes between 0.35 and 0.56, but the Mn# [Mn/(Mn+Fe<sup>2+</sup>+Fe<sup>3+</sup>) at.] is relatively stable between 0.28 and 0.36.

TABLE 9: SELECTED CHEMICAL ANALYSES OF CGM

Sample	VI1A	VI2AA	VI2BA	VI2E	VI2R	VI3A1
WO <sub>3</sub>	1.17	0.16	0.00	2.39	1.27	1.30
Nb <sub>2</sub> O <sub>5</sub>	38.40	28.00	26.00	64.30	64.60	38.60
Ta <sub>2</sub> O <sub>5</sub>	40.50	53.30	55.90	9.65	9.92	41.30
TiO <sub>2</sub>	0.62	0.50	0.38	2.08	1.51	0.73
ZrO <sub>2</sub>	0.09	0.00	0.00	0.00	0.00	0.09
SnO <sub>2</sub>	0.58	0.17	0.22	0.00	0.00	0.36
UO <sub>2</sub>	0.10	0.01	0.00	0.05	0.00	0.00
As <sub>2</sub> O <sub>3</sub>	0.03	0.01	0.01	0.03	0.02	0.03
Y <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.01	0.02	0.00
Sb <sub>2</sub> O <sub>3</sub>	0.00	0.01	0.00	0.03	0.03	0.01
Bi <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	0.08	0.06
MgO	0.00	0.01	0.01	0.02	0.01	0.00
CaO	0.02	0.00	0.00	0.00	0.01	0.01
MnO	6.19	5.61	5.69	6.06	6.12	5.71
FeO	10.59	9.95	9.46	13.19	12.91	11.60
ZnO	0.03	0.06	0.00	0.00	0.00	0.04
PbO	0.00	0.00	0.00	0.01	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	0.90	1.28	1.93	0.68	0.66	0.00
Total	99.22	99.07	99.60	98.50	97.16	99.84
W	0.082	0.012	0.000	0.147	0.079	0.091
Nb	4.705	3.639	3.396	6.890	7.020	4.715
Ta	2.985	4.167	4.392	0.622	0.648	3.035
Ti	0.126	0.108	0.083	0.371	0.273	0.148
Zr	0.012	0.000	0.000	0.000	0.000	0.012
Sn	0.063	0.019	0.025	0.000	0.000	0.039
U	0.006	0.001	0.000	0.003	0.000	0.000
As	0.005	0.002	0.002	0.004	0.003	0.005
Y	0.000	0.000	0.000	0.001	0.003	0.000
Sb	0.000	0.001	0.000	0.003	0.003	0.001
Bi	0.000	0.000	0.000	0.000	0.005	0.004
Mg	0.000	0.004	0.004	0.007	0.004	0.000
Ca	0.006	0.000	0.000	0.000	0.003	0.003
Mn	1.421	1.366	1.392	1.217	1.246	1.307
Fe <sup>2+</sup>	2.400	2.392	2.287	2.614	2.595	2.621
Zn	0.006	0.013	0.000	0.000	0.000	0.008
Pb	0.000	0.000	0.000	0.001	0.000	0.000
Fe <sup>3+</sup>	0.184	0.277	0.420	0.121	0.119	0.000
CTotal	12.001	12.001	12.001	12.001	12.001	11.989

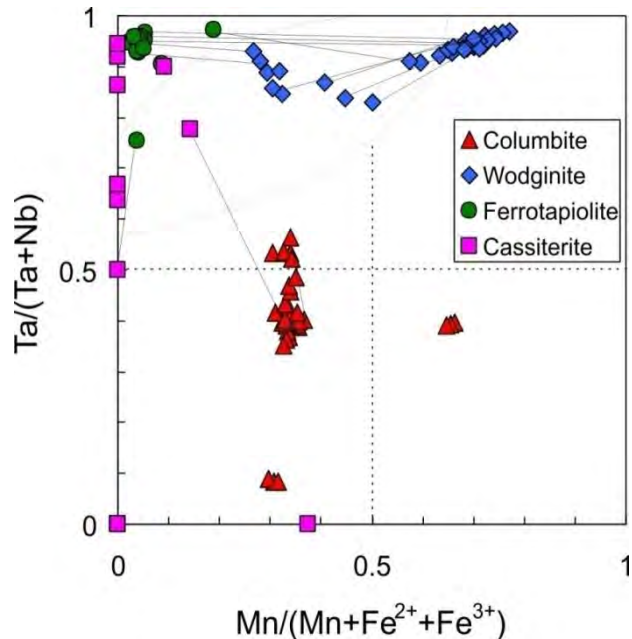


Figure 31: Plot of the compositions of CGM, WGM, tapiolite-(Fe) and Cassiterite in the columbite quadrilateral (tie lines link coexisting phases).

In general, the content of TiO<sub>2</sub> is significant, as it attains 2.08% and averages at 0.76% wt. %. The SnO<sub>2</sub> content is also high, with a maximum of 2.66% and an average of 0.68%. Inclusions of other minerals are minor, although rare, rounded grains of cassiterite are observed. The structural state of the columbite-group

minerals varies from disordered to moderately ordered (cf. Galliski & Černý 2006).

### Wodginite-group minerals

For a long time, the Mn- and Sn- dominant wodginite (Nickel *et al.* 1963) was an isolated mineral species in the systematics of the Nb-Ta-bearing oxide minerals. Four other derived phases were identified only relatively recently (Voloshin *et al.* 1990, Ercit *et al.* 1992, Tindle *et al.* 1998, Galliski *et al.* 1999), but their general abundance remain very subordinate to that of wodginite *sensu stricto*. However, of the five current members of the wodginite group (all of them Ta-dominant), three are represented in La Viquita.

The general formula of the wodginite-group minerals is  $ABC_2O_8$  where  $A = \text{Mn, Fe}^{2+}$  (Li, □),  $B = \text{Sn, Ti, (Ta, Fe}^{3+}, \text{Zr, Hf)}$ ,  $C = \text{Ta (Nb, W)}$ . In the wodginite-group minerals from La Viquita, the  $A$  site is dominated by Mn or  $\text{Fe}^{2+}$  (Table 10). The calculated Li content is significant, but in all cases below 12% of the total site-occupancy. The quantities of the other relevant cations analyzed are negligible. In the  $B$  site, Sn is the dominant cation in most of the samples, but does not invariably fill 50% of the site. Full occupancy of the  $C$  site is achieved by complementing all of Nb and negligible W by dominant quantities of Ta, and the remainder of Ta occupies the  $B$  site (up to 30% of its population). This site also hosts moderate to dominant Ti, major  $\text{Fe}^{3+}$  and significant Zr, which attains 1.63 wt.% oxide (0.350 *apfu*), almost in the range shown by the zirconian-hafnian wodginite exsolved from the Annie Claim #3 cassiterite in Manitoba (Masau *et al.* 2000). Hafnium, not sought in La Viquita samples, attains there up to 1.59 wt. %  $\text{HfO}_2$ ; the Hf content of Zr-rich wodginite may also be significant at La Viquita.

The wodginite-group minerals are distributed from the inner part of the intermediate zone inward, increasing in abundance to the core-margin association. They are observed in three different assemblages. (I) Wodginite-group minerals occur as wedge-shaped, dark brown, anhedral to subhedral crystals up to 0.8 mm in size, with small inclusions of tapiolite-(Fe). This kind of wodginite is enclosed in porous white albite, especially on some curved discontinuous surfaces covered by yellow mica. (II) Wodginite-group minerals also occur as sparse subhedral 0.2-4 mm crystals in a fine-grained groundmass of greenish mica and white albite. (III) More commonly, wodginite-group minerals form intergrowths with a fine-grained association of yellow mica and pink albite of the inner intermediate zone, or

in the core-margin association). In this assemblage, wodginite-group minerals are present in clusters up to 1 cm across, formed by euhedral crystals that individually are  $\leq 2\text{-}4$  mm in size.

Sample	VI13B	VI14B	VI14J	VI3AC	VI3BA	VI7A	VI7B	VI8AB
WO <sub>3</sub>	0.07	0.00	0.00	0.06	0.00	0.01	0.00	0.21
Nb <sub>2</sub> O <sub>5</sub>	2.12	4.10	7.77	1.83	7.36	1.43	1.58	4.93
Ta <sub>2</sub> O <sub>5</sub>	73.18	68.03	63.18	72.39	63.80	72.78	73.67	64.88
TiO <sub>2</sub>	0.36	2.76	6.72	0.26	6.90	0.13	0.19	0.74
ZrO <sub>2</sub>	1.05	0.71	0.29	1.38	0.42	1.19	1.24	0.44
SnO <sub>2</sub>	10.76	11.33	8.94	10.61	8.06	12.09	10.48	14.95
UO <sub>2</sub>	0.06	0.01	0.00	0.33	0.00	0.13	0.16	0.02
As <sub>2</sub> O <sub>3</sub>	0.03	0.03	0.03	0.03	0.02	0.04	0.04	0.03
Sb <sub>2</sub> O <sub>3</sub>	0.00	0.01	0.05	0.00	0.00	0.01	0.01	0.02
Bi <sub>2</sub> O <sub>3</sub>	0.00	0.02	0.00	0.08	0.03	0.00	0.00	0.00
MgO	0.00	0.01	0.01	0.01	0.07	0.01	0.00	0.02
CaO	0.02	0.05	0.03	0.01	0.03	0.01	0.03	0.04
MnO	8.07	7.10	5.79	8.54	5.37	8.91	8.49	3.74
FeO	3.22	4.89	5.83	3.31	6.74	2.69	2.77	9.07
ZnO	0.02	0.00	0.00	0.00	0.00	0.00	0.10	0.00
PbO	0.00	0.12	0.03	0.05	0.00	0.00	0.00	0.19
Total	98.96	99.17	98.67	98.89	98.80	99.43	98.76	99.28
W	0.010	0.000	0.000	0.010	0.000	0.000	0.000	0.020
Nb	0.430	0.790	1.420	0.370	1.340	0.290	0.320	0.960
Ta	7.560	7.210	6.580	7.620	6.660	7.710	7.680	7.020
Sum C	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Ta	1.280	0.680	0.370	1.150	0.350	1.080	1.290	0.570
Ti	0.120	0.890	2.040	0.090	2.100	0.040	0.060	0.240
Zr	0.230	0.150	0.060	0.300	0.080	0.260	0.270	0.090
Sn	1.910	1.930	1.440	1.890	1.300	2.140	1.870	2.570
As	0.010	0.010	0.010	0.010	0.000	0.010	0.010	0.010
Fe <sup>3+</sup>	0.450	0.340	0.080	0.560	0.170	0.470	0.500	0.520
Sum B	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
U	0.010	0.000	0.000	0.030	0.000	0.010	0.020	0.000
Sb	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000
Bi	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.000
Mg	0.000	0.010	0.010	0.010	0.040	0.010	0.000	0.010
Ca	0.010	0.020	0.010	0.000	0.010	0.000	0.010	0.020
Mn	3.040	2.570	1.980	3.230	1.840	3.350	3.220	1.370
Fe <sup>2+</sup>	1.200	1.740	1.970	1.230	2.280	1.000	1.040	3.270
Zn	0.010	0.000	0.000	0.000	0.000	0.000	0.030	0.000
Pb	0.000	0.010	0.000	0.010	0.000	0.000	0.000	0.020
Sum A	4.270	4.350	3.980	4.520	4.170	4.370	4.320	4.690
CTotal	15.830	16.010	15.900	15.970	16.000	15.900	15.820	16.190

The chemical composition of the wodginite-group minerals (Table 10) shows a broad variation over the compositional fields of wodginite, ferrowodginite, and ferrotitanowodginite (Fig. 32). Wodginite is the most widespread phase. Normally, individual grains are quite homogeneous or with only minor compositional variations, but some grains carry irregular patches and rims of ferrowodginite (cf. the tie-lines in Fig 31). Ferrowodginite is also found locally intergrown with subordinate tapiolite-(Fe), or with granular wodginite.

Patchy intergrowths of wodginite, ferrowodginite, and locally ferrotitanowodginite form networks in comparatively larger grains of tapiolite-(Fe), with relationships very similar to those of wodginite and ferrotitanowodginite described by Tindle & Breaks (1998) and of wodginite and titanowodginite described by Huang *et al.* (2002).

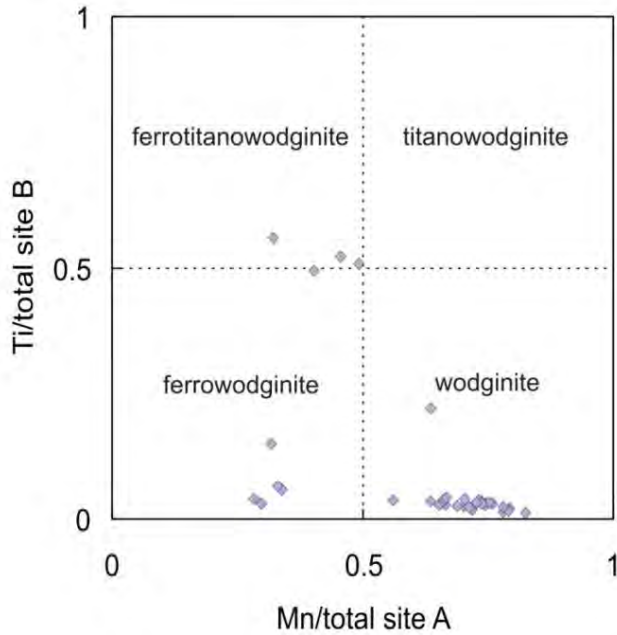


Figure 32: Compositions of the WGM from La Viquita pegmatite.

### Tapiolite-(Fe)

Tapiolite-(Fe) is quite common at La Viquita, and was initially identified by Arcidiácono (1974). It occurs as inclusions in wodginite and cassiterite, and as individual subhedral crystals associated with ferrotitanowodginite, in a matrix of muscovite, albite and quartz. In isolated crystals, commonly polysynthetically twinned, it commonly contains small irregular inclusions of hafnian zircon. The chemical compositions of individual crystals is fairly homogeneous, the contents of Sn and Ti are modest, and those of W and particularly Zr are very low (Table 11).

TABLE II : SELECTED CHEMICAL ANALYSES OF TAPIOLITE-(Fe)							
Sample	VI2AA	VH1C	VH1F	VH1G	VI11A	VI14A	VI15A
WO <sub>3</sub>	0.04	0.00	0.00	0.00	0.07	0.00	0.19
Nb <sub>2</sub> O <sub>5</sub>	1.47	8.61	6.53	7.59	4.98	1.79	13.78
Ta <sub>2</sub> O <sub>5</sub>	84.15	76.30	79.00	77.90	78.52	83.30	69.87
TiO <sub>2</sub>	0.13	0.07	0.30	0.30	0.15	0.41	0.24
ZrO <sub>2</sub>	0.00	0.00	0.00	0.00	0.14	0.00	0.00
SnO <sub>2</sub>	0.27	0.07	0.01	0.00	0.93	0.44	0.98
UO <sub>2</sub>	0.08	0.15	0.01	0.00	0.00	0.00	0.20
Sc <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.01
As <sub>2</sub> O <sub>3</sub>	0.03	0.03	0.01	0.05	0.03	0.00	0.06
Sb <sub>2</sub> O <sub>3</sub>	0.05	0.00	0.00	0.02	0.00	0.06	0.00
Bi <sub>2</sub> O <sub>3</sub>	0.00	0.11	0.05	0.06	0.17	0.00	0.03
MgO	0.00	0.02	0.01	0.01	0.00	0.01	0.00
CaO	0.01	0.02	0.02	0.00	0.01	0.04	0.02
MnO	2.59	0.64	0.50	0.64	1.17	0.72	0.54
FeO	11.27	14.14	13.66	14.26	12.63	12.82	13.98
PbO	0.06	0.00	0.00	0.00	0.09	0.06	0.00
Total	100.15	100.16	100.10	100.83	98.89	99.65	99.90
W	0.002	0.000	0.000	0.000	0.003	0.000	0.008
Nb	0.112	0.628	0.482	0.552	0.376	0.137	0.975
Ta	3.865	3.351	3.510	3.410	3.568	3.825	2.973
Ti	0.017	0.009	0.037	0.036	0.019	0.052	0.028
Zr	0.000	0.000	0.000	0.000	0.011	0.000	0.000
Sn	0.018	0.005	0.001	0.000	0.062	0.030	0.061
U	0.003	0.005	0.000	0.000	0.000	0.000	0.007
Sc	0.000	0.000	0.000	0.000	0.000	0.000	0.001
As	0.003	0.003	0.001	0.005	0.003	0.000	0.006
Sb	0.003	0.000	0.000	0.001	0.000	0.004	0.000
Bi	0.000	0.003	0.001	0.002	0.005	0.000	0.001
Mg	0.000	0.005	0.002	0.002	0.000	0.003	0.000
Ca	0.002	0.003	0.003	0.000	0.002	0.007	0.003
Mn	0.370	0.088	0.069	0.087	0.166	0.103	0.072
Fe <sup>2+</sup>	1.592	1.909	1.866	1.919	1.764	1.810	1.829
Pb	0.003	0.000	0.000	0.000	0.004	0.003	0.000
CTotal	5.990	6.009	5.972	6.014	5.983	5.974	5.964

### Cassiterite

Cassiterite, previously analyzed by Angelelli *et al.* (1978), is present in several forms in the La Viquita pegmatite, although it is not particularly abundant.

(I) Rounded intergrowths included in columbite-(Fe) occur in the middle intermediate zone. (II) Dark brown, mm-sized striated crystals of cassiterite are embedded



in fine-grained intergrowths of albite and quartz from the inner intermediate zone; they commonly carry inclusions of tapiolite-(Fe) with a higher Ta# than the host. (III) Cassiterite also occurs in brown crystals,  $\leq 1$  mm in size, in white lamellar albite of the inner part of the intermediate zone, or at the core-margin associations; this cassiterite is commonly intergrown with, or contains inclusions of tapiolite-(Fe). In the latter case, both minerals have almost the same Ta#. (IV) In a distinctly different association in the core-margin, cassiterite occurs with pink albite and yellow mica or in cavities of quartz with minor mica; it commonly forms equidimensional, isolated, euhedral, brown to dark yellow crystals 0.5 to 1 cm across.

Some crystals of cassiterite show high Ta content strongly dominant over that of Nb, except in the dark-yellow cassiterite of the type (IV) that is very poor in both elements, as well as Fe dominant over Mn (Table 12). Tungsten is minor, and Ti and Zr even more so. Even though the Ta# of the cassiterite tends in general to decrease from the outer to the inner zones, the variations do not follow a regular path.

Concluding Remarks

The mineralogical evolution history of the Nb-Ta-Ti-Sn oxides of the La Viquita pegmatite can be visualized in the Figure 33. This graph shows that the CGM crystallization with increasing #Ta give pass to WGM with progressive decreasing #Mn for finishing with tapiolite-(Fe) phase under increasing conditions of  $fO_2$ .

TABLE 12: SELECTED CHEMICAL ANALYSES OF CASSITERITE

Sample	VH2AA	VI11B	VI15B	VI16A	VI16B	VI16C
WO <sub>3</sub>	0.00	0.00	0.00	0.00	0.07	0.00
Nb <sub>2</sub> O <sub>5</sub>	0.13	0.81	0.50	0.13	0.08	0.07
Ta <sub>2</sub> O <sub>5</sub>	1.29	12.97	0.55	0.00	0.00	0.00
TiO <sub>2</sub>	0.10	0.04	0.00	0.00	0.05	0.07
ZrO <sub>2</sub>	0.06	0.23	0.01	0.00	0.00	0.01
SnO <sub>2</sub>	98.43	82.46	99.05	99.88	99.60	100.21
ThO <sub>2</sub>	0.01	0.00	0.02	0.06	0.00	0.03
As <sub>2</sub> O <sub>3</sub>	0.06	0.00	0.03	0.00	0.01	0.00
Sb <sub>2</sub> O <sub>3</sub>	0.03	0.01	0.10	0.06	0.07	0.09
Bi <sub>2</sub> O <sub>3</sub>	0.04	0.00	0.00	0.10	0.00	0.01
CaO	0.06	0.05	0.06	0.06	0.05	0.02
MnO	0.00	0.25	0.04	0.00	0.01	0.03
FeO	0.34	2.30	0.16	0.05	0.03	0.01
ZnO	0.04	0.00	0.09	0.00	0.00	0.00
PbO	0.00	0.14	0.12	0.05	0.02	0.00
Total	100.59	99.26	100.73	100.39	99.99	100.56
W	0.000	0.000	0.000	0.000	0.000	0.000
Nb	0.000	0.020	0.010	0.000	0.000	0.000
Ta	0.020	0.180	0.010	0.000	0.000	0.000
Ti	0.000	0.000	0.000	0.000	0.000	0.000
Zr	0.000	0.010	0.000	0.000	0.000	0.000
Sn	1.960	1.690	1.970	1.990	1.990	1.990
Th	0.000	0.000	0.000	0.000	0.000	0.000
As	0.000	0.000	0.000	0.000	0.000	0.000
Sb	0.000	0.000	0.000	0.000	0.000	0.000
Bi	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000	0.000	0.000
Mn	0.000	0.010	0.000	0.000	0.000	0.000
Fe <sup>2+</sup>	0.010	0.100	0.010	0.000	0.000	0.000
Zn	0.000	0.000	0.000	0.000	0.000	0.000
Pb	0.000	0.000	0.000	0.000	0.000	0.000
CTotal	1.990	2.010	2.000	1.990	1.990	1.990

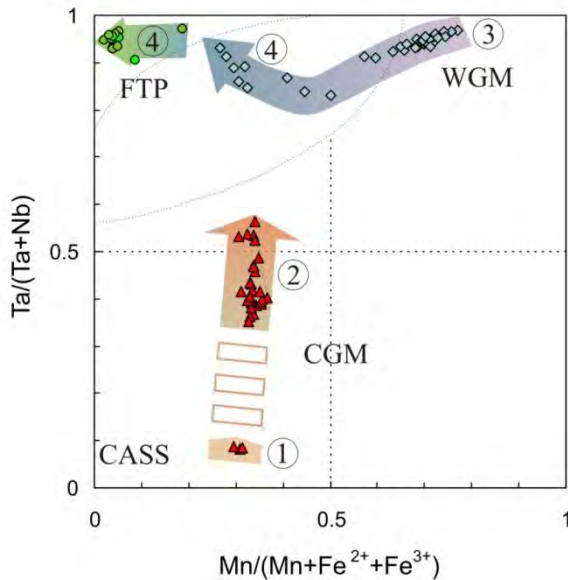


Figure 33: Schematic evolution of the Nb-Ta-Ti-Sn oxides from La Viquita in the CGM quadrilateral.

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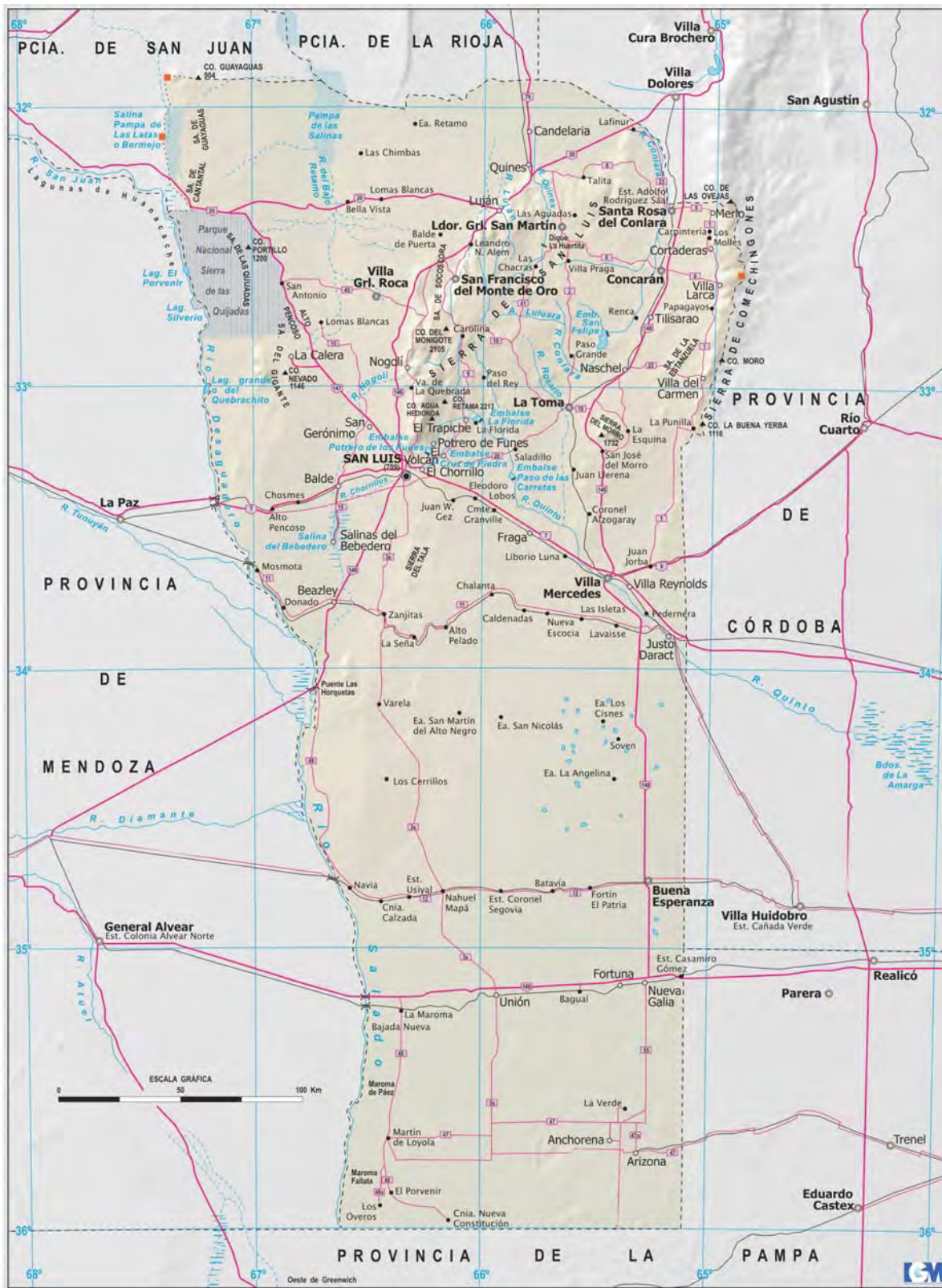
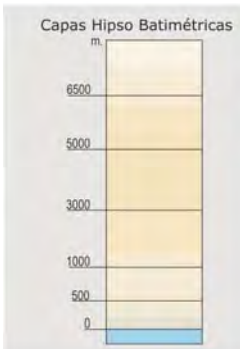
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