minerals

Review

The Li-Bearing Pegmatites from the Pampean Pegmatite Province, Argentina: Metallogenesis and Resources

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Abstract: The Li-bearing pegmatites of the Pampean Pegmatite Province (PPP) occur in a rare-element pegmatite belt developed mainly in the Lower Paleozoic age on the southwestern margin of Gondwana. The pegmatites show Li, Rb, Nb ≤ Ta, Be, P, B, Bi enrichment, and belong to the Li-Cs-Ta (LCT) petrogenetic family, Rare-Element-Li (REL-Li) subclass; most of them are of complex type and spodumene subtype, some are of albite-spodumene type, and a few of petalite subtype. The origin of the pegmatites is attributed predominantly to fractionation of fertile S-type granitic melts produced by either fluid-absent or fluid-assisted anatexis of a thick pile of Gondwana-derived turbiditic sediments. Most of the pegmatites are orogenic (530–440 Ma) and developed during two overlapped collisional orogenies (Pampean and Famatinian); a few are postorogenic (~370 Ma), related to crustal contaminated A-type granites. The pegmatites were likely intruded in the hinterland, preferably in medium-grade metamorphic rocks with PT conditions ~200–500 MPa and 400–650 °C, where they are concentrated in districts and groups. Known combined resources add up 200,000 t of spodumene, with variable grades between 5 and 8 wt.% Li_2O. The potential for future findings and enlargement of the resources is high, since no systematic exploration program has yet been developed.

Keywords: Li-bearing pegmatites; metallogenesis; lithium resources; Lower Paleozoic; Argentina

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1. Introduction

Assessment of the lithium resources for modern technological applications, especially for the rapidly growing demand for rechargeable Li-ion batteries for automotive vehicles, has produced a number of papers that contribute to the assurance that this strategic metal will be available in the next few years [1–5]. However, it is still necessary to assess the potential resources of many Li-rich ore deposits that were overlooked in the global inventory. Such is the case of the rare-element pegmatites present in the Pampean Pegmatite Province (PPP) that possess discrete mineralization of Li-ores. Some of these pegmatites were studied, explored, and mined for lithium resources from the 1960s to 1980s [6–15], but later, their small-scale mining progressively declined, even though the research continued [16–18]. Likewise, the reviews addressing the description and assessment of the resources of some districts of Li-bearing pegmatites [19], and some syntheses of the pegmatite lithium mining in Argentina, became outdated [20].

In this paper, we will present a summary of the location, geology, mineralogy, age, and estimated minimum resources of the main pegmatites carrying lithium from the principal economic districts of the PPP as a contribution to the global inventory of the hard rock potential resources of this strategic metal, and to the knowledge of the evolution and worldwide distribution of the rare-element pegmatites. We use the combined information to update the original hypothesis, and to predict the best regions for detailed exploratory research. We employ the nomenclature and categories established for the description of granitic pegmatites [21–23].

2. Geological Setting of the Pampean Pegmatite Province

The PPP extends for more than 800 km along a N–S belt situated eastward of the Andes, mostly in different units of the Pampean Ranges. The PPP main districts are located in the foreland of the Andes from 24°30′ to 33°30′ S. From 27° southward, this belt is included in a segment of flat subduction of the Nazca Plate that produced a set of faulted and tilted blocks of crystalline basement separated by basins partially and variably filled predominantly with clastic continental sediments from the Upper Paleozoic to recent years [24]. The different regional units comprise from the Eastern Cordillera in the north to the Eastern Pampean Ranges in the south (Figure 1). Southward, the PPP possibly extends for several hundred kilometers, mostly buried by recent sedimentary cover. The geological evolution of the basement of the Pampean Ranges developed during the Upper Precambrian to the Lower Paleozoic on the southwestern margin of Gondwana during two major overlapped tectonic and magmatic episodes known locally as the Pampean (~555–520 Ma) and the Famatinian (~505–440 Ma) Orogenies. During the Pampean Orogeny the attachment of the Pampia terrane that forms the Eastern Pampean Ranges to the Río de la Plata craton took place. The geodynamic arrangement of this episode is still debated, with interpretations that consider (i) collision of an oceanic ridge against an accretion prism associated with the Río de la Plata craton, (ii) active transportation and docking of the Pampean terrane by a transform fault extending to the Río de la Plata craton [25], and (iii) accretion of the Córdoba island arc terrane against the Río de la Plata craton, followed by an eastward subduction and collision of the Grenville-derived Pampia terrane [26]. This Pampean Orogeny was followed westward by extended sedimentation of a thick psamopelitic sequence represented by the Puncoviscana Formation (PVF) in the north and the Conlara Metamorphic Complex (CMC) in the south, forming a package that different studies consider equivalent, and from eastern provenance dominantly from Gondwana-based cratonic areas [25,27]. Accretion from the west of a ribbon of continental rocks with Laurentian affinities (the MARA block of Rapela [25]) or of more than one terrane with the same Grenville signature [28] produced the Famatinian collisional orogeny. Another interpretation [29] considers that both orogenies were formed by the eastward low-angle subduction and later accretion of the MARA block of the Laurentian provenance. In any case, the metasedimentary sequence underwent a predominantly low pressure–high temperature Abukuma-type metamorphism and an intrusion of I- and S-type magmatic rocks [17,30,31]. Following the uplift and erosion of the Famatinian orogen, a postorogenic volumetrically important intrusion of A-type batholiths consolidated the crystalline basement [17,30,32]. Some authors define this last magmatic episode as the main magmatic process of the Achalian Orogeny [33]. The rare-element pegmatites of the PPP in general, and the REL-Li subclass pegmatites in particular, are roughly linked in time and space to the above-mentioned S-type and A-type igneous rocks.

3. The Lithium-Bearing Pegmatite Belt and Its Main Pegmatite Districts

The rare-element pegmatites with lithium mineralization extend from Salta to San Luis provinces along ~800 km, grouped in several districts that define a segmented belt. To the west, this belt mostly contains districts of muscovite or muscovite-rare-element pegmatites, that carry beryl and, in some occurrences, sillimanite, kyanite, or andalusite [16,34] in the northern part, with no or just negligible lithium mineral occurrences. In the south, the pegmatites of the Valle Fértil district are dominantly of muscovite class, with minor units of muscovite-rare-element class. To the east, in some places, there are muscovite-rare-element to muscovite pegmatites mainly in the Eastern Pampean Ranges of Córdoba, which comprise the Alta Gracia and Comechingones districts [35,36]. The principal districts with Li-bearing pegmatites are, from north to south, El Quemado, Ancasti, Conlara, La

Estanzuela, and Totoral, with minor occurrences in Altautina (Figure 1), already in the Eastern Pampean Ranges of Córdoba.

3.1. El Quemado Pegmatite District (QPD)

The geology of the district consists of a thick turbiditic pile of pelitic and graywackic metasedimentary rocks belonging to the PVF of Precambrian to Lower Cambrian age [37], with medium-grade metamorphism that were intruded by epizonal plutons of trondhjemites and minor peraluminous leucogranites cupolas and pegmatites [38]. The district shows several pegmatite groups (Figure 2) with the known Li resources mostly concentrated in the pegmatites Aguas Calientes, Santa Elena Central, I and IV, and El Quemado. The sizes of the pegmatites are variable, with the main bodies concentrated in the Santa Elena Group, where lengths reach up to 800 m and widths up to 25 m (Table 1).

Table 1. Main parameters and mineralogy of lithium pegmatites from the El Quemado and Ancasti districts.

NAME	T	Ds	Gr	#	L	W	St	D	HR	Age (Ma) *	R	1	2	QAP	Spd	Lpd	Ms	Tur	Brl	Zrn	Ap	Aby	Trl-Trp	CGM	Mic	UM	BM	Reference
La Elvirita	S			3	40	≤2.5	N-S	45° E	tr					X	*		x	*	*	*	*	*	*	*	*	*	*	[15,17]
Aguas Calientes	P			1	270	25	N-S	75° W	ms			10–15		X	X		x	*	*	*	*	x	*	*				[15,17]
Anzotana	S			2	10	~3	N10° E	15° W	ms					X	*		x	x	x	*	x	*	*	x				[15,17]
Santa Elena C	P	El Quemado		1	200	30	~N40° W	~75° SW	ms	529.9 ± 11.5 * 480.6 ± 6.9 *				X	X	x	x	x	x	x	x	X	*	x	x	x	x	[15,39,40]
Santa Elena I	P			1	180	3–6	~N40° W	~75° SW	ms		>100 k			X	X	X	x	x	x	x	x	X	*	x		*		[15,17,39]
Santa Elena II	P			1	370	4	~N40° W	~75° SW	ms					X				x	x	*	x	x		x				[15,17,39]
Santa Elena III	P			1	320	4	~N40° W	~75° SW	ms					X			x	x	x	*	x	x		x				[15,17,39]
Santa Elena IV	P			1	800	6–12	~N40° W	70° SW	ms			15–20		X	X		x	x	x	*	x	x	*	x				[15,17,39]
El Peñón	B			1	60	4–10	~N40° W	~90°	ms	506.6 ± 6.07 * 502.4 ± 7.94 *				X			x	x	x	*	x	x	*	x	*	*	*	[15,39,40]
El Quemado	S			1	>40	~6	~N40° W	70° NE	ms	491.5 ± 3.74 *				X	X		x	*	x	x	x	x	*	x	x		x	[15,39,40]
Reflejos del Mar	S			1	600	4.50	N10° E	85° W	ms	343 ± 13	5175	25	8	X	X		x	x	x		x	*	*	*				[10,41,42]
La Culpable	S			1		4.50	N10° E	85° W	ms		5088	25	8	X	X		x	x	x		x	*	*	*				[10,41,42]
Loma Pelada	S		Vilisman	13	~ 600	~ 3	N10° E	72° W	ms		32,960	20	6.9	X	X		x	x	x		x	*	*	*				[41,43]
Juan Carlos	S	Ancasti		1	200	2	N7° E	68° W	ms		4500	25	7.3	X	X		x	x	x		x	*	*	*				[10,41]
Joyita	S			1	180	0.80	N8° E	75° W	ms		972	10	7.3	X	X		x	x	*		x	*	*	*				[10,41]
Pampa El Coco	S			1	90	0.85			ms		689	20		X	X		x	x	*		x	*	*	*				[41]
La Herrumbrada	S			3	161	1.68	~N-S	~90°	ms		3793	20	5.3	X	X		x	x	x		x	*	*	*				[41,43]
Campo El Abra	S			1	248	5	~N-S	~90°	ms		10,368	24		X	X		x	x	*		x	*	*	*				[41,43]
Ipizca I	S			1	700	6	N8° W	90°	ms			7–25		X	X		x	x	x		x	*	*					[9]
Ipizca II	S		El Taco	1	120	8	N7° W	45° E	ms	445 ± 17	2300	10–25	3.7	X	X		x	x	x		x	*	*	*				[8]
Santa Gertrudis	AS			3	520	4–10	N18° W	85° E	ms	709 ± 34	2175	7–25		X	X		x	x	x		x	*						[8]
Flor Morada	S			1	255	5–6	N7° E	78° W	ms			20		X	X		x	x	x		x	*	*	*				[41]

Note: T, type of pegmatite; S, spodumene; P, petalite; AS, albite-spodumene; B, beryl; Ds, district; Gr, group; #, number of dykes; L, length (m); W, width (m); St, strike; D, dip; HR, host rock; tr, trondhjemite; ms, mica schist; Age (Ma), number marked by * = LA-ICP-MS dating of columbite [40], all others are K-Ar ages [42]; R, Spd resources (t); 1, Spd (wt.%); 2, Li_2O (wt.%); QAP, Qz + Kfs + Pl; CGM, columbite group minerals; Mic, microlite group minerals; UM, U-bearing minerals; BM, Bi-bearing minerals. X = mayor mineral; x = abundant accessory; * = minor accessory. Mineral abbreviations as in [44].

The emplacement of the bodies is forced in the mica schist or mottled hornfels, and permissive in the trondhjemites, with tourmalinization of the host rock in the few cm near the contact. Zoning is well-developed, with 3 to 6 units where Li-minerals began to participate from the intermediate zones inwards. The mineralogy of these pegmatites is varied (Table 1), as is often the case in pegmatites of the rare-element class, and petalite and beryl subclasses. The Li-bearing dikes are pegmatites with spodumene-quartz intergrowth pseudomorphs after petalite ("*squi*", [45]), as was later identified [46], which carry spodumene, lepidolite, montebrasite, triphylite-lithiophilite, and derivatives. The columbite group minerals (CGM) include, predominantly, tantalite-(Mn), columbite-(Mn), tapiolite-(Fe), and bismutotantalite [47,48]. Two K-Ar muscovite ages give values of 564 $\pm$ 25 Ma for Santa Elena and 545 $\pm$ 15 Ma for Tres Tetas pegmatites [14]. The recently obtained Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) columbite ages give values between 529.9 $\pm$ 11.5 and 485.2 $\pm$ 7.5 Ma [40]. The pegmatites were only mined in the last century by CGM and bismuth, producing about 10 and 5 t of ore concentrates, with grades over 40% Ta_2O_5 and 50% Bi, respectively. The estimated potential resources, based on dimensional and modal mineralogy analyses along their lengths exceeds 100,000 t of spodumene [39].

3.2. Ancasti Pegmatite District (APD)

The Ancasti Pegmatite District (APD) is located in the Ancasti range where barren and rare-element class granitic pegmatites (Figures 1 and 3) were described in previous studies by several authors [6,8–10,12,49–51]. The main occurrences of the district were evaluated in detail [41]; meanwhile, other papers integrated the information and interpreted the geology [16,17,52]. The district comprises several groups that, from north to south, are named La Pampa-Unquillo, Vilismán, El Taco, and Santa Bárbara (Figure 3) [53]. The La Pampa-Unquillo Group comprises predominantly rare-element pegmatites of beryl type, intruding gneisses and migmatites of the Sierra Brava Complex. More than 90 pegmatites were exposed to artisanal mining for beryl and muscovite, and there are no records of Li-bearing mineralization.

In the Vilismán Group (Figure 3), Li-bearing pegmatites of the group 1, or spodumene and albite-spodumene types predominate, intruded in the mica schists of the Ancasti Formation. The pegmatites are single tabular dikes such as Reflejos del Mar, La Culpable or Juan Carlos, or groups of them, as occur in La Herrumbrada and Loma Pelada (Table 1). The lengths of the dikes range between 600 and 180 m and the widths between 0.80 and 5 m. The strike of the dikes is submeridional (avg. N10° E) and dips 70–90° W, and they are subconcordant with the strike of the hosting mica schists. The pegmatites are zoned with a thin border zone, usually aplitic, followed by wall and intermediate, to intermediate–core zones, and a relatively simple mineralogy, with spodumene as the main lithium ore, and amblygonite-montebrasite and triphylite as accessory phases. Black tourmaline, apatite supergroup, and CGM are minor accessory minerals. The modal contents of spodumene in the intermediate and core zones that carry it vary from 10 to 25%, and the grades are from 8 to 5.3 wt.% Li_2O (Table 1). There is one K-Ar date on muscovite from the intermediate zone of the Reflejos del Mar pegmatite that gave 343 $\pm$ 13 Ma [42]. The only known granite outcropping near (2–5 km) to the east of the pegmatites is the subcircular Vilismán two-mica syenogranite, studied recently [51]. According to these authors, it is a highly siliceous, peraluminous, high-K calcalcaline S-type granite that includes felsic dikes of aplitic and pegmatitic texture, and is possibly unrelated to the nearby Li-bearing pegmatites. The spodumene resources measured by the sum of the pegmatites of this group to a depth of 15 m is close to 65,000 t [41,43].

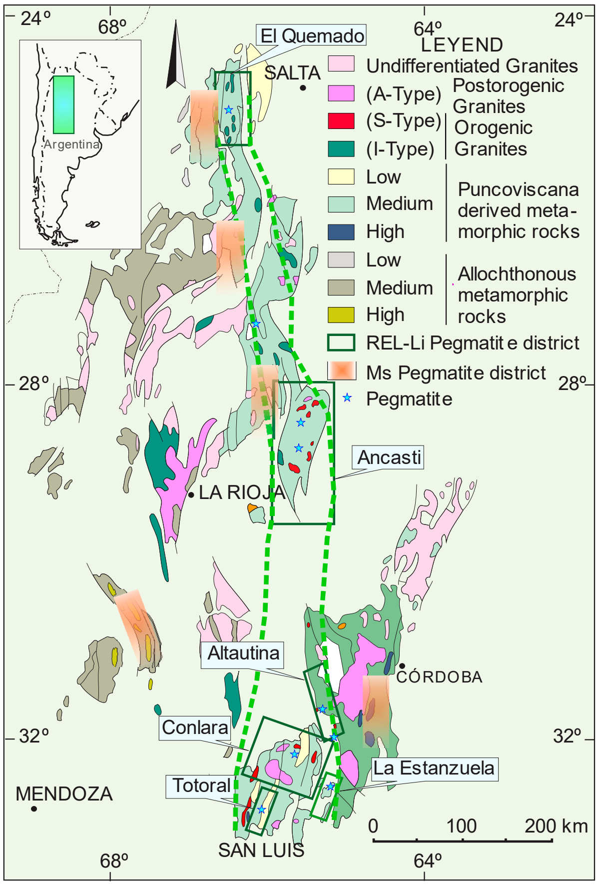

Figure 1. Geological map of the Pampean Pegmatite Province showing the rare-element pegmatite belt and the main districts (modified from [40]). The insets show the location of the Li-bearing pegmatite districts.

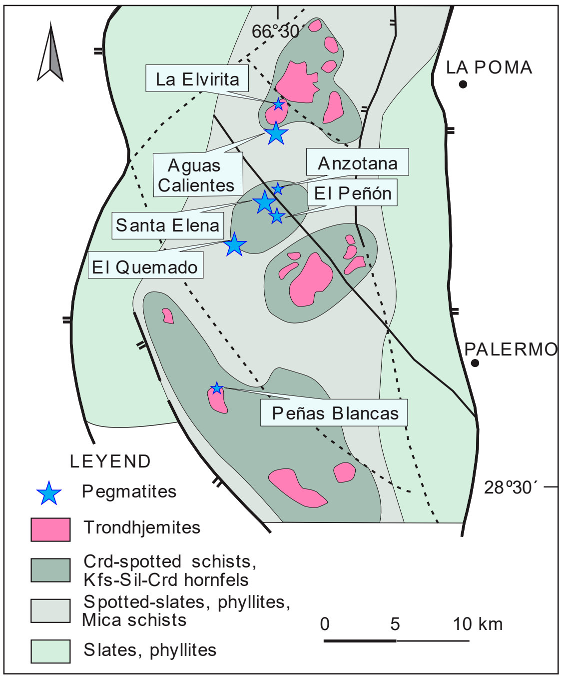

Figure 2. Geological map of the El Quemado pegmatite district with the main Li-bearing pegmatites (modified from [14]).

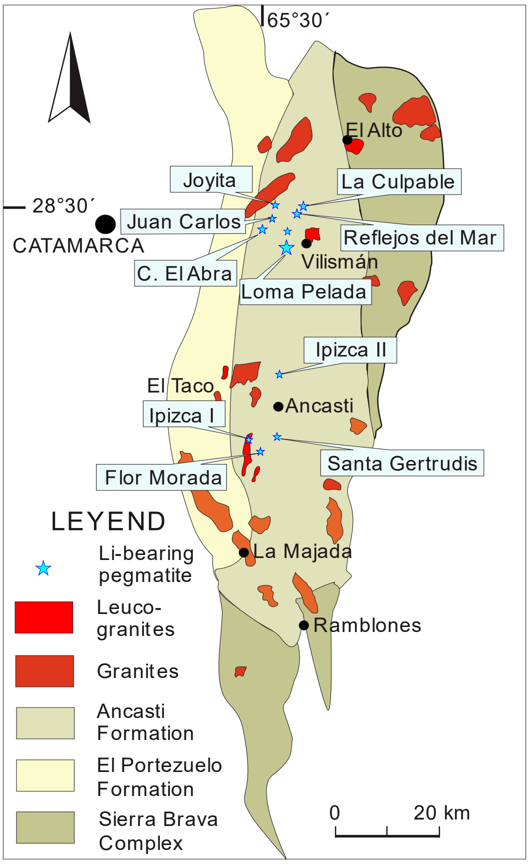

Figure 3. Geological map of the Ancasti district showing the distribution of the main Li-bearing pegmatite units.

To the south, the El Taco Group has rare-element pegmatites of REL-Li subclass and group 1 or beryl, spodumene, or albite-spodumene types and subtypes, respectively. The known Li-bearing pegmatites comprise four occurrences, from which Ipizca, Ipizca II, and Flor Morada are of rare-element class spodumene subtype, and Santa Gertrudis shows features of both spodumene subtype and albite-spodumene type. They are emplaced in mica schists in subconcordant attitude, with lengths that vary from 120 to 700 m and widths of 4 to 10 m. The internal structure consists of border, wall, intermediate, and core zones, except in Santa Gertrudis, where the intermediate zone is central. The grain size increases inward from a thin, fine-grain border zone, to the intermediate and core zones, where crystals of spodumene up to 0.5 m are common, usually in prismatic crystals perpendicular to the wall. Muscovite, schorl, beryl, and garnet are frequent accessory minerals, meanwhile, apatite, Li-phosphates, and CGM are rare or absent. Internal deformation and segmented outcrops are present in Santa Gertrudis. Two K-Ar muscovite ages for Ipizca II and Santa Gertrudis presented values of 445 $\pm$ 17 and 709 $\pm$ 34 Ma [42]. A LA-ICP-MS columbite age for the beryl-type San Isidro pegmatite located in the same group gave an average value of 486 $\pm$ 5.9 Ma [40].

Recent drilling and analyses achieved by Latin American Resources Ltd. in old properties gave estimated results of at least 120,000 t of spodumene for the Ancasti district, with grades of 6.6%, 7.1%, 6.3%, and 4.9% Li_2O in exposed spodumene [54].

3.3. Conlara Pegmatite District (CPD)

This district is located in the northern part of the San Luis Range. It is one of the most mined district of the PPP, and produced an important portion of the country’s beryl, mica, feldspars, and quartz, as well as minor quantities of tantalum and bismuth minerals. The basement of the range consists of a thick sequence of pelitic and psammitic rocks, with reduced mafic rocks, considered equivalent to the PVF in the north of the PPP [25,27]. This sequence underwent a mostly polyphasic medium-grade metamorphism during the Pampean and Famatinian Orogenies of Upper Proterozoic–Lower Paleozoic age [55], and its mica schists and gneisses were denominated Conlara Metamorphic Complex [33]. Intruding this sequence are minor basic, intermediate, or acid orogenic plutons such as Las Cañas [56], El Peñón [57], and S-type minor leucogranitic lenses, many rare-element class LCT pegmatites, mainly of group 1, or beryl and complex types [58], and the most voluminous magmatism that built the postorogenic Potrerillos-Las Chacras-Piedras Coloradas granitic batholith and its associated Nb-Y-F (NYF) pegmatites [32,59].

The distribution of Li-bearing pegmatites is mostly concentrated in the northern part of the district (Figure 4). Predominantly, they are zoned pegmatites of the rare-element REL-Li subclass, spodumene subtype, that contain spodumene in coarse to very coarse prismatic crystals as primary mineral in the intermediate to core zones. Usually, the pegmatites are intruded in mica schists with submeridional or NE strikes and outcrop near concordant lenses of leucogranites of ≤100 m wide and several to hundreds of meters long. The lengths of the pegmatites vary from 60 to 400 m and the average widths from 2 to 15 m, with few locally wider than 25 m (Table 2). Occasionally, segments of pegmatites barren in rare-elements pass to units located near the same structure that carry beryl and then to spodumene-rich bodies as occur in the La Puntillosa-Salomon-Rey David occurrences. In one individual pegmatite, the spodumene can be evenly distributed along the dikes (Cabeza de Novillo) or concentrated in a specific portion (e.g., the southern part of Las Cuevas). Ages of these pegmatites are variable; old K-Ar data on muscovite give values between 536 ± 27 to 413 ± 7 Ma [42] and recent LA-ICP-MS columbite data of CGM range from 512.6 ± 10.6 to 454.6 ± 4.2 Ma [40].

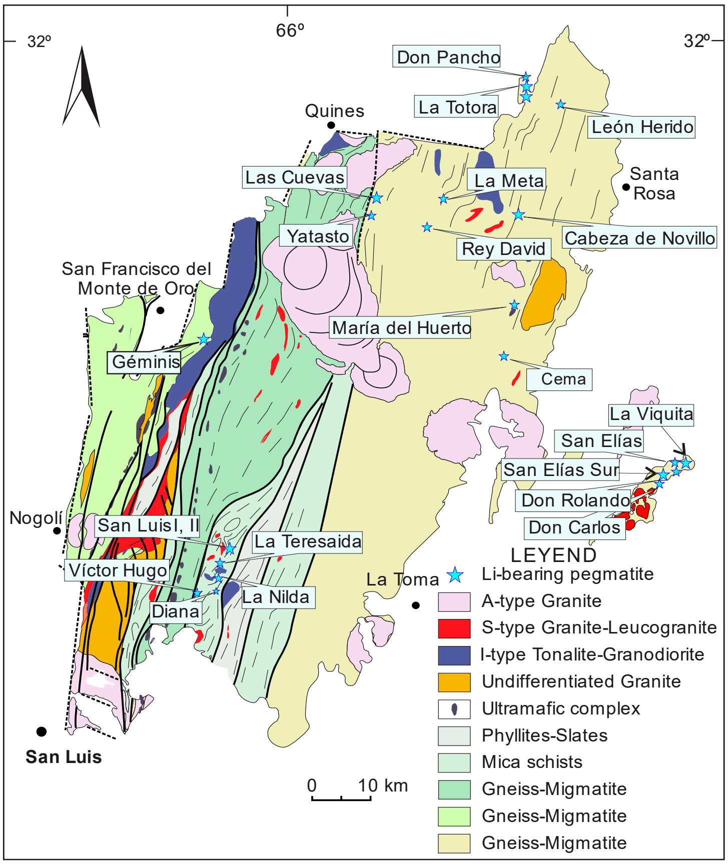

Figure 4. Geological map of the San Luis and La Estanzuela ranges with the distribution of the Li-bearing pegmatites (modified from [40]).

Table 2. Main parameters and mineralogy of lithium pegmatites from the Conlara, Totoral, La Estanzuela, and Altautina districts.

NAME	T	Ds	#	L	W	St	D	HR	Age (Ma) *	R	1	2	QAP	Spd	Lpd	Ms	Tur	Brl	Zrn	Grt	Ap	Aby	Trl-Trp	CGM	Mic	BM	Reference
La Totora	S	Conlara	2	60	2–7	N15° E	70–85° E	ms	469.7 ± 4.7 * 469.2 ± 4.7 *	150	20	7.9	X	X		x	x	x		*	x	*	*	*	*	*	[13,19,40,60]
Don Pancho	S		1	100	5.5	N20° E	~90°	ms		500	15	5.6	X	X		x	x	*			*	*		*	*		[13,19,60]
León Herido	S		1	100	4	N22° E	88° E	ms	505.9 ± 20.9 *	2300	25	6.5	X	X		x	*	x			x	*		*			[40,60,61]
C. Novillo	S		3	270	1.8–5	N7° W	~90°	ms		3200	15	7.5–8	X	X		x	x	x		*	x	*	*	*			[19,61]
La Meta	S		1	>200	<15	N-S	75° E	ms	463.5 ± 5.6 *	200	10	5–7.9	X	X		x	x	x			*		*	*			[13,19,20,40]
Las Cuevas	S		1	400	10	N2–10° W	31–82° W	ms	462.2 ± 9.7 * 510 ± 26	5700	10–15	6.7	X	X	*	X	x	*	*	x	x	x	*	x	*	x	[13,19,40,62]
Rey David	S		1	100	8	N30° E	~90°	ms	512.6 ± 10.6 * 509.9 ± 9.1 *				X	x	*	x	x	x		*	x	*	*	x		*	[40,63]
Géminis	S		1	~200	10	N52° E	0–50° SE	gn	477.3 ± 5.8 * 536 ± 27	6000	20–25	5.2	X	X	*	x	x	x	*	*	x	X	*	*	*	*	[20,61,64]
M. Huerto	S		2	370	6–8	N45°E	68–70°	ms		350	15	6.7–7.4	X	X		x	*	*	*	*	x	*		*	*	*	[13,19,65]
Cema	S		1	100	<25	N-S	52° SW	ms		150		0.3–8	X	x		x	x	x		*	x		*	*			[13,19,66]
San Luis I	AS	Totoral	1	>1000	2–35	NNE-SSW	60° SW	ms	317 ± 11	600	10–20	5.8–8.0	X	X		x	*	*		x	x		*	*			[6,19,67]
San Luis II	S		1	20	7	NW-SE	SW	ms	449.8 ± 8.6 *		20		X	X		x	x	x			x	*	x	*			[6,40,67]
La Teresaida	AS		1	100	5–12	NNW	~90	ms		4000	10	>5	X	X		x	x	x		*	x	*	*	*			[9,13]
V. Hugo	S		1	150	2–20	N-S	~90	ms	503 ± 24				X	X		x	x	x	*	*	x	*	*	*	*	*	[68]
La Viquita	S	La Estanzuela	1	190	40	N42°E	30–60° NW	ms	369.3 ± 3.8 * 320 ± 12	7800	10–25	5.1–7.8	X	X	x	x	x	*	x		x	x	x	x			[13,19,69,70]
San Elías	L		1	140	4.50	~N-S	80° E	ms	403 ± 16	200	Lpd	3.0–3.3	X	*	X	x	x	*	*		*	x	*	*			[13,19,71]
San Elías S	L		1	120	~5	~NE	~80° W	ms		100	Lpd	~ 3	X	*	X	x	x	*	x	*	*	*	*	*		*	[72]
Don Rolando	S		2	40–200	4–10	NW-NE	~65° SE	ms		6725	10–20	6.75	X	X		x	x	*	x		*		*	*			[19,20,61]
Don Carlos	AS		3	18–60	1.5–8	N30° E	55° SE	ms		1725	15	5.1–6.3	X	X		x	x		x		*						[19,20,61]
C. Namuncurá	B	Altau- tina	1	100	10	290°	80° SSW						X			x	x	*	*			*	*				[19,73]
Las Tapias	S		8	200	12–15	E-W	18–30° S	dr-am		700	10–15	7.9	X	X		x	x	x	*	*	*	*		*	*	x	[19,74]
La Juana	L		4	<15	<1			gr	370.3 ± 7.4 *				X		x	x	x		*	*	*			*	*		[40,75]

Note: T, type of pegmatite; S, spodumene; AS, albite-spodumene; L, lepidolite; B, beryl; Ds, district; #, number of dykes; L, length (m); W, width (m); St, strike; D, dip; HR, host rock; ms, mica schist; gn, gneiss; dr, diorite; am, amphibolite; gr, granite; Age (Ma), number marked by * = LA-ICP-MS dating of columbite [40], all others are K-Ar ages [42]; R, Spd or Lpd resources (t); 1, Spd (wt.%); 2, Li_2O (wt.%); QAP, Qz + Kfs + Pl; CGM, columbite group minerals; Mic, microlite-group minerals; BM, Bi-bearing minerals. X = major mineral; x = abundant accessory; * = minor accessory. Mineral abbreviations as in [44].

Most of the pegmatites were worked in quarries by open pit cuts, except some with small subsurface works (Géminis, Las Cuevas, Cabeza de Novillo), and the spodumene was manually concentrated. Estimated resources in old papers are discrete and very conservative. The content of spodumene in the pegmatites fluctuates between 10 and 25%, and the Li_2O wt.% grades from 0.3 to 8%, because, in some quarries, the spodumene is replaced by eucryptite + albite, as occurs in Las Cuevas, or suffered muscovitization or argillitization [62].

3.4. Totoral Pegmatite District (TPD)

This is the southern district of the PPP. It is contained in a thick psamopelitic sequence variably metamorphosed during the Upper Proterozoic–Lower Paleozoic ages, named Pringles Metamorphic Complex (PMC) [33]. This complex is intruded by I-type plutons, such as the Pampa del Tamboreo granodiorite of 470 ± 5 Ma [33], S-type leucogranites of Ordovician age, and the rare-element pegmatites spatially associated with them. The geology of the district was recently reviewed [76], and shows Li-bearing pegmatites of group 1, and albite-spodumene and spodumene subtypes. These pegmatites are spatially linked to the Paso del Rey leucogranite, and show estimated resources in excess of 600 t in one property; most of these correspond to fine–medium-grain spodumene only suitable for flotation concentration. The ages of the granites and pegmatites obtained by different authors and methods show striking variations, broadly comprised in the Ordovician Famatinian Orogeny [40,76]. The S-type leucogranites were subdivided into low T and higher T, and the former were considered to be produced by dominant muscovite dehydration melting, and the latter by muscovite plus biotite dehydration melting of the metapelites and metagraywackes of the PMC. The origin of both, leucogranites and the fractionated LCT rare-element pegmatites of TPD, was attributed to episodic anatexis that occurred during the late stage of the Famatina terrane-continent collision (≈450–460 Ma). Quartz chemistry of some of its pegmatites allowed us to classify them in the category of DPA-1 (direct product of anatexis enriched in Be-Nb-Ta-P-Li, [77].

3.5. La Estanzuela and Altautina Pegmatite Districts

The La Estanzuela district is located in the homonymous small range and its continuation to the south in the El Portezuelo range. The geology of both sectors shows a crystalline basement formed by metapelitic and metapsamitic Qtz-Pl-Kfs-Bt-Ms ± Grt-Sill-Tur-Sta schists, with some reduced banks of dolomitic marbles and minor calc-silicate schists, altogether belonging to the Upper Proterozoic–Lower Paleozoic CMC [33]. This basement is intruded by subconcordant lenses several meters thick of interspaced leucogranites folded and boudinaged, and by rare-element class pegmatites usually discordant to the foliation of the mica schists. The mined REL-Li subclass pegmatites are group 1 or of albite-spodumene type, such as Don Rolando, or spodumene or lepidolite subtypes, such as La Viquita and San Elías, respectively. In La Viquita, the spodumene begins to participate in the intermediate zone and continues in the core zone in green prismatic decimeter-sized crystals. The pegmatite also contains columbite and wodginite group minerals, as well as cassiterite. To the south, the group formed by the dikes outcropping in Don Rolando and Don Carlos occurrences comprises medium-to-small-sized albite-spodumene and spodumene pegmatites. In the southern extension of the La Estanzuela range, intruding the mined dolomitic marbles of Lujan quarry are the dikes of spodumene subtype pegmatites called La Cañada or Lujan. They are discrete-sized dikes with low contents of spodumene crystals in the intermediate and core zones. Muscovite dated by K-Ar gives an age of 320 ± 12 for La Viquita and 403 ± 16 Ma for San Elías [42]; meanwhile, CGM dating by LA-ICP-MS columbite gives an age of 369.3 ± 3.5 Ma for La Viquita [40].

The Altautina district, located immediately to the northeast, has only one significant rare-element class pegmatite of spodumene subtype and one minor occurrence with lepidolite, in addition to the existence of Li-phosphates in a beryl type pegmatite. The Las Tapias pegmatite was a large producer of beryl, and has some resources of spodumene, partially mined in the past, that are currently under exploration.

4. Discussion

4.1. Metallogenesis

The observation of the primary mineralogy quoted in Tables 1 and 2 shows noticeable resemblance in the Li-bearing pegmatites throughout the different districts of the PPP. Their contrast is mainly the result of internal fabric differences related to conditions of crystallization, or to assemblages of metasomatic and hydrothermal phases produced during postmagmatic hypogene reworking. Spodumene is the dominant lithium phase in most of the pegmatites, usually in decimetric-to-metric-sized prismatic crystals of grayish green color and incipient alteration, except in the albite-spodumene type pegmatites, where the size is smaller. Lepidolite only occurs at a minor number of localities, which means that the contents of fluorine was limited [17]; thus, resources of Li-micas are only significant in Santa Elena I and San Elías south pegmatites. In the same way, montebrasite is the dominant member in most of the pegmatites, instead of amblygonite. Tourmaline has been poorly studied, and the elbaite members are present in Santa Elena I, Las Cuevas, San Elías, San Elías south, and La Juana [15,75,78]. Beryl is present in all the pegmatites, and Las Tapias was the main producer in historic times; in several pegmatites, gahnite is an accessory phase. Regarding phosphates, apatite supergroup minerals are widespread; meanwhile, Fe-Mn $\pm$ Li-Mg-Ca primary phases are usually a minor accessory in nodules that are frequently transformed in several derivatives during postmagmatic processes [66]. One particular detail is that, in most of the pegmatites, the accessory phosphates of the transition elements show Mn > Fe with the exception of La Viquita, where Fe > Mn [70]. The CGM phases are always present in fine crystals disseminated, or in small nodules, usually in the intermediate zone or in core-margin assemblage. The evolutionary trend of this group involves different paths towards Ta- and Mn-enriched members [47] showing enrichment in Bi, Pb, and U, and depletion in Sn in normalized diagrams [40]; tapiolite-(Fe) occurs as a late-stage phase, cassiterite occurs in two pegmatites, whereas wodginite group minerals are only present in one occurrence [69]. Bismuth minerals are common as small nodules of bismuthinite and less frequently as bismuth, both with greater or lesser late-stage hydrothermal reworking [79,80]. With this mineralogy, the geochemistry of the pegmatites shows enrichment in Li, Rb, Nb $\leq$ Ta, Be, P, B, Bi, and the pegmatites belong to the LCT (Li-Cs-Ta) petrogenetic family and REL-Li subclass of rare-element pegmatites [22].

The phase diagram of the Li aluminosilicate polymorphs helps to envisage the pressure of the formation of the pegmatites [81–83]. The occurrence of "*squi*" in Santa Elena pegmatites of *QPD* allowed to us infer that the bulk crystallization of some of these starts in the stability field of petalite crossing during cooling to the field of spodumene + quartz, meaning pressures in the range of 200–300 MPa and temperatures comprised between ~400–650 °C [83,84]. Higher pressures of crystallization are present in the southern districts where only spodumene occurs, as occurs in the Totoral district, where values of 400–500 MPa were suggested [76]. The modal composition of lithium aluminosilicate phases is variable, being evenly distributed in albite-spodumene-type pegmatites, or more randomly in complex spodumene subtype bodies, with variations along the length or in the different internal units.

The origin of the granitic pegmatites of the PPP has been discussed in several papers, and is still debatable [7,17,40,76,85]. Herrera [17] interpreted the pegmatites as produced by crystallization of magmatic residual liquids that changed in composition along the fractionation, and that its present distribution is determined by the depth of the parental granitic intrusion [7,85]. All the rare-element pegmatites of the PPP were grouped following the classification of Černý [86,87] into two petrogenetic families, LCT and NYF or Mixed [17]. The Li-bearing and other beryl-type pegmatites were considered as belonging to the LCT petrogenetic family, and considered to be formed during the pre- to syn-collisional stages of the Famatinian Orogeny by fractionation of a suite of S(+I) parent granites along a rare-element pegmatite belt. It was mentioned in [17] that most of the pegmatites show signs of deformation, and that they were consistently not late-orogenic, as is usually the case in the LCT family [87]. More recently, pegmatites from the *TPD* were considered as generated by fractionation of low-T and higher-T S-type leucogranites formed by episodic anatexis of supracrustal micaceous-rich metamorphic rocks [76]. Recently [40], rare-element pegmatites with accentuated negative Eu anomalies in their CGM were interpreted to have formed by the bold fractionation of relatively large volumes of leucogranites, likely produced by anatexis of the micaceous metasediments; meanwhile, the pegmatites carrying CGM with low total contents of REE and more flattened patterns were possibly formed by fractionation of low-T leucogranites produced by anatexis of the same protoliths.

Considering the mineralogy, geochemistry, ages, and tectonic setting of the Li-bearing pegmatites, their petrogenesis is likely linked to parent leucogranites emplaced preferably in the hinterland of a collisional scenery, produced by fluid-absent [76] or fluid-assisted anatexis of micaceous metasediments. The hinterland relative position is considered appropriate since the dominant metaluminous magmatism of the Central Famatinian Domain [31] is located to the west of the Li-bearing pegmatite belt (Figure 1). Most of the considered pegmatites were formed during the Famatinian Orogenesis, but a few, such as La Viquita and La Juana, are postorogenic, and were likely generated by fractionation of A-type granites contaminated in the medium-to-upper crust by micaceous metamorphics [40].

Regarding the relative significance in the signature of the pegmatites between two proposed models, (i) the predominance of the nature of the source of pegmatitic melts [88] and (ii) the tectonic setting conditioning the the pattern of enrichment of felsic pegmatites [89], the ages of Li-bearing pegmatites of the PPP [40] preliminary show that both orogenic and postorogenic pegmatites can be Li-enriched and sourced totally or partially in a metasedimentary medium–upper crust.

4.2. Resources

The resources of the Li-bearing pegmatites of the PPP are known from measurements, estimations, and further information in past technical reports and papers. The sum of the resources quoted in Tables 1 and 2 gives a total close to 200,000 t of spodumene, with grades that range approximately between 5 to 8 wt.% of Li_2O. The QPD has a rough estimation > 100,000 t of spodumene, Ancasti was found to have resources of 65,845 t, most of them concentrated in the Vilismán group. In the southern districts, the CPD reaches up to 18,200 t, TPD > 600 t, and EPD plus APD 13,350 t. In most cases, the criteria used by different researchers were very conservative, and could be considered as the minimum resources available. Recent data for some districts, where drilling of the main occurrences was undertaken, are probably still being evaluated.

These numbers are smaller compared with the reserves of brines from salars of NW Argentina and elsewhere, and with pegmatites from other major occurrences, such as Greenbushes, Tanco, and Bikita [90]. The difference in size and Li-resources of pegmatites from the PPP related to the bigger rare-element LCT pegmatites of Proterozoic age, could be ultimately related with the progressive cooling of the Earth, as was interpreted in a global analysis [91].

Regarding the potential, since no systematic exploration program was carried out in the PPP for lithium or other rare-element pegmatite-derived ores, and that the known resources were obtained based in the carefully collected geological information obtained from specific studies in already-mined pegmatites, the potential for discovering new resources is latent. The most auspicious geological conditions are present along the rare-element pegmatite belt shown in Figure 1, specifically in the northern districts: QPD and APD.

5. Conclusions

The Li-bearing pegmatites of the PPP are distributed in a rare-element pegmatite belt developed mainly during the Lower Paleozoic in the southwestern margin of Gondwana.

Most of the pegmatites belong to the LCT petrogenetic family, REL-Li subclass, many of them are of complex type, spodumene subtype, and some of albite-spodumene type, and a few of petalite subtype. The origin of the pegmatites is attributed dominantly to fractionation of fertile S-type granitic melts produced by anatexis of a thick pile of turbiditic metasedimentary rocks during two overlapped collisional orogenies. The known resources sum in excess of 200,000 t of spodumene, with variable grades between 5 and 8 wt.% Li_2O. The potential for future findings is good, since no systematic exploration program has yet been developed.

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