

The phosphate mineral association of the granitic pegmatites of the Fregeneda area (Salamanca, Spain)

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Abstract

In the Fregeneda area different pegmatitic types can be distinguished on the basis of their mineralogy, internal structure and field relationships. The most common type corresponds with simple pegmatites with a homogeneous internal structure, but Li and Sn-bearing pegmatites are also relatively widespread, besides a minority group of Fe-Mn phosphate-bearing pegmatites that has recently been characterized. These pegmatites are located in an intermediate zone, between the barren pegmatites and the most evolved Li and Sn-bearing bodies, and they carry a complex association of phosphate minerals. The study of these phosphates has allowed the identification of the primary phases as wyllieite, graftonite, sarcopside, triplite-zwieselite and ferrisicklerite; the secondary phosphates are rosemaryite, heterosite-purpurite, alluaudite and väyrynenite. In this study, the main characteristics of these phosphate minerals are reported, including their chemical composition, analysed by electron microprobe, and their unit-cell parameters, calculated using X-ray powder diffraction techniques.

A common transformation mechanism in this phosphate association is the oxidation of the transition metal cations at the same time as Na-leaching in wyllieite to generate rosemaryite, and Li-leaching in ferrisicklerite to generate heterosite. The occurrence of sarcopside lamellae in ferrisicklerite and heterosite is evidence of the replacement processes of the former by the latter. A Na-metasomatic replacement of the early phosphates as ferrisicklerite and graftonite, producing alluaudite, is also a well developed process.

Phosphate minerals occur in pegmatites with an intermediate degree of fractionation, appearing between the barren and the more evolved pegmatites with Li and Sn, which is in agreement with the pegmatite field zonation established in the literature.

KEYWORDS: Fe-Mn phosphates, granitic pegmatites, Fregeneda, Spain.

Introduction

In the Fregeneda area different types of pegmatites have been established according to their mineralogy, morphology, internal structure, etc. (Fig. 1, Table 1). This area is located in the NW part of the province of Salamanca, Spain (Fig. 1), in the western extremity of a narrow metamorphic band with an E-W strike,

in the Hesperic Massif. This band is bordered by the Lumbrales granite to the south, and by the Saucelle granite to the NE. Both units are peraluminous, two-mica granites, and belong to a group of syntectonic massifs, which have been deformed during the third phase of Hercynian deformation (López Plaza and Carnicero, 1988; López Plaza and Martínez Catalán, 1988). The studied pegmatites intrude into rocks of

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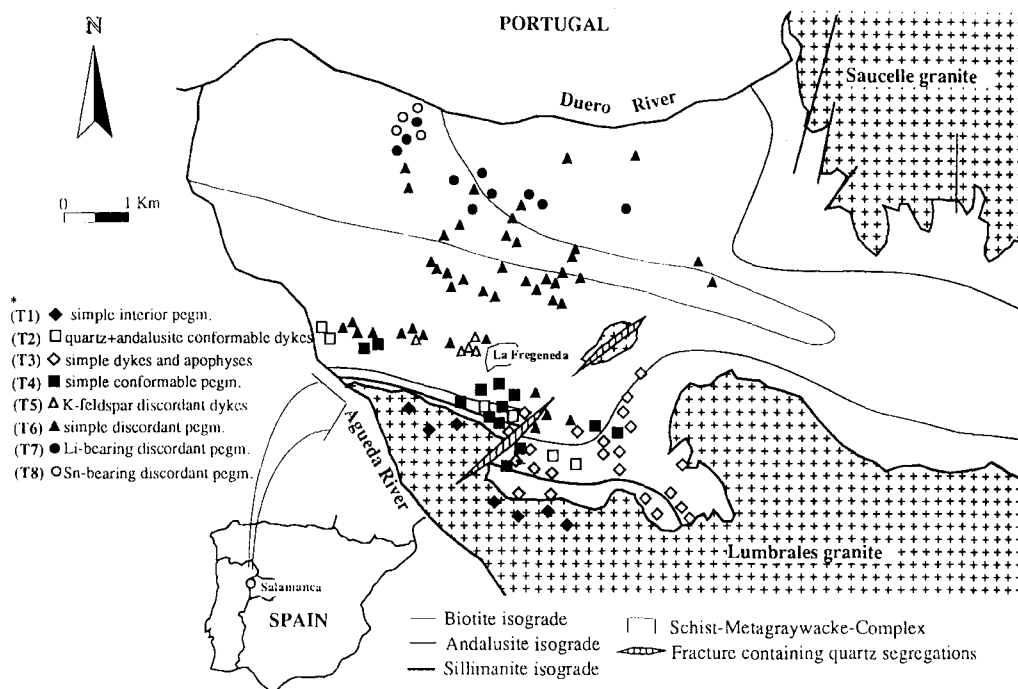


FIG. 1. Distribution of the pegmatite groups recognized in the Fregeneda area (* numbers of pegmatite types as in Table 1).

the Schist-Metagreywacke Complex, which in this area consists of an alternation of quartzites, greywackes, schists and pelites, with abundant thin calcisilicate layers. Previous works on the description of the pegmatite bodies, their mineralogy and their petrogenesis have been published (Roda, 1993; Roda *et al.*, 1993, 1995, 1996).

The different groups of pegmatites which crop out in the area display a grade of differentiation which increases away from the Lumbrales granite (Fig. 1; Table 1). In the border zones of the granite intragranitic pegmatites (T1) occur, and these are mainly composed of quartz and K-feldspar. Close to the Lumbrales granite, in the andalusite-cordierite zone, dykes composed mainly of quartz and andalusite (T2) crop out. Another group of barren bodies, located near the Lumbrales granite, comprise dykes and apophyses showing aplitic and pegmatitic facies (T3), mainly composed of quartz, K-feldspar and muscovite. Also in close proximity to the granite, the conformable pegmatites, composed mainly of quartz, K-feldspar, muscovite and albite (T4) appear. In an intermediate zone, between the barren and the most evolved dykes, pegmatites composed mainly of K-feldspar (T5) and discordant pegmatites that consist of quartz, K-feldspar, albite and muscovite

(T6) crop out. The pegmatites of the T6 group that appear near to the Lumbrales granite carry a complex paragenesis of Fe-Mn phosphates, whereas in the T6 pegmatites which appear farthest from the Lumbrales granite, ambygonite may be present. Finally, in the area furthest from the granite, discordant Li-mica-bearing pegmatites (T7) and pegmatites, consisting mainly of quartz, cassiterite and albite (T8) appear.

The main purpose of this study is to establish the characteristics and relationships between the phosphates that appear in the various different pegmatite bodies, as well as to specify the mineralogical and geochemical role of the phosphate minerals in the evolution of the Fregeneda pegmatites.

Data collection and analyses

The studied phosphate minerals were mainly collected from the pegmatites of type 6 nearest to the Lumbrales granite (Fig. 1). In some cases, it was possible to separate the crystals by hand-picking them under the binocular microscope and grinding by hand in an agate mortar, but due to very fine-grained impurities it was not possible to obtain pure amounts of all the phases. The various phosphate minerals have been identified by optical properties in thin

TABLE 1. Main characteristics of the groups of pegmatites recognized in the fregeneda district

Type	Mineralogy		Nature of the host rock		Morphology and structure	Outcrop area	Remarks	Enrichments
	Main minerals	Other important minerals	Tourmalinization	Country-rock				
T1	Qtz Ksp	msc ab tur	-	(intragranitic)	dyke-like thickness < 50 cm	within the Lumbrales granite	scarce, within the Lumbrales granite	K, Al, Si, (B,P)
T2	Qtz and	msc tur Ksp chlorite	-	Andalusite zone	conformable dyke-like thickness < 50 cm	close to the Lumbrales granite	not abundant; boudinage structures. Qtz & and their main minerals	Al, Si, (B,K)
T3	Qtz Ksp msc	ab tur bi	-	Sillimanite, andalusite and biotite zones	irregular and bulbous masses ellipsoidal, lenticular or turnip-shaped forms	S-E of the area near the Lumbrales granite	abundant; aplite-pegmatite facies; graphic texture	K, Al, Si, (B)
T4	Qtz Ksp msc ab	tur bi and chl gt	✓	Sillimanite and andalusite zones	conformable dyke-like locally with internal zonation thickness 1 m	near the Lumbrales granite	abundant; in some cases internal zoning, and graphic texture	B, Al, Na
T5	Qtz Ksp	msc pyrite	-	Biotite zone	unconformable dyke-like thickness > 1 m	1 km from the Lumbrales granite	not very abundant; main component is pink K-feldspar	K
T6	Qtz Ksp ab msc	± Fe-Mn pho ± amb ± tur	✓	Biotite and chlorite zones	unconformable dyke-like thickness < 10 cm–2 m	1–4 km from the Lumbrales granite	most abundant Near the Lumbrales granite, internal zoning can be present	K, Na, Al, Si, (P,Li)
T7	Qtz ab Li-mica msc Ksp	amb spd cass apt be	✓	Biotite and chlorite zones	unconformable dyke-like locally with internal zoning thickness < 1 m–15 m	4–6 km from the Lumbrales granite	not very abundant; can show internal zonation. Li-bearing minerals are very abundant	Li, Sn, P, (Rb,Cs)
T8	Qtz cass ab	msc Ksp	✓	Chlorite zone	unconformable dyke-like, thickness < 50 cm locally with internal zoning	N of the studied area	scarce, folded, abundant cassiterite	Sn, K, (P)

PHOSPHATES IN GRANITIC PEGMATITES

In 'Mineralogy', the following abbreviations have been used: Qtz – quartz; Ksp – K-feldspar; msc – muscovite; ab – albite; tur – tourmaline; and – andalusite; chl – chlorite; bi – biotite; gt – garnet; py – pyrite; pho – phosphates; amb – amblygonite; spd – spodumene; cass – cassiterite; apt – apatite; be – beryl.

TABLE 2. List of the identified phosphate minerals in the different pegmatite types of the Fregeneda area

Phosphate minerals	Ideal formula	Pegmatite type							
		1	2	3	4	5	6	7	8
Wyllieite-rosemaryite	$\text{Na}_2(\text{Mn}, \text{Fe}^{2+}, \text{Fe}^{3+})_2\text{Al}(\text{PO}_4)_3$								
Graftonite	$(\text{Ca}, \text{Fe}^{2+}, \text{Mn}^{2+})_3(\text{PO}_4)_2$								
Sarcopside	$(\text{Fe}^{2+}, \text{Mn}, \text{Mg})_3(\text{PO}_4)_2$								
Ferrisicklerite	$\text{Li}, (\text{Fe}^{3+}, \text{Mn}^{2+})_3(\text{PO}_4)$								
Sicklerite	$\text{Li}, (\text{Mn}^{3+}, \text{Fe}^{2+})_3(\text{PO}_4)$								
Heterosite	$(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{PO}_4)$								
Purpurite	$(\text{Mn}^{3+}, \text{Fe}^{3+})(\text{PO}_4)$								
Triphylite-Wieselite	$(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Ca})_2(\text{PO}_4)(\text{F}, \text{OH})$								
Allauadite	$(\text{Na}, \text{Ca})(\text{Fe}^{2+}, \text{Mn}^{2+})\text{Fe}_2^{3+}(\text{P}_4\text{O}_{13})$								
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F})$								
Amblyg.-montebras	$\text{LiAl}(\text{PO}_4)(\text{F}, \text{OH})$								
Väyrynenite	$\text{MnBe}(\text{PO}_4)(\text{OH})$								

section, X-ray powder diffraction techniques and electron microprobe analyses. Chemical analyses were performed at the Université Paul Sabatier (Toulouse, France), with a Camebax SX 50 electron microprobe, using an operating voltage of 15 kV and a beam current of 20 nA for all the elements.

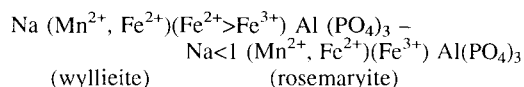
Unit-cell parameters were obtained by means of X-ray powder diffraction using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 20 mA) and graphite monochromator. Runs were made by scanning through 2° to 70° at $1^\circ 2\theta$ per minute for each sample, using silicon as an internal standard. Unit cell refinements were performed according to the procedure of Appleman and Evans (1973).

Petrographic and chemical data

The study of these phosphate minerals has allowed the identification of the phases listed in Table 2. In the following, the more important phosphates will be described, as they may provide valuable aid in explaining the crystallization history of the phosphate associations as well as of the pegmatites themselves.

Wyllieite-rosemaryite. This phase adopts the following general structural formula (Moore and Ito, 1979): $\text{X}(2)_4 \text{X}(1a)_2 \text{X}(1b)_2 \text{M}(1)_4 \text{M}(2a)_4 \text{M}(2b)_4 (\text{PO}_4)_{12}$, where $\text{X}(2) = \text{Ca}, \text{Na}$ and K ; $\text{X}(1b) = \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ca}$ and Na ; $\text{M}(1) = \text{Fe}^{2+}$ and Mn^{2+} ; $\text{M}(2a) = \text{Fe}^{3+}, \text{Mg}, \text{Li}, \text{Zn}$ and Fe^{2+} ; and, finally, $\text{M}(2b) = \text{Al}, \text{Fe}^{3+}$ and Mg . Wyllieite can undergo a topotactic alteration, with oxidation of the

transition metal cations at the same time as Na-leaching, to generate rosemaryite (Roda, 1993; Fransolet, 1995). Both phosphate minerals constitute a little-known sequence, with problems similar to those shown by the triphylite-ferrisicklerite sequence (Quensel, 1937; Mason, 1941). Thus, rosemaryite shows a lower Na content, and this is accompanied by a higher content of ferric iron to maintain the charge equilibrium in the following way (Fig. 2a):



This is the first time wyllieite and rosemaryite appear intergrown, a fact that allowed us to confirm the inter-relation between both phases, as has been suggested by previous workers (Roda, 1993; Fontan *et al.*, 1994; Fransolet, 1995). Wyllieite appears as xenomorphic grains, usually $< 1 \text{ cm}$, with a slight pleochroism ranging from green to light-green. Some of these grains show more pleochroic yellow to greenish-yellow areas of rosemaryite.

The finely intergrown nature of the wyllieite and rosemaryite has not allowed us to obtain pure samples of such phases, in order to calculate their unit-cell parameters. The compositional variation for wyllieites is small for some elements (Table 3; Fig. 2a, b and c), with Al_2O_3 values that range from 6.12 to 7.84% and MnO from 18.35 to 18.92%; and finally, Na_2O varies between 4.75 and 6.40%.

TABLE 3. Representative analyses of wylieite (WY) and rosemaryite (RO), from the simple discordant pegmatites (type 6). (Data obtained by electron microprobe from the same sample; cation values on the basis of $(\text{PO}_4)_{12}$)

		WY-1	WY-2	RO-1	RO-2
Al ₂ O ₃		6.26	7.84	7.21	7.29
FeO		19.90	18.82	10.92	6.83
MgO		0.10	0.06	0.15	0.11
MnO		18.69	18.65	16.54	16.24
CaO		0.52	0.38	0.41	0.48
Na ₂ O		6.40	4.75	3.24	3.06
Fe ₂ O ₃		4.87	5.67	13.73	17.97
P ₂ O ₅		44.06	44.86	43.50	44.33
Total		100.80	101.03	95.70	96.31
M(2b)	Al ³⁺	2.377	2.924	2.780	2.746
	Fe ³⁺	0.179	1.076	1.220	1.254
	Mg	0.039	0.038	0.000	0.000
	Fe ²⁺	0.405	0.000	0.000	0.000
M(2a)	Fe ³⁺	0.000	0.272	2.147	3.066
	Mg	0.000	0.038	0.078	0.058
	Fe ²⁺	4.000	3.690	1.775	0.876
M(1)	Fe ²⁺	0.948	1.285	1.201	0.948
	Mn ²⁺	3.052	2.715	2.799	3.052
X(1)	Mn ²⁺	2.049	2.279	1.762	1.345
	Ca	0.174	0.133	0.137	0.173
	Na	1.777	1.588	2.056	1.901
	□	0.000	0.000	0.045	0.581
X(2)	Na	2.223	1.317	0.000	0.000
	□	1.777	2.683	4.000	4.000
Fe _{tot} /Fe _{tot} +Mn		0.52	0.56	0.58	0.58

Therefore, rosemaryite exhibits a very homogeneous Al₂O₃ content, that changes from 7.21 to 7.77%, from 3.00 to 3.32% in Na₂O content, and from 16.24 to 17.32% MnO content. With regard to Fe content, two Mössbauer spectra have been obtained, evidencing a mixture of wylieite-rosemaryite: FeO = 9.38% and Fe₂O₃ = 12.10% (calculated from 12 microprobe analyses).

Graftonite. This phosphate mineral, considered a primary phase (Moore, 1982), appears as very fine-grained masses, being indistinguishable in hand specimen. Identified by its optical properties in thin section, this mineral usually shows sarcopside lamellae. Therefore, graftonite appears growing in association with heterosite, alluaudite and ferrisicklerite in the simple discordant pegmatites (type 6). Its chemical composition is shown in Table 4 and Fig. 2b and c.

Sarcopside. This is another of the primary phosphate minerals to be found in the simple discordant pegmatites (type 6), in association with graftonite, ferrisicklerite and heterosite. According to Moore (1982), this phosphate cannot occur as a sole primary phase, but is an exsolution product of triphylite or graftonite. Nevertheless, in some cases its occurrence has been described as irregular grains growing in close association with triphylite (Fransolet *et al.*, 1986). In our case, sarcopside has only been detected as lamellae, growing inside graftonite, ferrisicklerite and heterosite. Its chemical composition is shown in Table 4 and Fig. 2b and c, and the unit-cell parameters are listed in Table 5.

Ferrisicklerite-sicklerite. Ferrisicklerite occurs in association with graftonite, heterosite, and sarcopside in the simple discordant pegmatites (type 6), whereas sicklerite appears with purpurite and alluaudite in the

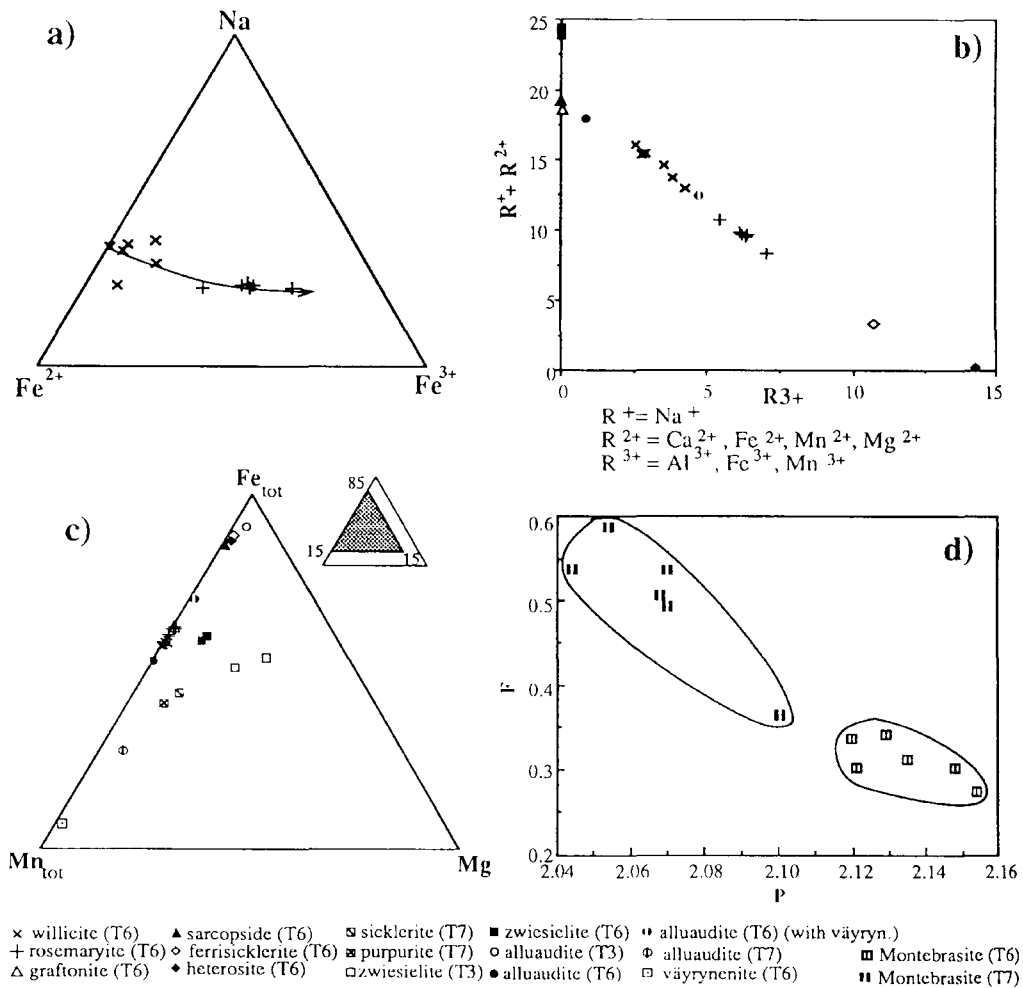


FIG. 2. (a) Plot of the variation in the contents in Na, Fe^{2+} and Fe^{3+} for the wyllicites and rosemaryites associated with the simple discordant pegmatites (type 6); (b) Plot of $R^+ + R^{2+}$ vs. R^{3+} for the different phosphates associated with the discordant pegmatites (type 6); (c) Plot of the chemical composition of the major phosphate minerals from the Fregeneda pegmatites, analysed by electron microprobe, in the triangular diagram Fe_{tot} - Mn_{tot} -Mg. (* numbers of the pegmatite type as in Table 1); and (d) Plot of P vs. F for montebrasites associated with simple discordant pegmatites (type 6) and Li-bearing pegmatites (type 7).

Li-bearing pegmatites (type 7). Table 4 lists their chemical compositions. It is noteworthy that the Fe, Mn and Mg content for ferrisicklerite and sicklerite are very similar to those of the associated heterosite and purpurite, respectively (Fig. 2b and c), suggesting an evolution according to the sequence defined by Quensel (1937) and Mason (1941). On the basis of this sequence, the Li-leaching in triphylite (not detected here) would generate ferrisicklerite-sickler-

ite and later heterosite-purpurite. Thus, ferrisicklerite shows a lower Li content than triphylite, and this is accompanied by a higher content of ferric iron to maintain the charge equilibrium, in a similar fashion to the wyllicite-rosemaryite series. According to this, ferrisicklerite-sicklerite and heterosite-purpurite would be topotactic alteration products formed metasomatically (Fontan *et al.*, 1976). In our case, as stated by other authors (Keller and Von Knorring,

TABLE 4. Chemical composition of some phosphate minerals associated with the simple discordant pegmatites (type 6) and with the Li-bearing pegmatites (type 7) (Data obtained by electron microprobe, *values calculated to balance the formula of sicklerite). The cation numbers are calculated on the basis of 16 oxygen per unit-cell for sarcopside (SA), ferrisicklerite (FS), heterosite (HT), sicklerite (SC) and purpurite (PU); and on the basis of 8 oxygens for graffonite (GR)

	GR(T6)	SA(T6)	FS(T6)	HT(6)	SC(T7)	PU(T7)
TiO ₂	—	—	—	—	0.05	0.01
Al ₂ O ₃	0.06	0.03	0.04	0.01	0.06	0.08
Fe ₂ O ₃	—	—	42.62	42.72	22.25	20.68
Mn ₂ O ₃	—	—	—	13.01	—	26.72
FeO	32.23	46.34	—	—	—	—
MgO	0.05	0.21	0.26	0.30	2.26	1.72
ZnO	0.16	0.13	0.02	0.05	—	—
MnO	22.38	14.89	11.01	—	22.87	—
CaO	4.78	0.03	0.13	0.13	0.34	0.41
[Li ₂ O*]	—	—	—	—	[4.36]	—
Na ₂ O	0.04	0.04	0.07	0.08	0.27	0.78
K ₂ O	—	—	—	—	0.07	0.12
P ₂ O ₅	39.03	38.20	42.37	41.72	45.23	44.95
Total	98.73	99.87	96.52	98.02	97.76	95.47
Ti	—	—	—	—	0.004	0.001
Al	0.004	0.004	0.005	0.001	0.007	0.010
Fe ³⁺	—	—	3.472	3.382	1.749	1.628
Mn ³⁺	—	—	—	1.042	0.000	2.127
Fe ²⁺	1.609	4.671	—	—	—	—
Mg	0.004	0.038	0.042	0.047	0.352	0.268
Zn	0.007	0.012	0.002	0.004	—	—
Mn ²⁺	1.132	1.520	1.010	—	2.023	—
Ca	0.306	0.004	0.015	0.015	0.038	0.046
[Li*]	—	—	—	—	[1.831]	—
Na	0.005	0.009	0.015	0.016	0.055	0.158
K	—	—	—	—	0.009	0.016
P	1.973	3.898	3.883	3.716	3.999	3.980
Fe _{tot} /Fe _{tot} +Mn	0.59	0.75	0.77	0.76	0.46	0.43

TABLE 5. Unit cell parameters of some of the phosphate minerals, mainly associated with the simple discordant pegmatites (type 6)

	apat(T6)	sarc(T6)	sarc(T6)	heter(T6)	heter(T6)	heter(T6)	heter(T1)	allu(T6)	ferris(T6)
<i>a</i>	9.389(7)	10.545(4)	10.494(4)	5.820(7)	5.763(6)	5.914(4)	5.820(1)	10.982(5)	5.9354(1)
<i>b</i>	9.389(7)	4.795(4)	4.727(7)	9.76(1)	9.635(5)	9.724(6)	9.747(3)	12.59(1)	10.0969(7)
<i>c</i>	6.851(8)	6.053(1)	6.034(3)	4.790(6)	4.809(2)	4.763(5)	4.769(1)	6.441(3)	4.78259(9)
β	—	—	—	—	—	—	—	96.16(4)	—
V	523.1(8)	306.0(1)	299.3(4)	272.3(5)	267.0(2)	273.9(2)	270.6(1)	885.8(6)	286.62(1)

TABLE 6. Chemical composition of zwieselite (ZW), apatite (AP), amblygonite (AM) and väyrynenite (VA), associated with dykes and apophyses with aplitic and pegmatitic facies (T3); simple conformable pegmatites (T4); simple discordant pegmatites (T6), and Li-bearing pegmatites (T7). (Data obtained by electron microprobe; N = number of points of analyses; *bluish apatite; **values calculated from the end member MnBe(PO₄)(OH)). Cation numbers on the basis of 1(PO₄³⁻) per cell for zwieselite and väyrynenite, 26 (O, F) for apatites and 9 (O, F) for amblygonite

N	ZW(T3) 2	ZW(T6) 2	AP(T4) 1	AP(T6) 1	AP(T6)* 3	AP(T8) 2	AM(T6) 5	AM(T7) 5	VA(T6) 7
Al ₂ O ₃	0.02	0.01	0.24	0.33	0.02	0.24	37.87	36.35	0.90
TiO ₂	—	—	—	—	—	—	—	—	0.01
FeO	33.57	34.78	0.56	0.29	1.24	0.06	0.00	0.05	7.65
MgO	5.97	2.22	0.00	0.00	0.00	0.00	0.01	0.01	0.22
ZnO	0.00	0.31	—	—	—	—	0.00	0.05	—
MnO	20.34	22.67	2.66	0.52	4.87	0.18	0.01	0.01	31.22
CaO	0.69	0.82	52.77	54.94	50.15	56.25	0.04	0.02	0.17
Na ₂ O	0.06	0.01	0.04	0.00	0.12	0.02	0.02	0.02	0.02
P ₂ O ₅	30.88	30.88	41.64	41.68	41.58	41.64	47.91	47.31	38.04
[BeO**]	—	—	—	—	—	—	—	—	[13.41]
[H ₂ O**]	—	—	—	—	—	—	—	—	[6.71]
F	6.70	7.75	2.96	3.73	3.15	4.40	1.88	3.09	—
	97.83	99.45	100.86	101.49	101.13	102.78	85.84	86.91	—
-O=F	2.82	3.26	1.25	1.57	1.33	1.85	0.79	1.30	—
Total	95.01	96.19	99.61	99.92	99.80	100.93	85.05	85.61	98.36
Al	0.001	0.000	0.047	0.062	0.005	0.046	2.230	2.212	0.030
Ti	—	—	—	—	—	—	—	—	0.000
Fe ²⁺	1.074	1.113	0.077	0.039	0.172	0.008	0.001	0.002	0.200
Mg	0.340	0.127	0.001	0.000	0.000	0.000	0.001	0.001	0.010
Zn	0.000	0.001	—	—	—	—	0.000	0.002	—
Mn	0.655	0.734	0.373	0.071	0.683	0.024	0.000	0.000	0.820
Ca	0.028	0.034	9.350	9.557	8.896	9.615	0.002	0.001	0.010
Na	0.005	0.001	0.012	0.001	0.038	0.005	0.002	0.002	0.000
P	1.000	1.000	5.830	5.729	5.829	5.625	2.135	2.068	1.000
F	0.810	0.940	1.548	1.916	1.651	2.220	0.313	0.505	—
[Be**]	—	—	—	—	—	—	—	—	[1.000]
[OH**]	—	—	—	—	—	—	—	—	[1.390]
Fe _{tot} /(Fe _{tot} +Mn)	0.62	0.60	0.17	0.35	0.20	0.25	—	—	0.20

1989; Corbellá and Melgarejo, 1990), primary triphylite has not been observed. Therefore, although an origin for the ferrisicklerite from triphylite cannot be definitively rejected, it is possible to propose a direct crystallization for the ferrisicklerite, which has been obtained experimentally as a primary phase from hydrous aluminosilicate melts (Shigley and Brown, 1986).

Heterosite-purpurite. Heterosite is found not only in the discordant pegmatites (type 6), but also in the interior pegmatites (type 1), whereas purpurite has been detected in the Li-bearing dykes (type 7). As has been said previously, heterosite is associated with ferrisicklerite in type 6 pegmatites, the former being

an alteration product of the latter. This substitution has been described by other authors (Fontan *et al.*, 1976; Fransolet *et al.*, 1986; Corbellá and Melgarejo, 1990; Moore, 1982). It occurs as fine-grained masses, showing its characteristic purple colour, with small orange-brownish spots of the previous ferrisicklerite in thin section. Chemical composition is shown in Table 4 and Fig. 2b and c, and the unit-cell parameters are listed in Table 5. These contents are very similar to those observed in the associated ferrisicklerite. On the other hand, heterosite associated with the interior pegmatites (type 1) appears strongly altered, mainly to clay minerals. For this reason, its microprobe analyses would not be reliable.

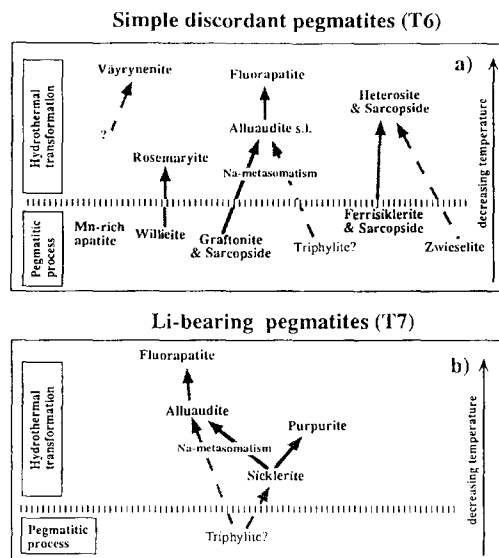


FIG. 3. Schematic representation of the alteration sequences of the early crystallized phosphate minerals from (a) the simple discordant pegmatites (type 6), and (b) the Li-bearing pegmatites (type 7). (Dashed lines correspond with hypothetical evolutive paths).

In this case, ferrisicklerite relics have not been observed.

With regard to the purpurite associated with the Li-bearing pegmatites, it has only been detected in one of these bodies, associated with alluaudite and sicklerite, and is probably an alteration product of the latter. It appears as very fine grains of subhedral habit with a deep purple colour.

Triplite/zwieselite. Members of this series have been found in the aplitic and pegmatitic apophyses (type 3), and in the discordant pegmatites (type 6). Their Fe content is higher than that of Mn, so that they can be classified as zwieselites (Fig. 2c). In the type 3 bodies, a high Mg content is observed, much higher than that of the zwieselite associated with simple discordant pegmatites (Table 6).

Zwieselite generally appears in brown masses consisting of crystals smaller than 1 cm. According to Moore (1982), its origin can be either primary or metasomatic, growing in the intermediate zones of the pegmatites. In the sole discordant pegmatite where it has been found, the larger crystals appear disposed parallel to the pegmatitic layered internal structure. This fact, as well as its textural relationships with the rest of the pegmatitic phases, lead us to suppose a primary origin for this zwieselite. In the

case of the aplitic and pegmatitic apophyses (type 3), zwieselite appears closely related to alluaudite. We found insufficient criteria to determine if its origin is primary or metasomatic.

Alluaudite. Alluaudite constitutes a complex group that includes a sequence of metasomatic components of which the chemistry and structural nature were detailed by Moore and Ito (1979). This term constitutes an extremely complex and diverse group of species whose crystal chemistry is complicated by the fact that several non-equivalent cation positions occur in the unit cell.

This phase appears associated with the aplitic and pegmatitic apophyses (type 3); with the discordant pegmatites (type 6) occasionally associated with vayrynenite; and with the Li-bearing dykes (type 7) showing important compositional differences between them (Table 7, Fig. 2b and c). Alluaudite from type 3 pegmatites is the richest in Fe (ferroalluaudite), whereas that from the discordant pegmatites shows the highest Ca (hagendorfite), and the highest Mn values correspond to alluaudite associated with the Li-bearing pegmatites.

Alluaudite is a replacement product of triphylite-lithiophilite and other phosphate minerals, when an important Na-metasomatism occurs. The replacement of ferrisicklerite by alluaudite in this way has been suggested (Huvelin *et al.*, 1972), and also the substitution of graftonite by alluaudite (Pesquera *et al.*, 1986). So, bearing in mind that triphylite has not been detected in the Fregeneda pegmatites, it is possible that alluaudite is a product of Na-metasomatism undergone by these primary phases.

Apatite. Apatite is the most widespread phosphate in these pegmatites. It has been found in all the pegmatite types except in the interior pegmatites (type 1) and in the K-feldspar pegmatites (type 5). Generally, it occurs as anhedral fine to medium sized crystals. In addition, a bluish variety of prismatic apatite is associated with the simple discordant pegmatites (type 6). In this case, apatite appears in the intermediate zones of pegmatites, whereas in the rest of the cases this phase occurs in the core as well as in the border zones. It is noteworthy that a porphyroblastic apatite growing in a lepidoblastic matrix is associated with the quartz and andalusite dykes (type 2) and with the most deformed simple concordant pegmatites (type 4). Unit cell parameters of bluish apatite of type 6 pegmatites are listed in Table 5. With regard to their chemical composition, the Mn content of the bluish apatite is higher than that of the rest of the apatites (Table 6), which is in agreement with previous workers (Deer *et al.*, 1992). Nevertheless, the Mn content of apatites associated with simple concordant pegmatites is also relatively high, and in this case their colour is not bluish. There is a certain positive correlation between Fe and Mn,

TABLE 7. Representative microprobe analyses of ferroalluaudite (FA) from the dykes and apophyses with aplitic and pegmatitic facies (T3); hagendorfite (HA) and alluaudite (ALL) from the simple discordant pegmatites (T6); and alluaudite from the Li-bearing pegmatites (T7). (*alluaudite associated with väyrynenite). Number of cations on the basis of $(\text{PO}_4)_{12}$. The structural formulae are calculated following the procedure suggested by Moore (1971)

	FA(T3)	HA(T6)	ALL(T6)*	ALL(T7)
Al_2O_3	0.03	0.07	0.98	0.07
TiO_2	—	—	—	0.05
FeO	37.09	24.90	14.30	—
MgO	0.64	0.13	0.21	1.00
ZnO	0.00	0.03	—	0.06
MnO	8.92	22.67	15.64	27.11
Fe_2O_3	—	—	16.85	17.15
CaO	0.58	7.12	1.40	0.37
Na_2O	5.37	3.65	5.48	7.72
PO_5	41.51	41.50	41.88	41.60
Total	94.2	100.07	95.16	95.20
M(2) Al^{3+}	0.012	0.027	0.386	0.021
Fe^{3+}	4.966	0.816	4.292	4.403
Fe^{2+}	2.696	6.296	3.322	0.000
Mg	0.000	0.000	0.000	0.512
Mn^{3+}	0.000	0.000	0.000	0.512
Ti	0.000	0.000	0.000	0.021
Zn	0.000	0.000	0.000	0.021
Mn^{2+}	0.000	0.000	0.000	2.510
M(1) Fe^{2+}	2.929	0.000	0.726	0.000
Mn^{2+}	1.071	4.000	3.274	4.000
X(1) Mn^{2+}	1.509	2.558	1.221	0.780
Ca	0.212	1.442	0.509	0.143
Na	2.279	0.000	2.270	3.077
X(2) Na	1.276	2.417	1.330	1.933
Ca	0.000	1.163	0.000	0.000
K	0.000	0.000	0.060	0.041
\square	2.724	0.420	2.610	2.047
$\text{Fe}_{\text{tot}}/\text{Fe}_{\text{tot}}+\text{Mn}$	0.80	0.52	0.65	0.36

the apatites of the Sn-bearing pegmatites being the poorest in these elements, whereas the richest is the bluish apatite, associated with the simple discordant pegmatites (type 6). On the other hand, as all the apatites exhibited a high F content (3.08–6.40%) we shall classify them as fluorapatites.

Apatite is associated with all the stages of pegmatite evolution (including pegmatitic and subsequent hydrothermal stages). As evidenced by its textural characteristics, the crystallization of the Mn-rich apatite in the simple discordant pegmatites (type 6) is associated with a late pegmatitic stage (Fig. 3), whereas the rest of the observed apatites

(fluorapatites) would stem from late hydrothermal stages, as is common in apatites of such composition.

Amblygonite. Members of the amblygonite-montebasite series appear associated with some of the simple discordant pegmatites (type 6) and mainly with the Li-bearing pegmatites (type 7). Grain size is very heterogeneous, generally <1 cm in the type 6 pegmatites, and fine to coarse in the type 7 pegmatites, showing an anhedral habit in both cases. This phosphate generally shows a polysynthetic twin, sometimes double, with an oblique relation between them. Frequently, amblygonite appears strongly altered to clay minerals, as well as replaced by Li-mica.

The end members of this solid-solution are amblygonite $\text{LiAl}(\text{PO}_4)\text{F}$ and montebrasite $\text{LiAl}(\text{PO}_4)\text{OH}$. In fact, this series varies from amb_0 to amb_{92} , members richer in F than amb_{65} being rare (Greiner and Donald Bloss, 1987). Although the term 'amblygonite' is most frequently used to name any member of this series, most of the analysed crystals correspond with montebrasite (Dubois *et al.*, 1973; Loh and Wise, 1976). In this way, in Table 6 and in Fig. 2d, it is possible to observe that all the analysed crystals correspond with montebrasite, with a F content <4%. Nevertheless, it must be noted that amblygonite associated with Li-bearing pegmatites (Type 7) is richer in the amblygonite term than that associated with the simple discordant pegmatites (type 6).

Members of this series usually appear in the interior zones of pegmatites, as well as in the quartz cores of the zoned Li-rich pegmatites (London and Burt, 1982). On the contrary, in the Li-bearing pegmatites of the Fregeneda area this phosphate appears not only in the cores, but also in the border and intermediate zones.

Väyrynenite. This rare beryllium phosphate has been identified by means of X-ray powder diffraction spectra, and its chemical composition is shown in Table 6 (Fig. 2c). Väyrynenite of the Fregeneda pegmatites occurs as very fine grained crystals, showing an anhedral habit. It has only been detected in the simple discordant pegmatites (type 6), associated with alluaudite. It is remarkable that although this secondary phosphate is characteristic of Be-bearing pegmatites, up to now, the presence of beryl has not been detected in these bodies.

Discussion and conclusions

Most of the pegmatitic types of the Fregeneda area show phosphate minerals, particularly the simple discordant pegmatites (type 6), and mainly those occurring near the Lumbrales granite, which carry a variety of relevant phosphates. The following phosphate minerals have been reported: wylleite, graffonite, ferrisicklerite, sarcopside, zwieselite, rosemaryite, heterosite, alluaudite, Mn-rich apatite, F-apatite, and väyrynenite. To a lesser extent, the Li-bearing pegmatites (type 7) show other phosphate minerals, with montebrasite being the most common, whereas sicklerite, purpurite and alluaudite have only been detected in one of these dykes.

The presence of patches of rosemaryite within wylleite showing a crystallographic continuity suggests that both phases are closely related. Rosemaryite may be formed by the topotactic alteration of the wylleite, due to the oxidation of the transition metal cations (iron and minor manganese) simultaneous with the Na-leaching.

This mechanism is similar to that shown by the ferrisicklerite-heterosite sequence, with the Li-leaching in ferrisicklerite to generate heterosite (sicklerite and purpurite respectively in the Li-bearing pegmatites). So, rosemaryite, heterosite and purpurite are believed to be topotactic alteration products (Moore, 1971; Fontan *et al.*, 1976; Keller and Von Knorring, 1989) (Fig. 3). The first sequence is therefore evidenced in Fig. 2b, where a good correlation between $(\text{R}^{2+}+\text{R}^+)$ and (R^{3+}) for wylleite and rosemaryite can be observed. The occurrence of sarcopside lamellae in ferrisicklerite and heterosite is also evidence of the replacement processes of the former by the latter. On the other hand, the Na-metasomatic replacement of the early phosphates ferrisicklerite and graffonite, to produce alluaudite, is also well developed in this association. The replacement of wylleite by alluaudite is improbable because of the immobile character of the Al.

With regard to the väyrynenite, this phosphate appears closely associated with alluaudite, although its genetic relationships have not yet been established.

The occurrence of this Fe-Mn phosphate association in the simple discordant pegmatites (type 6) is in agreement with the pegmatite fields zonation established by Černý (1991), so that these phosphate-bearing pegmatites exhibit an intermediate degree of fractionation, and they appear between the barren and the more evolved pegmatites with respect to Li and Sn.

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