Boron vs. Phosphorus in granitic pegmatites: the Cap de Creus case (Catalonia, Spain)

Bór vs. fosfor v granitických pegmatitech: příklad Cap de Creus (Katalánsko, Španělsko) (Czech summary)

(12 text-figs, 1 tab.)

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Four granitic pegmatite types are distinguished in the metapelite-hosted Cap de Creus pegmatite field: barren microcline-rich pegmatites (type I), beryl-columbite subtype pegmatites (type II), beryl-columbite-phosphate subtype pegmatites (type III) and albite type pegmatites (type IV). The abundance of tourmaline is inversely proportional to that of the phosphates: it is widespread in all the internal zones of the P-poor type I and II pegmatites, becomes very rare in the P-rich type III pegmatites and it is absent in the type IV. Nevertheless, tourmalinization is developed in the exocontacts of all the pegmatite types. All of the tourmaline crystals in the pegmatites and exocontacts belong to the schorl-dravite and schorl-foitite series, although Li phosphates are essential components in the most evolved pegmatites. In the less evolved, P-poor pegmatites, tourmaline crystallization, as well as that of other ferromagnesian silicates, depletes the concentration of Mg and Fe in the magma, and Fe/(Fe+Mg) in tourmalines increases during the course of crystallization of the pegmatite. Meanwhile, in the most evolved P-rich pegmatites, Fe-Al-Li-Mg phosphates are formed instead of silicates, boron is fractionated with excess phosphorus into the residual fluids, and tourmaline and apatite are formed by metasomatism of the host rock.

Key words: tourmaline, electron microprobe, phosphorus, boron, granitic pegmatite

Introduction

The composition of tourmaline is highly sensitive to the chemical composition of the parental system. This mineral provides valuable information about the petrogenesis and bulk chemistry of the system in which it forms (Power 1968, Manning 1982, Shearer et al. 1984). Tourmaline is the most common boron-bearing phase in granitic pegmatites, and this element plays a significant role in the petrogenesis and petrology of these rocks: it lowers the solidus and liquidus and increases the solubility of H_2O in the magma (Pichavant 1987, Dingwell et al. 1996, Wolf – London 1997).

Several studies on the variation in the tourmaline composition have been carried out in order to obtain information about the petrology and petrogenesis of pegmatites (Staatz et al. 1955, Foord 1977, Joliff et al. 1986, London – Manning 1995, Roda et al. 1995, Keller et al. 1999, Trumbull – Chaussidon 1999).

The present work examines the variation of the tourmaline composition within the pegmatite field of Cap de Creus. It establishes the evolution of different components, such as Mg, Fe and B, by examination of tourmaline throughout the pegmatite field and throughout the different zones of individual pegmatite bodies, and it correlates the mineralogy of Li with the abundance of phosphorus.

Geological setting

The Cap de Creus (NE Spain) is the easternmost outcrop of the Hercynian basement of the Pyrenees. The area consists of Paleozoic series of a 2000 m-thick pelitic sequence with minor limestones, acid volcanics and coarser sediments (Carreras – Casas 1987). This series has been affected by two main episodes of Hercynian deformation: the first generated the main foliation, and the second folded the foliation and terminated with the development of NW-SE trending shears (Carreras – Casas 1987). A low pressure, high temperature regional metamorphism took place between the two deformation episodes. Metamorphism ranges from a chlorite-muscovite zone in the south to cordierite-andalusite, sillimanite-muscovite and K-feldspar-sillimanite (migmatite) zones in the north, with isograds trending NW.

The intrusive rocks in the Cap de Creus area consist of pre-Hercynian porphyritic granites and two types of Hercynian granitoids: (1) small syntectonic leucogranite to quartz gabbro masses related to the northern migmatite zone (Carreras et al. 1975, Carreras – Druguet 1994, Druguet 1997); and (2) the late Roses and Rodes granodiorites and quartz diorite stocks emplaced within lower grade rocks, in the south and southwest. In the easternmost part of the Cap de Creus peninsula, a pegmatite field is exposed, which consists of more than 400 pegmatite bodies. (Fig. 1). Based on the classification of Černý (1991), four pegmatite types have been established according to internal structure and mineralogical criteria (Corbella – Melgarejo 1990): microcline-rich (type I); beryl-columbite (type II); beryl-columbite-phosphate (type III) and albite (type IV). All of these types are progressively distributed along to the metamorphic gradient: type I occurs in the sillimanite+K-feldspar zone, and type IV in the cordierite+andalusite zone. The number and size of the pegmatite bodies decrease from the type I, which is comprised of nearly 200 bodies, to type IV pegmatites, with
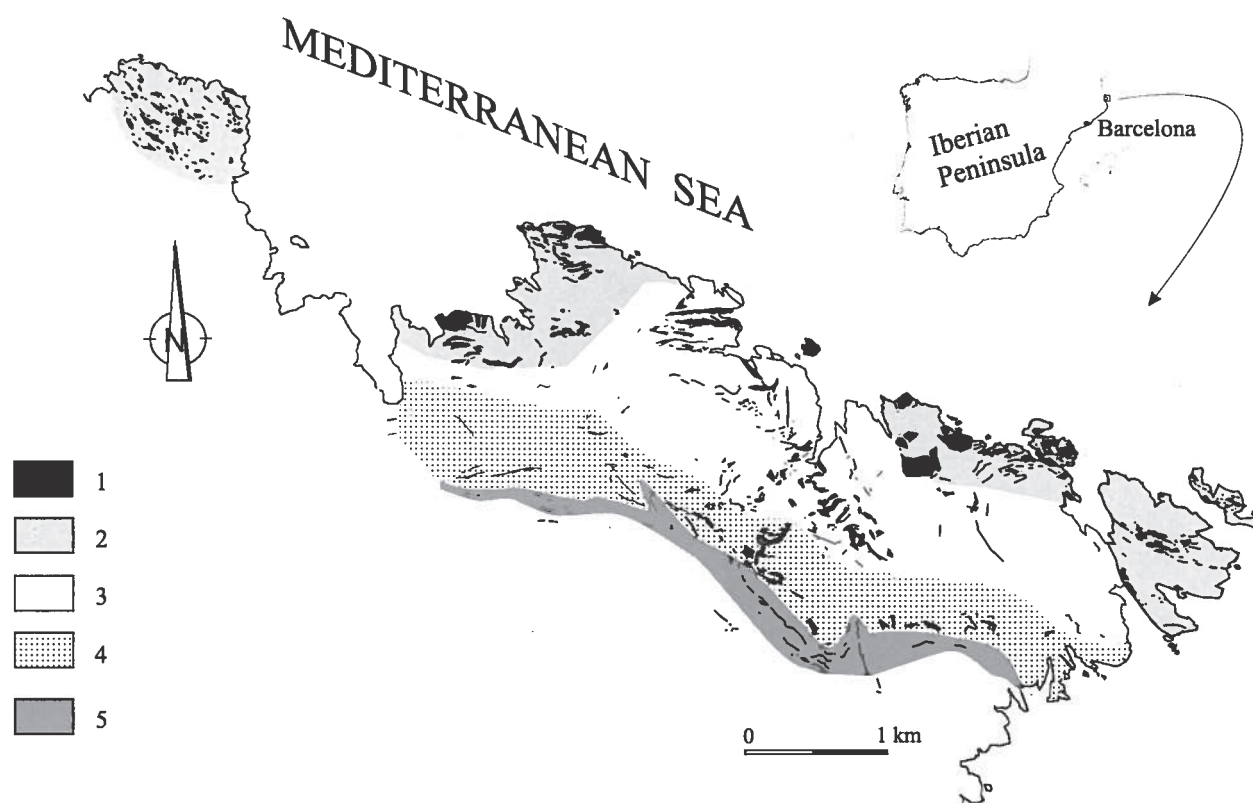
Fig. 1. Pegmatite distribution in the Cap de Creus Peninsula: 1 – pegmatite body; 2 – area with type I microcline pegmatites, barren; 3 – area with type II transitional pegmatites, with Ca-Fe-Mn-Mg phosphates, Be mineralization and Ti-Nb-Ta-W-U sparse mineralization; 4 – area with type III microcline-albite pegmatites, with Li-Na-Fe-Mn-Be phosphates, Be mineralization, and common Nb-Ta-(Sn) ores; 5 – area with type IV albite pegmatites, with Al-Li-Be-Na-Fe phosphates, Be mineralization and Ta-Nb-Sn-REE ores. Modified from Carreras (1975).

about 10 bodies. Structure and mineralogy increase in complexity from type I to type IV pegmatites (Fig. 2).

Structure and Mineralogy of the Cap de Creus pegmatites

Type I or microcline pegmatites are microcline-rich and poorly zoned: there is a centimeter-size border zone followed by the wall aplitic zone, intermediate zones (first and second, according to the grain size), synkinematic crystallization in necking zones, and quartz or schorl veins also occur as the latest products. Major minerals in these zones are quartz, macroperthitic microcline and albite; the main accessory minerals are sillimanite, biotite, cordierite, tourmaline, almandine, muscovite and scarce niobian rutile and columbite-tantalite. These pegmatites are synkinematic, as evidenced by boudinage structures in the bodies coupled with coarse-grained pegmatite crystallization in the necking zones, with decimeter-size crystals (Fig. 3). In these necking zones the sequence of crystallization starts with blocky microcline (associated with muscovite, garnet and schorl) and ends with quartz. True quartz-cores are absent in these pegmatites, but some small quartz pods do occur locally. Late schorl veins crosscut all of the pegmatite. Tourmalinization is widespread in the exocontact.

Type II or beryl-columbite pegmatites are well zoned, with a border, wall, first intermediate and second inter-

mediate zones. These zones mainly consist of microcline, albite and quartz; common Al-rich accessories are muscovite, almandine, tourmaline, beryl (partly replaced by an association of chrysoberyl, phenakite and euclase), gahnite and andalusite (in some cases, partly pseudomorphosed by fibrolitic sillimanite), with minor niobian rutile, columbite, wolframite and uraninite. Primary Ca-Mn-Mg-Fe-rich phosphate minerals are formed in the second intermediate zones and also in the quartz core. This mineral association is comprised of sarcopside, graftonite, wyllieite and magniotriplite. Late albitization stage produces the replacement of K-feldspar and the development of albite veins; in these veins columbite-tantalite minerals are especially common. Phosphates of Be (hurlbutite and hydroxyl-herderite) and apatite are formed by the destabilization of all of the above Be-silicates and chrysoberyl during the late stage of pegmatite formation. According to Burt (1975), this association suggests a low F_2O^{-1}, high P_2O_5 activity in the pegmatite-forming fluids during this stage. Moreover, all these phosphates are replaced by alkali metasomatic phosphates and supergene phosphates (Corbella – Melgarejo 1990). Tourmalinization occurs in the host rocks.

Type III or beryl-columbite-phosphate pegmatites have similar zonal patterns. A significant mineralogical difference with respect to the other two types is that many of the pegmatites from this type are Al-poor: garnet and tourmaline only occur in a few pegmatite bodies. Here, the
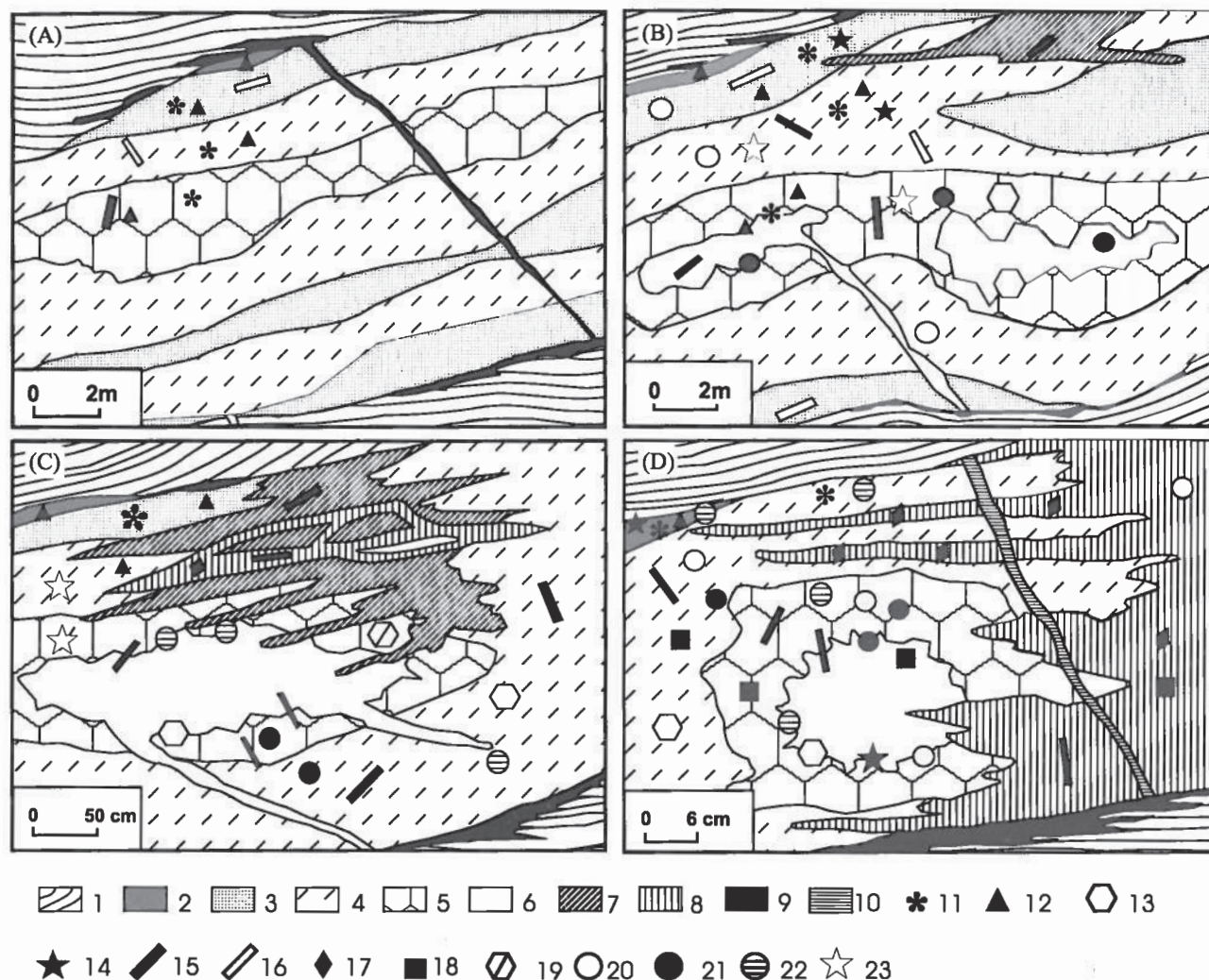
Fig 2. Idealised models on internal structure and ore distribution in pegmatite types from Cap de Creus pegmatite field: A – Type I pegmatites; B – Type II pegmatites; C – Type III pegmatites; D – Type IV pegmatites. 1 – country rock; 2 – border zone; 3 – wall zone; 4 – 1st intermediate zone; 5 – 2nd intermediate zone; 6 – quartz core; 7 – albitic replacements; 8 – quartz-muscovite veins; 9 – schorl veins and tourmalinization; 10 – Al-Li-Be phospates within late veins; 11 – Al-rich silicate minerals; 12 – schorl; 13 – beryl; 14 – chrysoberyl; 15 – columbite-tantalite 16 – rutile and other Ti-rich oxides; 17 – cassiterite; 18 – REE bearing oxides; 19 – Be-phosphates pseudomorphic after beryl; 20 – lazulite; 21 – Ca-Fe-Mn-Mg phosphates; 22 – primary Li phosphates; 23 – Be-phosphates pseudomorphic after chrysoberyl.

intermediate zones mainly consist of quartz, microcline and albite; beryl, Nb-Ta minerals and primary Li-phosphates (montebrasite and triphilite) or Al-Ca-Mn-Fe phosphates (wyllieite, graftonite, sarcopside) are very common. The quartz core is well developed, and replacement bodies are widespread. Two types of replacement bodies can be distinguished: albite units (constituted by sugary albite, very rich in Ta-rich columbite-tantalite minerals, tapiolite, fergusonite and cassiterite), and quartz-muscovite veins. Albitization of the early- formed K-feldspar is also common, and hurlbutite and hydroxyl-herderite replace beryl. Metasomatic alkali phosphates and Ta-rich oxides are also related to the replacement processes (Alfonso et al. 1995). Zircon (commonly rich in uraninite inclusions) is a common accessory mineral in all of the zones. Tourmalinization is widespread at the exocontact.

Type IV, or albitic pegmatites mainly consist of albite with minor quartz and muscovite; K-feldspar is absent.

Border, wall, intermedite zones, quartz core and veining are well developed. Common accessories in the border zone and in the intermediate zones are montebrasite, scorzalite, graftonite, sarcopside, gahnite, chrysoberyl and beryl, columbite-tantalite, aeschynite and Ta-rich rutile. Tourmaline only occurs in the border zone. In the quartz core, scorzalite nodules can occur. Quartz-muscovite veins are strongly mineralized in cassiterite, gahnite (locally destabilized to nigerite), Ta-rich members of the columbite-tantalite series, microlite and other minerals with HREE. Phosphate veins crosscut the pegmatite bodies; these veins contain berlinite as an early-formed phosphate, but it is replaced by trolleite, scorzalite, wyllieite and montebrasite. A very late fissural mineralization with chlorite, euhedral albite and LREE-rich allanite can also be distinguished in some pegmatites. Hf-rich zircon is common in all of these units. Graphitization, phosphatization (apatite), muscovitization
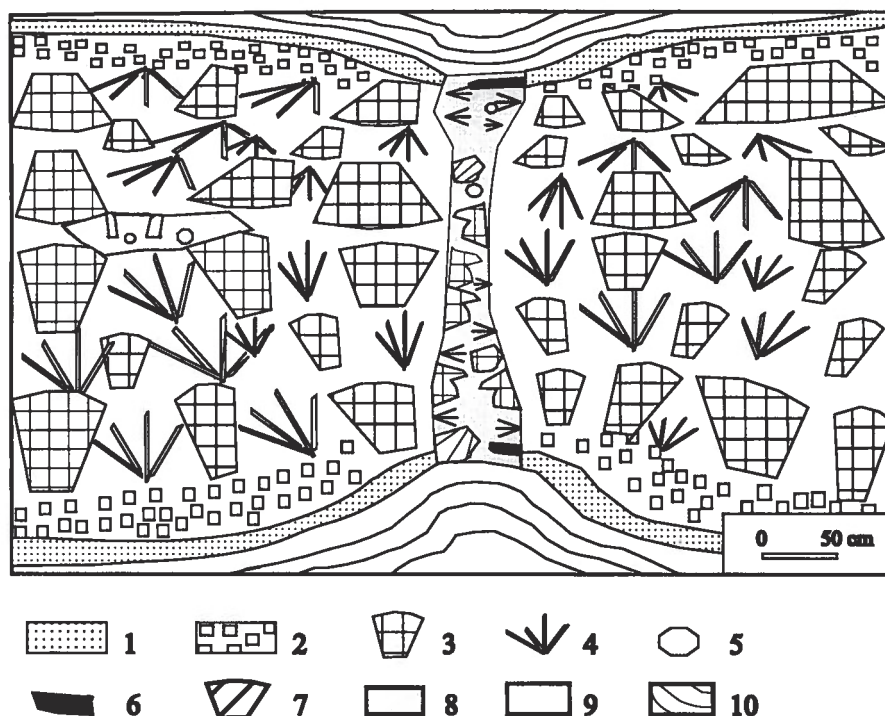
Fig. 3. Structure and mineralogy of a syntectonic pegmatite of type I, showing the mineral growth in a necking zone related to boudinage phenomena. 1 – wall zone; 2 – first intermediate zone; 3 – blocky microcline in the second intermediate zone; 4 – branching aggregates of muscovite and biotite; 5 – garnet; 6 – tourmaline; 7 – albite; 8 – quartz; 9 – fine- to coarse-grained aggregates of microcline, quartz, albite, biotite, muscovite, tourmaline, garnet, cordierite and sillimanite; 10 – country rock.

and tourmalinization are common metasomatic phenomena in the pegmatite exocontact.

The mineralogical and geochemical data suggest that all of these pegmatites were formed by fractionation processes operating from a single source (Corbella – Melgarejo 1990, Alfonso 1995). The most remarkable geochemical variations from type I to type IV pegmatites are: increasing albitization and replacement phenomena, increasing P and Li mineralization, increasing Hf/(Zr+Hf) in zircon (Corbella – Melgarejo 1993) and increasing Ta/(Ta+Nb) and Mn/(Fe+Mn) in columbite-tantalite minerals (Alfonso et al. 1995). Furthermore, type IV pegmatites are enriched in HREE-Sn-Ta-Hf. The evolution of the composition of Nb-Ta minerals depends not only on the pegmatite type in which they occur, but also on the pegmatite unit (Alfonso et al. 1995): the Ta-rich minerals occur in the last units to crystallize (albite and quartz-muscovite replacement units).

Sampling and Experimental Methods

The Cap de Creus pegmatite field is well exposed, so a systematic sampling was completed. Samples of tourmaline crystals were selected from all the pegmatite types in the zones where it was present. Profiles from 41 crystals in 24 samples with 4 to 15 analyses were obtained.

Single crystals were analyzed with an electron microprobe CAMECA SX50 at the Serveis Cientifico Tècnics de la Universitat de Barcelona. The analytical conditions were conduced at an accelerating voltage of 15 kV and 15nA beam current for Si, Al, Ti, Fe, Mn, Mg, Ca, Na and K, and 6 kV for B and F. The boron contents were determined with a multi-layer crystal of Mo/B4C with a 2d spacing of 20.5 nm. The objective of this study was to characterize the chemical variations in some elements among the different populations of tourmaline, in spite of the absence of direct analyses of Li.

Results

The chemical composition of the tourmalines from the Cap de Creus pegmatites (Table 1) indicates that all of them belong to the schorl-dravite and the schorl-foitite series. These analyses plot in the fields 2 and 4 of the diagram of Henry – Guidotti (1985) (Fig. 4), which represent the field of the tourmaline from Li-poor granitic rocks and their associated aplites and pegmatites and the field of metapelite and metapsamite suites. Those from this later field are mainly tourmalines from the exocontact, border and wall zones.

Crystal chemistry of the tourmaline

All the tourmaline crystals from the Cap de Creus pegmatites belong to the schorl-dravite and the schorl-foitite series: $XY_3Z_6(BO_3)_3 Si_6O_{18}(OH)_4$, with X=Na, Ca, K, $\square$, Y=Fe, Mg, Ti, Mn and Z= A2 (Fig. 5).

Tourmaline shows deviations from these end members. Firstly, the Y sites, in addition to Fe, Mg, Mn and Ti, also contain Al. coupled substitutions can maintain charge balance (Foit – Rosenberg 1977, Manning 1982, Foit et al. 1989): $R^+ + R^{2+} = R^{3+} * \square$ or $(OH)^- + R^{2+} + = R^{3+} + O^{2-}$. The first replacement produces an alkali-free end member (foitite, MacDonald et al. 1993), and the second, a proton-free end member. Manning (1982) proposes a diagram R^{3+} *versus* $R^+ + R^{2+}$ to evaluate the importance of both substitutions. Tourmaline crystals from the Cap de Creus pegmatites (Fig. 6) are located far away from the schorl-dravite,

Table 1. Chemical compositions of tourmaline crystals, obtained by electron microprobe.

Zone	2nd intermediate		Necking		Exocontact		Wall		1st intermediate		2nd intermediate		Core		Wall	1st i.	Exo.
Pegmatite. type	I		I		II		II		II		II		II		III	III	IV
Crystal zone	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	core	rim	n. c	n. c	n. c
SiO_2	35.70	35.75	35.78	35.30	35.81	36.03	34.77	35.14	33.68	34.92	34.86	34.03	35.23	34.81	34.55	34.81	35.09
Al_2O_3	35.50	34.97	35.46	35.80	32.60	33.88	34.02	34.27	34.80	34.44	32.70	34.77	35.09	34.28	35.02	35.17	33.16
TiO_2	0.76	0.56	0.02	0.31	–	–	0.80	0.74	0.05	0.11	0.02	0.17	0.22	0.41	0.15	0.06	0.06
B_2O_3	9.90	9.94	10.02	10.31	11.54	11.4	9.46	9.54	10.67	10.35	10.89	10.85	10.7	10.64	11.90	9.84	11.01
FeO	6.22	7.84	12.52	10.04	8.15	7.34	6.75	8.79	11.28	11.42	11.58	11.73	8.10	8.05	11.31	12.68	8.50
MgO	6.07	5.39	1.88	2.95	6.26	6.36	5.55	4.81	2.16	2.38	1.35	1.87	4.92	4.79	1.66	1.27	5.42
MnO	–	0.09	–	0.15	0.06	0.07	0.08	0.18	0.31	0.31	0.24	0.24	0.04	0.06	0.18	0.26	0.20
CaO	0.42	0.46	–	0.05	0.48	0.43	0.09	0.24	0.03	0.01	0.04	0.12	0.09	0.12	0.02	0.03	0.04
Na_2O	1.67	1.58	0.94	1.74	2.05	1.97	1.90	2.08	1.90	1.84	1.37	1.75	1.88	2.71	1.81	1.57	2.00
K_2O	0.04	0.04	–	0.05	0.06	0.03	0.06	0.06	0.03	0.06	0.01	0.03	0.06	0.04	0.05	0.07	0.03
F	0.13	0.05	0.10	0.45	0.18	0.15	–	0.53	0.36	0.08	0.43	0.33	0.28	–	0.18	0.05	0.52
H_2O*	3.58	3.61	3.56	3.41	3.59	3.56	3.52	3.32	3.37	3.53	3.43	3.41	3.51	3.61	3.55	3.53	3.30
Total	99.99	100.28	100.28	100.56	100.78	100.74	97.00	99.70	98.64	99.47	99.81	99.30	100.12	99.52	100.37	99.34	99.33
O=F	0.05	0.02	0.04	0.19	0.08	0.11	–	0.22	0.15	0.03	0.12	0.14	0.12	–	0.08	0.02	0.22
Total	99.93	100.26	100.24	100.37	100.70	100.63	97.00	99.48	98.49	99.44	99.69	99.16	100.00	99.52	100.30	99.32	99.11

atoms p. f. u. based on 31 (O, OH, F)

Zone	2nd intermediate		Necking		Exocontact		Wall		1st intermediate		2nd intermediate		Core		Wall	1st i.	Exo.
Si (T)	5.989	5.896	5.952	5.840	5.840	5.838	5.923	5.903	5.702	5.863	5.801	5.729	5.795	5.785	5.703	5.884	5.827
Al (T)	0.011	0.104	0.048	0.160	0.160	0.162	0.77	0.097	0.298	0.137	0.199	0.271	0.205	0.215	0.279	0.116	0.173
T	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Al (Z)	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
B	2.811	2.829	2.876	2.943	3.247	3.199	2.781	2.765	3.117	2.998	3.127	3.151	3.037	3.051	3.389	2.870	3.010
Al (Y)	0.758	0.691	0.901	0.818	0.103	0.306	0.751	0.685	0.643	0.676	0.802	0.625	0.595	0.497	0.513	0.888	0.758
Ti	0.010	0.008	–	0.004	–	–	0.011	0.010	0.001	0.002	–	0.002	0.003	0.006	0.002	0.001	0.008
Fe^{2+}	0.856	1.081	1.741	1.388	1.111	0.909	0.961	1.234	1.596	1.603	1.611	1.651	1.114	1.118	1.560	1.792	1.082
Mg	1.325	0.466	0.466	0.727	1.521	1.540	1.409	1.204	0.545	0.596	0.320	0.469	1.206	1.186	0.408	0.320	1.406
Mn	0.013	–	–	0.021	0.008	0.010	0.012	0.026	0.044	0.044	0.034	0.034	0.006	0.008	0.025	0.037	0.011
pos. Y	3.117	3.108	3.108	2.959	2.743	2.765	3.144	3.160	2.830	2.920	2.758	2.781	2.924	2.815	2.509	3.038	3.265
Ca	0.081	–	–	0.009	0.084	0.075	0.016	0.043	0.005	0.002	0.007	0.022	0.016	0.021	0.004	0.014	0.036
Na	0.505	0.303	0.303	0.558	0.648	0.619	0.627	0.677	0.623	0.605	0.442	0.571	0.599	0.873	0.579	0.514	0.626
K	0.008	–	–	0.011	0.012	0.006	0.013	0.013	0.006	0.009	0.002	0.006	0.013	0.008	0.011	0.015	0.004
Pos. X	0.595	0.303	0.303	0.577	0.744	0.700	0.657	0.733	0.635	0.618	0.451	0.599	0.628	0.902	0.593	0.544	0.666
F	0.026	0.053	0.053	0.235	0.093	0.077	–	0.281	0.193	0.042	0.147	0.176	0.146	–	0.094	0.027	0.205
OH	3.974	3.947	3.947	3.765	3.907	3.923	4.000	3.719	3.807	3.957	3.853	3.824	3.854	4.000	3.906	3.973	3.795

* Theoretic value calculated based on 4 (OH, F). 1st i.= first intermediate, Exo = exocontact, nc= not concentrically zoned.

toward the alkali-free and proton-free end members. No important differences can be observed among the tourmalines from different pegmatite types. The crystals from the exocontact have the most restricted compositional range.

An important possibility in the tourmaline group is the substitution of Fe+Mg by Li+Al, leading to elbaite. Since Li cannot be analyzed with EMP, London – Manning (1995) provided a diagram based on the charge-balance estimates of the Li content. According to this diagram, the Li content of the Cap de Creus tourmalines is very low or absent (Fig. 7), which is in agreement with the lack of Li silicates in this field (Alfonso 1995).

Intracrystalline compositional variation

Tourmaline crystals usually exhibit a concentric zonation, mainly due to a variation in Fe/(Fe+Mg). In type I and type II pegmatites, tourmaline crystals from the exocontact and the outermost zones show an increase in Fe/(Fe+Mg) from the core to the rim (Fig. 8a). In the last tourmaline crystals formed in these pegmatites, (i. e. tourmaline from the necking zone in type I, and tourmaline from the contact between intermediate zones and core in type II pegmatites), Fe/(Fe+Mg) decreases from the center to the border.

In type III pegmatites, the tourmaline crystals from the host rocks and the wall zone exhibits the same compositional trend as those in the type I and II pegmatites, with an increase in Fe/(Fe+Mg). Crystals from other pegmatite zones usually do not exhibit any compositional zonation, or it is of patchy style. When they are concentrically zoned, the zoning is similar to that in the inner zones of the previously mentioned pegmatites, as Fe/(Fe+Mg) decreases from the core to the rim.

This behavior is correlated with the total Fe and Mg content in the crystals. In those cases where Fe/(Fe+Mg) increases to the rim, the bulk composition of the crystal is richer in the schorl end member and when Fe/(Fe+Mg) decreases to the rim, those crystals are richer in the dravite end member.

Some of the Al can occupy the same position as the Fe and Mg (Y-site). Al(Y) increases from the core to the rim of crystals from the first stages of type I and II pegmatites; nevertheless, during the crystallization of the intermediate zones the trend becomes inverse. Increase in Al(Y) correlates with increase in foitite component.

Other minor elements also exhibit intracrystalline zonation. From core to rim, the Ca and Ti contents increase and Mn decreases. The Na content is constant across the crystals (Fig. 8b).

The number of vacancies in the X site increases from the core to the rim of the crystals from type I pegmatites, except for the necking zone. In type II, these vacancies decrease from core to rim, except for tourmaline crystals from the exocontact. Vacancies increase with increasing temperature of crystallization (Rosenberg – Foit 1985), but in some cases the opposite correlation has been found (e. g. Manning 1982). In the Cap de Creus tourmalines, the vacancies in Y sites are high and may be due to the presence of some Li or Fe^{3+}.

Compositional variation in the pegmatite bodies

The composition of tourmaline changes throughout the pegmatite zones. In all cases, the chemical composition of the tourmaline of the host rock is the richest in Mg. In type I and type II pegmatites, initially, there is an increase in Fe/(Fe+Mg) from the outer to the innermost zones (Fig. 9). In the necking zone of type I pegmatites
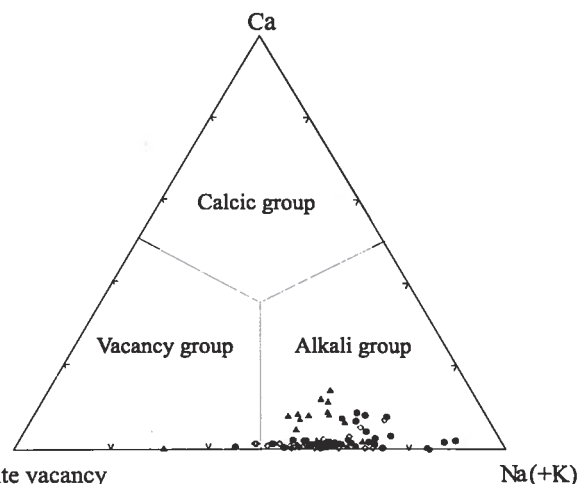
Fig. 5. Distribution of the tourmaline compositions from Cap de Creus in the classification diagram of Hawthorne – Henry (1999). Symbols as in Fig. 4.

and in crystals in the second intermediate-core contact, the Fe/(Fe+Mg) decreases. In type III pegmatites, Fe/(Fe+Mg) decreases from the earliest to the latest zones. However, the number of vacancies roughly increases from the exocontact and the early formed zones towards the late units (Fig. 10).

In type I and II pegmatites, tourmaline from the exocontact have minor Al(Y) contents, 0.10 to 0.34 apfu, but
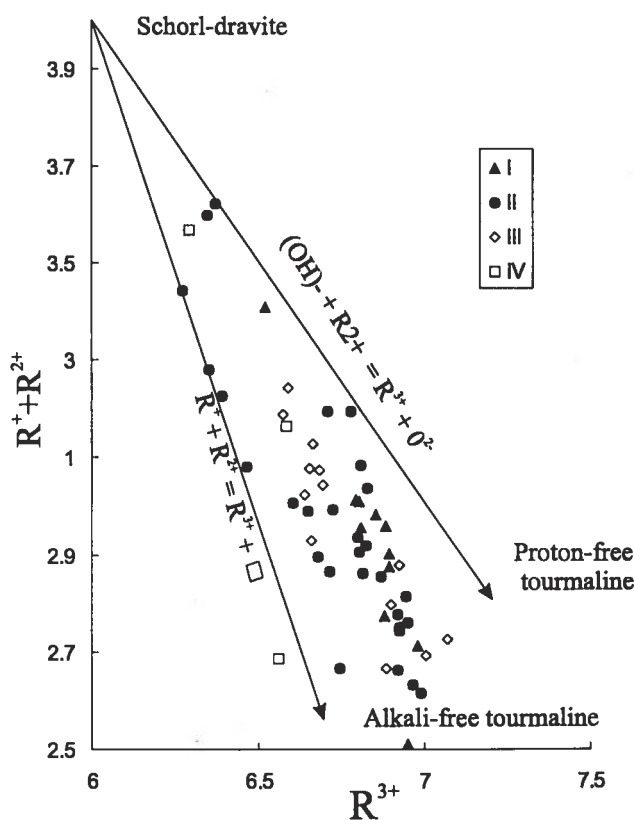
Fig. 4. Al-Fe(tot)-Mg diagram (in atomic proportions) for tourmaline (modified from Henry – Guidotti 1985) from the Cap de Creus pegmatites. Triangles, type I pegmatites ; circles, type II ; diamonds, type III and squares, type IV pegmatites. Numbers: 1 – Li-rich granitic pegmatites and aplites, 2 – Li-poor granitoids and their associated pegmatites and aplites, 3 – hydrothermally altered granites, 4 – metapelites and metapsamites not coexisting with Al-saturated phases, 6 – Fe-rich quartz-tourmaline rocks, calc-silicate rocks, and metapelites, 7 – low-Ca meta-ultramafic and Cr-V rich metasedimentary rocks, and 8 – metacarbonates and metapyroxenites.

Fig. 6. Representation in the R+ R2+versus R3+ diagram (Manning 1982) of the tourmaline compositions from the different pegmatite types of Cap de Creus. I – type I pegmatites; II – type II pegmatites; III – type III pegmatites; IV – type IV pegmatites.
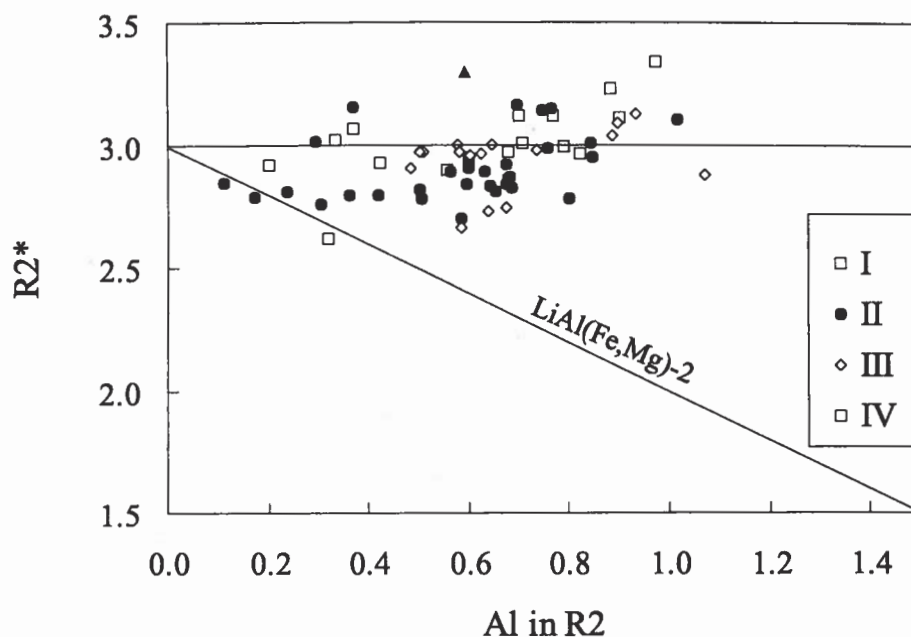
Fig. 7. Representation of the tourmaline compositions from the different pegmatite types of Cap de Creus in the R2* versus Al in R2 diagram (London-Manning 1995). I – type I pegmatites; II – type II pegmatites; III – type III pegmatites; IV – type IV pegmatites.

inside the pegmatite body the values range from 0.40 to 0.90 *apfu*. In type III pegmatites, the Al(Y) content is still higher, from 0.47 to 1.10 *apfu*, and in the exocontact and border zone of type IV the values range from 0.54 to 0.76 *apfu*. Type II pegmatites have he most extensive distribution of tourmaline; the Fe and Al contents of tourmaline systematically increase as the pegmatite melt evolves (Fig. 11).

Compositional variation among the different pegmatite types

The chemical composition of tourmaline from successive pegmatite types shows progressive differences. There is a general tendency of an increase in the Fe content and a decrease in Mg from the outermost to the inner zones of individual pegmatites, and from pegmatite type I to IV (Fig. 12).

Discussion

The chemical composition of tourmaline indicates an exchange between the host rock and the pegmatites. The higher Mg contents in the exocontact tourmalines could be explained by the interaction of boron from the pegmatite and Mg and Fe from the destabilization of biotite in the host rock (Shearer et al. 1984). The higher Al content in the rim
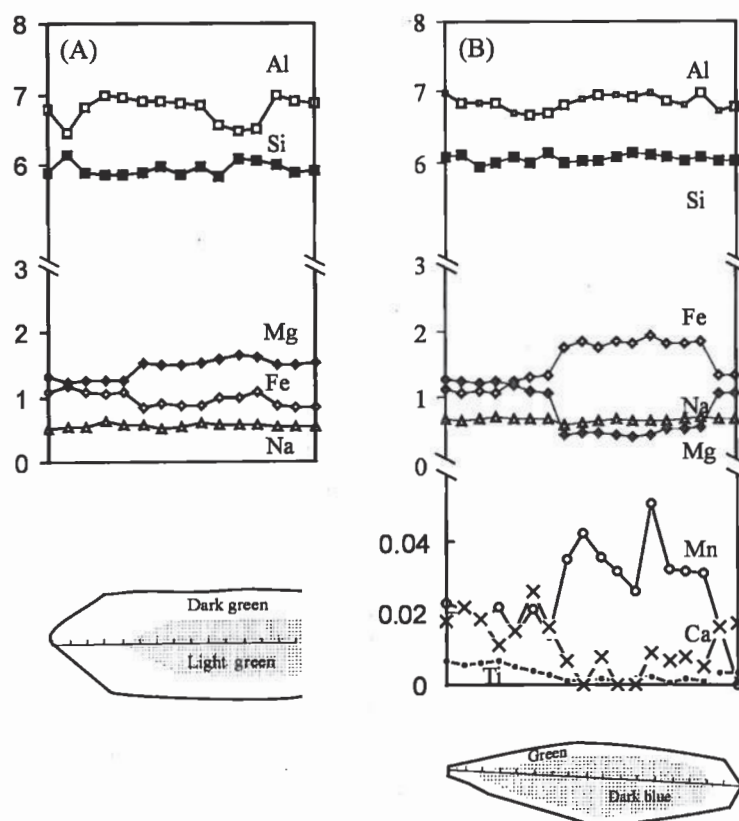
of these crystals could be due to Al-rich metamorphic fluids from the host rock.

The Fe/(Fe+Mg) increases and the tourmaline composition evolves from dravite-rich compositions to schorl with the fractionation of the pegmatitic fluid and with the progress of solidification of a pegmatite body. This trend has been postulated during the magmatic differentiation by Power (1968). A similar increase in the Fe-rich com-

Fig. 8. Compositional variation in tourmaline crystals: (A) second intermediate zone from type I pegmatites, and (B) second inrtermediate zone-core contact from type II pegmatites.

ponent with the degree of evolution has been reported in many other pegmatite fields (Neiva 1974, Manning 1982, Jolliff et al. 1986, Roda et al. 1995).

On the other hand, the Fe/(Fe+Mg) range is similar in all the different pegmatites, suggesting that decreas-

ing temperature has little or no influence on the fractionation of these elements. Alternatively, the tourmaline composition is affected by the early crystallization of other phases such as garnet, biotite and phosphates that can deplete the magma in Fe and Mg.
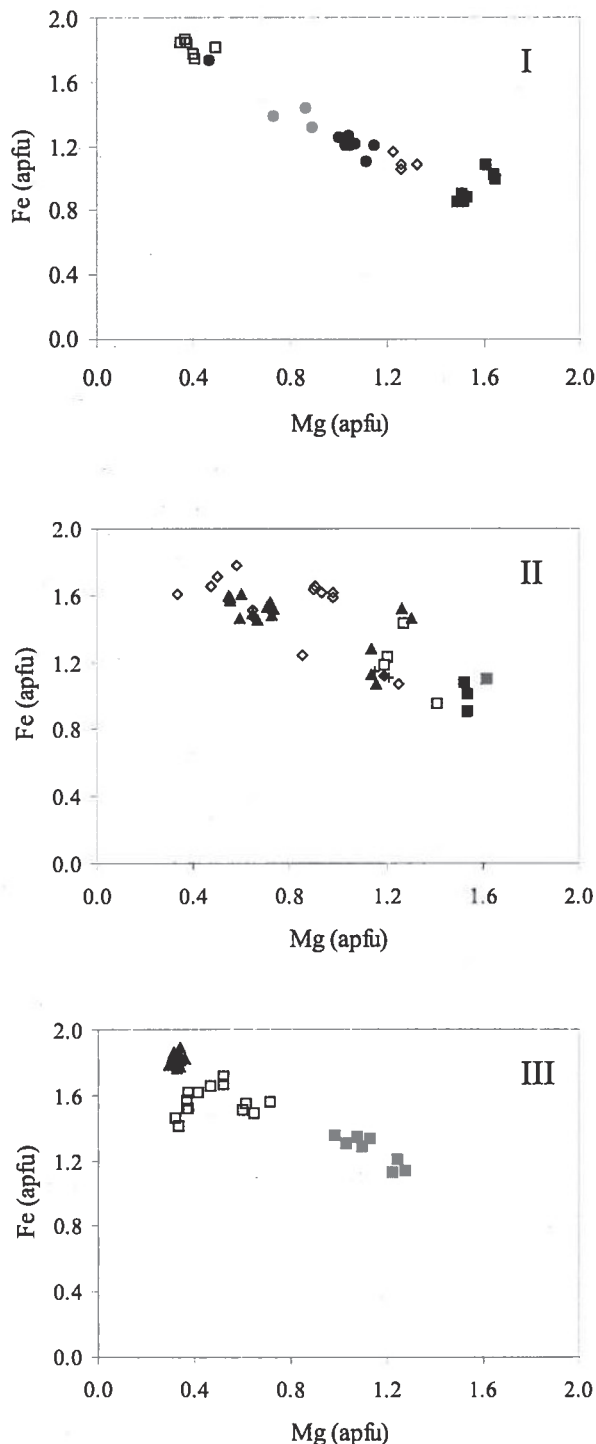
Fig. 9. Variation in Fe/Mg in tourmaline from (I) type I pegmatites, (II) type II pegmatites and (III) type III pegmatites. Filled squares, exocontact; open squares, wall zone; triangles, first intermediate zone; diamonds, second intermediate zone; circles, necking zone; crosses, contact second intermediate zone-core.
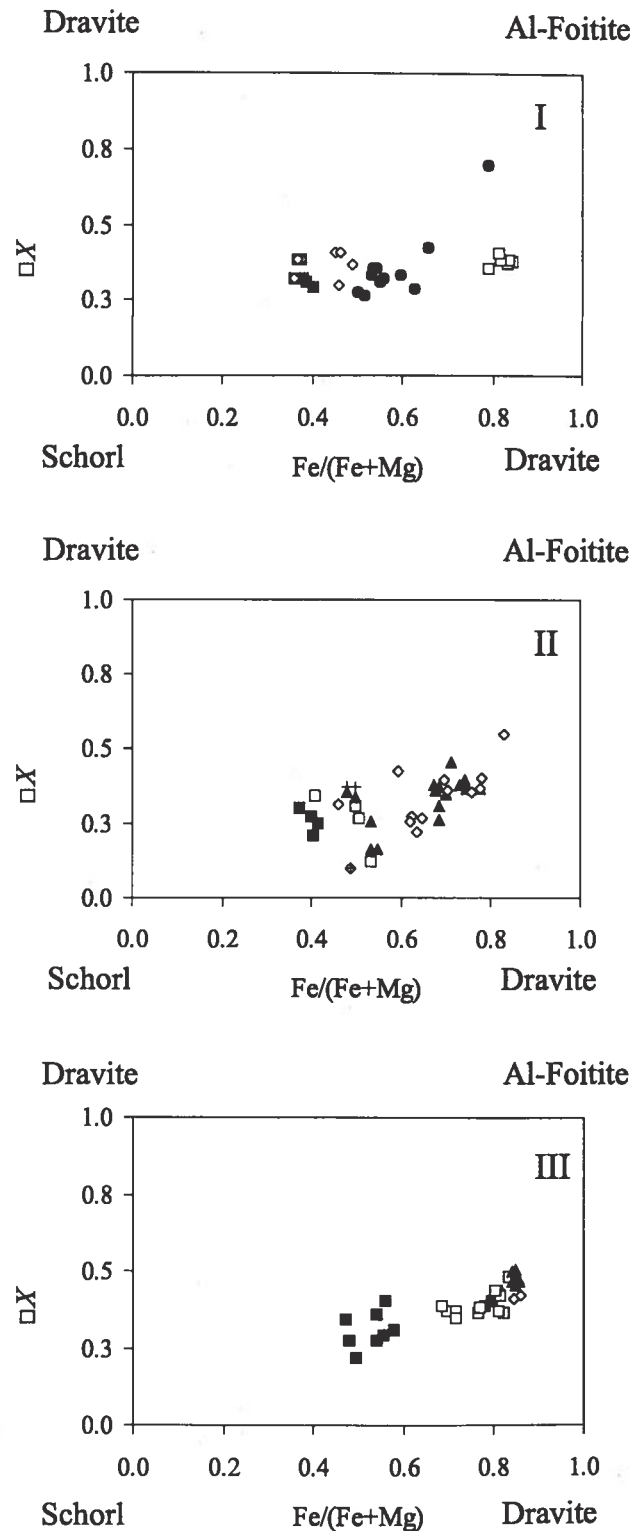
Fig. 10. At X-site versus Fe/(Fe+Mg) at Y-site diagram (modified from Henry – Dutrow 1996) of the tourmaline compositions from the different zones of pegmatite types from Cap de Creus. Symbols as in Fig. 9.
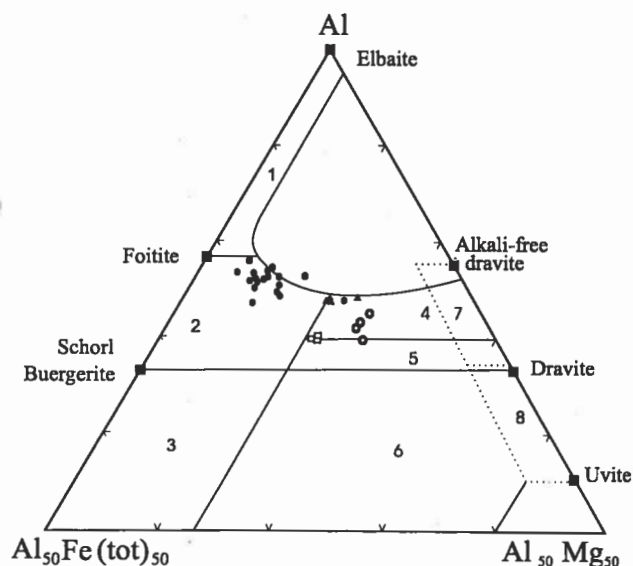
Fig. 11. Chemical compositions of tourmaline from each zone in type II pegmatites, in the Al-Fe(tot)-Mg diagram (in atomic proportions) (modified from Henry – Guidotti 1985). Open circles, exocontact; squares, border zone; triangles, wall zone; filled circles, intermediate zones. Numbers same as in Fig. 4.

The tourmaline compositions in type I and type II pegmatites reflect a late stage Mg enrichment with 0.73 *apfu* Mg in schorl in the necking zone of type I and 1.21 *apfu* in the dravite in the core of type II. Two stages in the pegmatite crystallization can be distinguished from these observations: in the first one, there is a decrease in the Mg and an increase in the Fe content in the pegmatitic fluid. During the end of crystallization of the second intermediate zone, an inverse trend starts, as the fluid becomes Mg-richer and Fe-poorer. A similar situation is reported by Jolliff et al. (1986) who observed the Mg content elevated to 0.10 *apfu* in elbaite of the third intermediate zone in the Bob Ingersoll pegmatite. As these authors propose, the cause of this Mg enrichment could be the lack of crystallization of Mg-bearing minerals

during the second intermediate zone. In the case of the necking zone in type I pegmatites, however, the increase of Mg is related to the influx of metamorphic fluids that mix with the residual pegmatite fluids. This explains the Fe-rich cores and Mg-rich rims of these crystals.

In albitic pegmatites (type IV), tourmaline only occurs in the border zone and in the exocontact. The occurrence of tourmalinization in the exocontact in the absence of tourmaline in the inner parts of the pegmatite was reported previously from many other localities, such as the Harding pegmatite (Jahns – Ewing 1977).

The main factor contributing to the precipitation of tourmaline is the boron content of the magma. The boron concentration necessary to form tourmaline is highly reduced in the presence of excess Al in the melt (Wolf – London 1997). As all of the pegmatites from the Cap de Creus are peraluminous with abundant Al-rich silicates, this condition for tourmaline crystallization is attained. Therefore, the lack of tourmaline crystallization in the inner parts of these pegmatites could by attributed to a high chemical potential of other anions that also bond to Fe and Mg, such as PO_4^{3-}. The presence of phosphorus also decreases the stability of tourmaline by lowering the activity of Al in the melt (Wolf – London 1994). Nevertheless, Keller et al. (1999) report the coexistence of tourmaline and Fe-Mn phosphates in Fregeneda, Spain, and they justify the lack of tourmaline in the intermediate zones from Namibian pegmatites by the low concentration of boron in the melt. In the Cap de Creus pegmatites, the tourmalinization of the exocontact could be indicative of relatively B-rich pegmatite melts. The Al content in type IV pegmatites is high, but no peraluminous silicates are formed. This is interpreted as a result of the high concentration in phosphorus that generate Al-rich phosphates in these pegmatites. The extraordinary abundance of P in the Cap de Creus pegmatites is manifested not only by the presence of Al-phosphate minerals, but also by the high P content in the feldspar (up to 1.1 % P_2O_5, Alfonso et al. 1996). Moreover, in the Cap de Creus field, the tourmalinized exocontacts

Fig. 12. Compositional ranges of tourmaline (atomic proportions) in the different pegmatite types. A – exocontact; B – border; C – wall; D – first intermediate zone; E) necking zones in syntectonic type I pegmatites; F – second intermediate zone G – contact second intermediate zone-core.
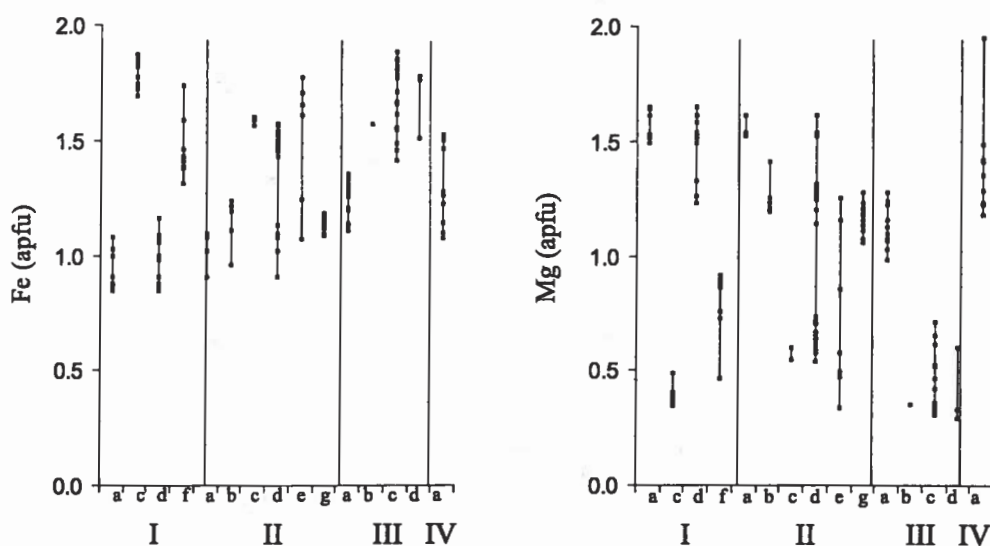
of the P-rich type IV pegmatites are also accompanied by crystallization of metasomatic apatite. In these pegmatites, internal tourmaline is absent, and the Fe-Mg phosphates are very common. These characteristics indicate a decisive influence of P in the crystallization of the early pegmatite units, because it has the same role as B in these less evolved pegmatites: to scavenge Fe and Mg extracted from the host rock. In this case, boron becomes fractionated towards the residual fluids that produce tourmalinization and apatitization of the exocontact, in late stages.

Other possible complementary factors that can explain the lack of tourmaline in the most evolved pegmatites could be the increase in alkalis, F, and H_2O. The alkalis decrease the tourmaline stability (London 1986, 1987), as their increase boosts the $^{IV}B/^{III}B$ ratio. Moreover, Wolf – London (1994) pointed out that the crystallization of tourmaline is suppressed when the F activity is high. This is the case of the most evolved pegmatites of the Cap de Creus, as reflected in the increase in the amblygonite component of the amblygonite-montebrasite phosphates (Alfonso 1995).

Conclusions

All the tourmalines from the Cap de Creus pegmatites belong to the schorl-dravite and schorl-foitite series, and the elbaite component is absent even in the most Li-rich pegmatites of the field. This fact, as well as the lack of Li-silicates and the absence of Li in the associated muscovite (Alfonso et al., 1996) suggests that high phosphorus activity in the pegmatitic magma, lithium is concentrated in phosphates rather than in silicates (e. g. Burt – London 1982, Fig. 7).

The compositional variation within individual tourmaline crystals and in the tourmaline from the early to the latest zones of the pegmatite bodies indicates the existence of two different episodes with respect to Fe/(Fe+Mg): (1) during early crystallization Fe/(Fe+Mg) increases; (2) during the latest events of the pegmatite crystallization, Fe/(Fe+Mg) decreases. This decrease is probably due to the end of the crystallization of other Mg-bearing minerals, increasing the Mg content in the melt.

Although the boron content in the pegmatite fluid is high in all the pegmatites, as evidenced by widespread tourmalinization of the wallrocks, tourmalines are restricted to the exocontact (where phosphatization also occurs) in the most evolved P-F-rich pegmatites. Therefore, the higher are the activities of F and P_2O_5, the lower is the stability of tourmaline. The existence of abundant Al-Fe-Li phosphates in early-formed pegmatite units seems to be incompatible with the crystallization of tourmaline in late pegmatite units.

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Bór vs. fosfor v granitických pegmatitech: příklad Cap de Creus (Katalánsko, Španělsko)

V pegmatitovém poli Cap de Creus, situovaném v metapelitech, jsou definovány čtyři kategorie granitických pegmatitů: nezrudnělé mikroklinové pegmatity (typ 1), pegmatity beryl-columbitového subtypu (typ 2), beryl-columbit-fosfátový subtyp (typ 3), a albitový typ (typ 4). Množství turmalínu je nepřímo úměrné k množství fosfátů: turmalín je hojný ve všech vnitřních zónách fosforem chudých pegmatitů I a II, je však vzácný ve fosforem bohatých pegmatitech III a chybí v pegmatitech IV. Turmalinizace exokontaktu je však vyvinuta kolem pegmatitů všech čtyř kategorií. Všechen turmalín v pegmatitech a jejich exokontactech náleží k řadám skoryl-dravit a skoryl-foitit, i když jsou fosfáty Li podstatnou složkou nejvíce diferencovaných pegmatitů. V méně vyvinutých, fosforem chudých pegmatitech snižuje krystalizace turmalínu a jiných silikátů Fe a Mg koncentrace těchto prvků v magmatu a hodnoty Fe/(Fe+Mg) v turmalínu během krystalizace jednotlivých pegmatitů stoupají. V nejvíce frakcionovaných fosforem bohatých pegmatitech jsou však místo silikátů stabilizovány fosfáty Fe, Al, Li a Mg, bór je frakcionován společně s přebytkem fosforu do zbytkového fluida, a turmalín s apatitem vznikají metasomaticky v boční hornině.