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TOURMALINE IN GRANITIC PEGMATITES AND THEIR COUNTRY ROCKS, FREGENEDA AREA, SALAMANCA, SPAIN

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ABSTRACT

In the northwestern part of the province of Salamanca (Spain), many Li-, Sn-bearing and barren granitic pegmatites occur. These bodies display a zonal distribution northward from the Lumbrales granite, with a degree of evolution increasing with distance from the granite contact. Tourmaline appears as an accessory mineral in the barren pegmatites, as well as in their country rock. In both cases, the tourmaline belongs to the schorl–dravite solid-solution series. Tourmaline shows textural and compositional variations in relation with pegmatite type. Subhedral to euhedral prismatic, very fine- to medium-grained (<6 mm – 10 cm), zoned grains are most common. In the country rock, tourmaline appears as prismatic–euhedral, very fine-grained (<6 mm) crystals. Their Fe/Mg value changes considerably among the different pegmatite types, providing insight into the degree of evolution of the associated pegmatites: those richest in Fe and poorest in Mg are associated with the most evolved bodies. Tourmaline from the country rocks shows compositional characteristics inherited from the host schists: similarity of the shape of the *REE* patterns for tourmaline and the schists, and a high content in Cr, Hf, Th and U.

Keywords: tourmaline, granitic pegmatite, schorl–dravite, Fregeneda, Spain.

SOMMAIRE

Dans le secteur nord-ouest de la province de Salamanca, en Espagne, se trouvent plusieurs massifs de granite pegmatitique, soit lithinifères, stannifères ou stériles. Ces différents faciès sont disposés d'une façon zonaire à partir du granite de Lumbrales vers le nord, et montrent un degré d'évolution progressivement plus avancé en s'éloignant du contact. La tourmaline est un minéral accessoire dans les pegmatites stériles, de même que dans les roches encaissantes. Dans les deux cas, la tourmaline fait partie de la série schorl–dravite. La tourmaline montre des différences texturales et chimiques selon le faciès de la pegmatite. Les prismes subidiomorphes à idiomorphes, à granulométrie très fine ou moyenne (<6 mm – 10 cm) et zonés sont les plus courants. Dans les roches encaissantes, la tourmaline est prismatique et idiomorphe, et possède une granulométrie très fine (<6 mm). La valeur Fe/Mg varie considérablement d'un faciès à l'autre, de façon à indiquer le degré d'évolution de la pegmatite hôte. La tourmaline la plus riche en Fe et la plus pauvre en Mg est associée avec la pegmatite la plus évoluée. La composition de la tourmaline des roches hôtes reprend les traits compositionnels de celles-ci, par exemple une ressemblance dans l'enrichissement relatif des terres rares et une teneur élevée en Cr, Hf, Th et U.

(Traduit par la Rédaction)

Mots-clés: tourmaline, pegmatite granitique, schorl–dravite, Fregeneda, Espagne.

INTRODUCTION

In the Fregeneda area of Spain, different types of granitic pegmatites can be established on the grounds of mineralogical and geological criteria and spatial distribution around the Lumbrales granite (Fig. 1). The most common type corresponds to simple pegmatites without internal zonation. Zoned, Li-bearing pegmatites also are relatively common, as are pegmatitic veins containing quartz, muscovite, feldspars, and cassiterite. Tourmaline appears as an accessory or major mineral in many of these pegmatites, and it is also common in the country rock, near the contacts with pegmatite bodies.

The composition of the tourmaline reflects the bulk chemistry of the system in which it forms, and some studies have established its value as a petrogenetic indicator (*e.g.*, Shearer *et al.* 1984, Henry & Guidotti 1985, Jolliff *et al.* 1986, Kassoli-Fournaraki 1990, Pirajno & Smithies 1992, Kassoli-Fournaraki & Michailidis 1994, Michailidis & Kassoli-Fournaraki 1994, Hellingwerf *et al.* 1994). In this study, petrographic and chemical data on representative samples of tourmaline selected from the various groups of pegmatites in the Fregeneda area and their extensively tourmalinized country-rock are given. The chemical variations are discussed in order to determine whether these different types of pegmatite 1) are related by a

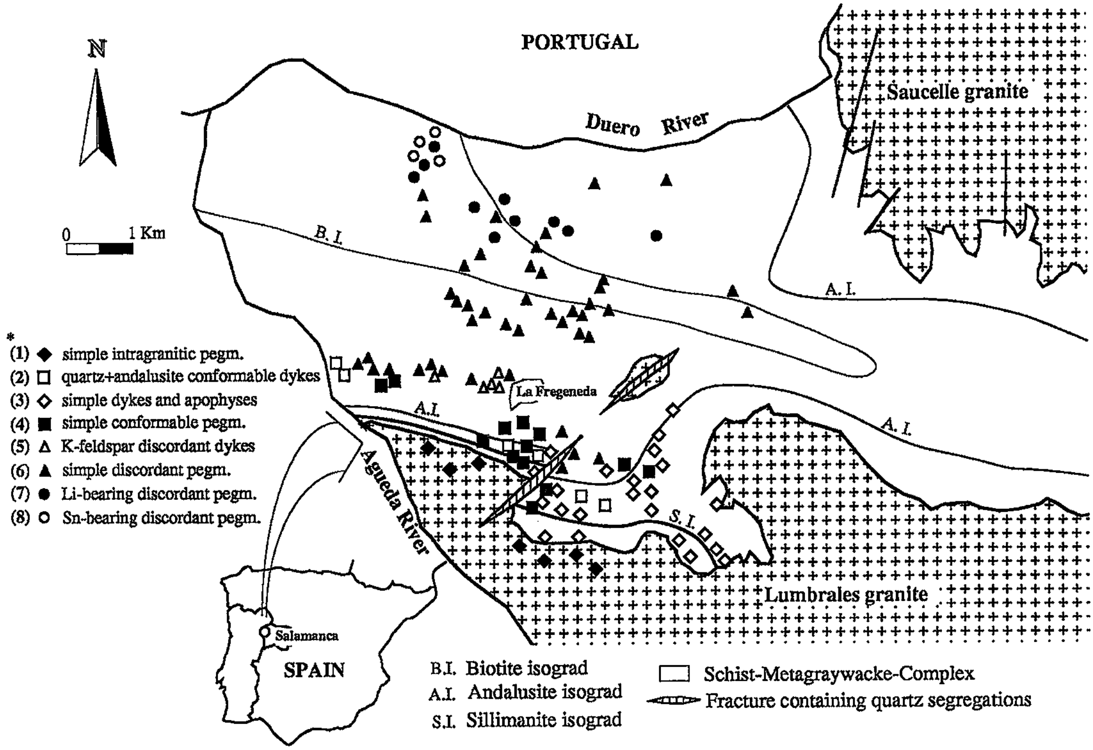

FIG. 1. Distribution of the pegmatite groups recognized in the Fregeneda area. The pegmatite types are labeled as in Table 1.

common path of fractionation, and 2) are related to the nearby Lumbrales granite.

GEOLOGICAL SETTING

The pegmatites of the Fregeneda area appear in the Hesperic Massif, in the western part of a narrow metamorphic belt, with an E–W strike. This belt, situated in northwestern Salamanca, is bordered by the Lumbrales pluton to the south, and by the Saucelle pluton to the northeast (Fig. 1). Both granites and pegmatites are intrusive into pre-Ordovician metasediments of the Schist–Metagraywacke Complex. In this area, this Complex comprises a sequence of quartzites, graywackes, schists and pelites, with abundant thin layers of calcsilicate. These materials have undergone two main phases of Hercynian deformation, with the later event of lower intensity (Martínez Fernández 1974). The earlier phase gave rise to a regional metamorphism that in the Fregeneda area shows a distribution of isograds parallel to the Lumbrales granite, locally reaching the sillimanite zone, whereas the biotite zone is the most extensive (Fig. 1). The regional metamorphism, of medium to high grade, and intermediate pressures, determined by the sillimanite – K-feldspar isograd, led to incipient partial melting of the metasedimentary units at approximately 650°C and 3.5 kbars, coinciding, in general, with the appearance of cordierite – K-feldspar in the migmatitic leucosome (García Luis 1991). The episode of regional metamorphism preceded the second phase of Hercynian deformation (Carnicero 1982), and it is superimposed by a contact metamorphism that may be due to the presence of a hidden granitic pluton, which has been detected at depth by drilling (López Plaza *et al.* 1982).

One of the main characteristics of this area is the great diversity of granites that outcrop there. The most common group is that of the peraluminous leucogranites, to which the Lumbrales and Saucelle plutons belong (Fig. 1). The former is part of the Meda-Penedono-Lumbrales granitic complex (Bea *et al.* 1988), and consists of a parautochthonous, heterogeneous, fine- to medium-grained two-mica granite (Carnicero 1981). With regard to the Hercynian deformation, this pluton is included in the group of syntectonic massifs that have been deformed during a third phase of Hercynian deformation (López Plaza & Carnicero 1988, López Plaza & Martínez Catalán 1988), with a Rb–Sr isochron age of 284 ± 8 Ma (García Garzón & Locutura 1981). In spite of its

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	Tourmal-inization	Country-rock				
1	quartz K-Feldspar	albite tourmaline muscovite	-	(intragranitic)	dyke-like thickness < 50 cm	within the Lumbrales granite	scarce, within the Lumbrales granite	K, Al, Si, (B, P)
2	quartz andalusite	muscovite tourmaline K-Feldspar chlorite	-	Andalusite zone	conformable dyke-like thickness < 50 cm	close to the Lumbrales granite	not abundant; boudinage structures. quartz & andalusite their main minerals	Al, Si, (B, K)
3	quartz K-Feldspar muscovite	albite tourmaline biotite	-	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)
4	quartz K-Feldspar muscovite albite	tourmaline biotite andalusite chlorite garnet	√	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
5	K-Feldspar	quartz muscovite pyrite	-	Biotite zone	disconformable dyke-like thickness > 1 m	1 km from the Lumbrales granite	not very abundant; main component is pink K-feldspar	K
6	quartz K-Feldspar albite muscovite	±Fe-Mn phosphates ±amblygonite ±tourmaline	√	Biotite and chlorite zones	disconformable 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)
7	quartz albite Li-mica muscovite K-Feldspar	amblygonite spodumene cassiterite apatite	√	Biotite and chlorite zones	disconformable 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)
8	quartz cassiterite albite	muscovite K-Feldspar apatite	√	Chlorite zone	disconformable dyke-like, thickness < 50 cm locally with internal zoning	N of the studied area	scarce, folded, abundant cassiterite	Sn, K, (P)

evident petrological continuity, the Lumbrales pluton shows a clear tectonic control westward, whereas to the east the deformation decreases, and the emplacement of the granite seems to have been free of external stress (Gonzalo Corral 1981, López Plaza *et al.* 1982). Another characteristic of this body is the presence of a migmatitic facies in the border as well as in the inner zones, mainly to the east of the Fregeneda area. As is the case for the Lumbrales pluton, the Saucelle pluton is a peraluminous, fine-grained, two-mica granite, and it belongs to the group of syntectonic massifs that were deformed during the third phase of Hercynian deformation (López Plaza & Carnicero 1988). With regard to their degree of rare-element enrichment, they contain 170–230 ppm Li, 343 ppm Rb and 218 ppm Ba (García Garzón & Locutura 1981, Bea & Ugidos 1976). The high contents in Li and Rb are noteworthy, as are the low contents of Ba in both series. The K/Rb ratio also is low, with values below 160 (Bea 1976, Bea & Ugidos 1976), characteristic of granitic pegmatite and highly differentiated granites (Ahrens *et al.* 1952).

PEGMATITE TYPES

On the basis of mineralogy, morphology, and internal structure, several groups of granitic pegmatites have been recognized. These groups display a degree of differentiation that increases away from the Lumbrales granite. With increasing distance from the contact, the groups are (Roda *et al.* 1991, Roda & Pesquera, in press) (Fig. 1, Table 1):

(1) Intragranitic bodies of pegmatite consisting of quartz, K-feldspar (microcline and orthoclase), muscovite, albite and schorl; these bodies are relatively abundant in the border zones of Lumbrales pluton.

(2) Dykes composed mainly of quartz, andalusite and minor muscovite, schorl and K-feldspar (microcline and orthoclase), of pegmatitic grain-size. They are concordant to the country-rock fabric, showing related deformation, with a boudinage structure. These bodies appear in the andalusite–cordierite zone, close to the Lumbrales granite.

(3) Dykes and apophyses showing aplitic and pegmatitic facies, consisting of quartz, K-feldspar (microcline and orthoclase), muscovite and minor albite, schorl, and biotite. Their grain size changes abruptly from an aplitic to a pegmatitic facies, and their shapes vary greatly. These bodies are located to the southeast of the area studied, near the Lumbrales granite, associated with the sillimanite, andalusite, and biotite zones.

(4) Conformable bodies of pegmatite of narrow width (<1.5 m), locally showing internal zoning. They are composed mainly of quartz, muscovite, K-feldspar (microcline and orthoclase), schorl, albite, and minor andalusite, chlorite, garnet, and biotite. Host rocks commonly display strong tourmalinization near the contacts. These bodies are located close to the Lumbrales granite. They are associated mainly with the andalusite zone and, to a lesser extent, with the sillimanite and biotite zones.

(5) Pegmatite bodies mainly composed of K-feldspar (microcline and orthoclase). Other phases that may be present are quartz, muscovite and pyrite. They are discordant to the country rock, appearing near the contact with the Lumbrales granite, associated with the biotite zone.

(6) Discordant bodies of pegmatite that, in some cases, show a layered internal structure. They consist of quartz, K-feldspar (microcline and orthoclase), muscovite, and albite. In the bodies farthest from the Lumbrales granite, amblygonite may appear, whereas close to the granite, phosphates of Fe–Mn ± Li are common, as well as tourmaline as an accessory mineral. Moreover, the host rock can show a variable degree of tourmalinization. Situated in an area between 1 and 4 km to the north of the Lumbrales pluton, group 6 is the most abundant. The host rocks exhibit low-grade regional metamorphism (biotite and chlorite zones).

(7) Discordant bodies of Li-mica-bearing pegmatite. These bodies usually display a zoned internal structure. They are composed of quartz, Li-bearing mica, albite, K-feldspar (microcline and orthoclase), muscovite and minor amblygonite, spodumene, cassiterite, apatite, and columbite–tantalite. Tourmaline has not been found in these pegmatites, although tourmalinization is variably developed around the pegmatites. These dykes crop out along a narrow band, 4–6 km north of the Lumbrales granite. As is the case with the previous category, these bodies of pegmatite are associated with the biotite and chlorite zones.

(8) Bodies of pegmatite consisting of quartz and minor fine-grained muscovite, albite, microcline and cassiterite. Their country rock exhibits a variable degree of tourmalinization; as in the previous group, tourmaline has not been found as a constituent of the pegmatites. These dykes locally show internal zonation, being folded, with the axial plane nearly horizontal. They appear in the northern zone of the area studied, being cut by some bodies of the previous category. These dykes are only associated with the chlorite zone.

PETROGRAPHY

Textural and paragenetic differences among the tourmaline samples from the various types of pegmatite have been observed (Table 2). Three modes of occurrence can be established. The first one is a medium to very fine-grained (5 cm – <6 mm), prismatic tourmaline, that appears homogeneously distributed in the intragranitic pegmatites (1), in the quartz–andalusite dykes (2) and in the apophyses with aplitic and pegmatitic facies (3). Commonly, this type of tourmaline grows with quartz in the core zone in the

TABLE 2. TOURMALINE DISTRIBUTION IN THE FREGENEDA PEGMATITES AND THEIR TOURMALINIZED COUNTRY-ROCK

PEGM. TYPE*	TOURMAL. TYPE	OCCURRENCE	MINERAL ASSOCIATION	TEXTURE	GRAIN SIZE**
1	1	mainly in the intermediate zone	quartz, K-Feldspar, albite, muscovite	sub- to euhedral prismatic, zoned grains	fine to medium
	1	within the pegmatites	quartz, K-Feldspar, albite, muscovite, Fe-Mn pho	subhedral	very fine
2	1	within the dykes	quartz, andalusite, muscovite, K-Feldspar	euhedral, slender, prismatic grains	very fine to fine
3	1	within the aplitic and pegmatitic bodies	quartz, K-Feldspar, muscovite, albite, biotite	euhedral	fine to medium
	2	within the aplitic and pegmatitic bodies	quartz, K-Feldspar, muscovite, albite, biotite	subhedral, interstitial	fine
4	1	mainly in the core zone	quartz, K-Feldspar, albite, muscovite, andalusite, garnet, apatite	sub- to euhedral prismatic grains	fine to medium
	2	in the aplitic facies of some pegmatites	quartz, K-Feldspar, albite, muscovite, biotite	an- to subhedral interstitial	very fine to fine
	3	country rock	muscovite, biotite, quartz, K-Feldspar, albite	prismatic-euhedral	very fine
6	1	mainly in the wall zone and aplitic facies of some pegmatites	quartz, albite, K-Feldspar, muscovite, Fe-Mn±Li phosphates	subhedral	fine to medium
	3	country rock	muscovite, biotite, quartz, K-Feldspar, albite	prismatic-euhedral	very fine
7	3	country rock	muscovite, biotite, quartz, K-Fsp, albite	prismatic-euhedral	very fine
8	3	country rock	muscovite, biotite, quartz, K-Fsp, albite	prismatic-euhedral	very fine

* number of the pegmatite types as in Table 1; **grain size: very fine =< 6 mm; fine = 6 mm to 2.5 cm; medium = 2.5 cm to 10 cm.

simple conformable pegmatites (4); less commonly, the crystals are perpendicular to the contact with the country rock in the border zones of the simple discordant pegmatites (6). This type of tourmaline usually shows an internal concentric zonation, with a variable, occasionally intense pleochroism, ranging from yellow to brown-orange in the border zones, and from bluish green to blue or colorless near the core of the prism.

The second type of tourmaline is interstitial and fine to very fine grained (2 cm – <6 mm). It occurs in the apophyses with aplitic and pegmatitic facies (3) and in the simple conformable pegmatites (4). Generally, this type of tourmaline shows a pleochroism ranging from yellow to brown-orange.

The third type is very fine grained (<6 mm) and is found in the country rock, at some pegmatite – country rock contacts. Crystals are euhedral and show a variable pleochroism, ranging from brown to greenish yellow in the border zones and from bluish green to deep blue in the inner zones.

DATA COLLECTION AND ANALYSIS

The tourmaline samples studied have been selected from the most representative bodies of pegmatite of the area, as well as from their tourmalinized country-rock. Tourmaline crystals from at least four different bodies of each type of pegmatite have been analyzed. The samples were prepared by magnetic separation and

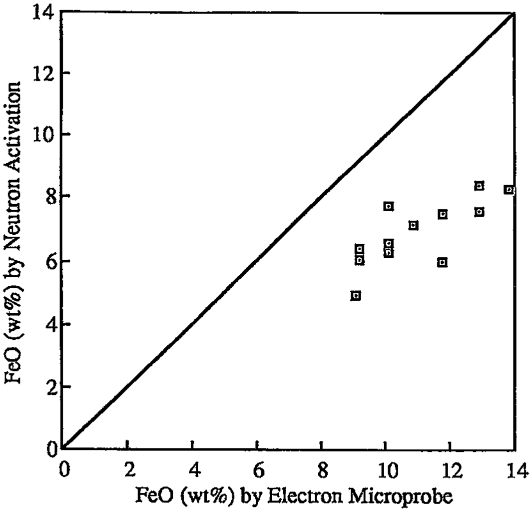

FIG. 2. FeO in tourmaline measured by electron microprobe ans neutron-activation analysis. The latter method shows the "boron shielding effect" (King *et al.* 1988), and the results so obtained are between 24 and 49% lower than those produced with an electron microprobe. The trace-element concentrations were corrected by the ratio Fe_{EM}/Fe_{NA}.

hand-picking, and the separates were examined with a binocular microscope to remove contaminated grains. They were ground by hand in an agate mortar and analyzed for major elements using a Camebax SX 50 electron microprobe. Operating conditions were: voltage 15 kV and beam current 10 nA. Wollastonite, corundum, hematite, graftonite, albite, orthoclase and MgO were used as internal standards. Finally, the concentrations of Li and Sn was determined by atomic absorption spectrometry (AA); concentrations of Sc, Co, Zn, As, Se, Rb, Sr, Mo, Ag, Cs, Ba, *REE*, Ta, W,

TABLE 3. AVERAGE COMPOSITION OF TOURMALINE FROM THE DIFERENT TYPES OF PEGMATITE AND THEIR TOURMALINIZED COUNTRY-ROCK

*Peg.type	(T1)	(T2)	(T3)	(T4)	(T4)CR	(T6)	(T6)CR	(T7)CR	(T8)CR
SiO2	34.72	35.47	34.67	34.99	34.98	35.45	36.17	36.14	35.64
TiO2	0.48	0.90	0.40	0.58	0.40	0.16	0.70	0.99	0.84
Al2O3	33.05	33.99	34.11	34.24	32.47	34.13	32.75	31.43	31.59
FeO	12.24	8.42	12.03	10.14	13.82	12.89	9.87	9.80	11.01
MnO	0.17	0.05	0.13	0.11	0.12	0.22	0.08	0.03	0.13
MgO	1.56	3.64	2.45	3.27	1.23	0.87	4.18	5.07	3.90
CaO	0.07	0.49	0.09	0.24	0.06	0.11	0.38	0.31	0.64
Na2O	1.61	1.49	1.75	1.68	1.69	1.58	2.02	2.21	2.05
K2O	0.05	0.04	0.04	0.05	0.04	0.03	0.05	0.08	0.05
Total	83.95	84.49	85.67	85.30	84.81	85.43	86.20	86.06	85.86
N	14	4	8	14	6	15	13	4	6
Structural formula on the basis of 24.5 atoms of oxygen									
Si	5.949	5.913	5.822	5.841	5.985	5.973	5.978	6.000	5.970
Al	6.675	6.683	6.753	6.739	6.549	6.779	6.381	6.148	6.240
Al T	0.051	0.087	0.178	0.159	0.015	0.027	0.022	0.000	0.030
Al Z	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Al Y	0.624	0.596	0.575	0.580	0.534	0.751	0.359	0.148	0.210
Ti	0.062	0.113	0.050	0.072	0.051	0.020	0.086	0.124	0.105
Si Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.000
Fe^{2+}	1.754	1.175	1.689	1.416	1.978	1.816	1.364	1.360	1.542
Mn	0.025	0.008	0.018	0.016	0.018	0.032	0.011	0.004	0.018
Mg	0.398	0.906	0.613	0.813	0.314	0.217	1.029	1.254	0.975
Y total	2.860	2.796	2.946	2.897	2.894	2.837	2.849	2.912	2.850
Ca	0.012	0.088	0.016	0.042	0.012	0.020	0.067	0.056	0.116
Na	0.533	0.483	0.569	0.545	0.560	0.516	0.649	0.709	0.666
K	0.011	0.008	0.007	0.011	0.008	0.007	0.011	0.016	0.011
X total	0.557	0.579	0.592	0.598	0.580	0.542	0.727	0.782	0.793

*pegmatite type as in Table 1; N: number of analyses; CR: tourmaline from the country rock. All Fe is calculated as FeO.

Th and U were determined by neutron activation (INAA). Trace-element analyses were performed by X-Ray Assay Labs of Don Mills, Ontario.

According to King *et al.* (1988), the determination of trace-element and *REE* concentrations in tourmaline by neutron activation is hampered by the problem of the incident neutron-flux suppression in the sample, arising from the large neutron-capture cross section of B. This effect has been checked using the Fe concentrations obtained by neutron activation and electron-microprobe analyses (Fig. 2). The concentrations obtained by neutron activation seem to be between 24 and 49% lower than those measured by electron microprobe. These deviations can be corrected with the factor Fe_{EM}/Fe_{NA}, to permit comparisons among the various samples of tourmaline.

Tourmaline samples were analyzed with an X-ray diffractometer using silica as the internal standard by scanning over the interval 5–70° 2θ using Cu$K\alpha$ radiation. Unit-cell dimensions were obtained using the program of Appleman & Evans (1973).

MINERAL CHEMISTRY

All of the tourmaline samples analyzed belong to the schorl–dravite series, mainly the Fe^{2+}-rich end member (Tables 3, 4, Fig. 3). Nevertheless, the data show compositional variations that correlate with pegmatite type (Figs. 3, 4, 5, 6). It is also remarkable that in no case was a difference found between the composition of tourmaline from the core and that from the wall of the same body of pegmatite.

In general, tourmaline crystals from pegmatites show higher concentrations of Fe and lower concentrations of Mg than those growing in the country rock (Fig. 3). Tourmaline taken from the simple discordant pegmatites (6) has the highest Fe/Mg value, whereas tourmaline from the quartz and andalusite dykes show the lowest Fe/Mg value (Fig. 3a). Among samples of tourmaline taken from the country rock (Fig. 3b), those found in schist near bodies of Li-rich pegmatite (7) have the lowest Fe/Mg value, whereas those from the host rock of the simple concordant pegmatites (4) shows the lowest concentrations of Mg and the highest concentrations of Fe.

The total number of cations in the Y site implies vacancies, with a deficiency in R^+ ($Na^+ + 2Ca^{2+} + K$) and R^{2+} ($Fe^{2+} + Mg^{2+} + Mn^{2+}$) and an excess of R^{3+} ($Al^{3+} + 4/3\ Ti^{4+}$) (Table 3, Fig. 4). These may be due to the effect of two coupled substitutions (Foit & Rosenberg 1977) involving (1) alkali defect: $(OH)^- + R^{2+} = R^{3+} + O^{2-}$, and (2) proton loss: $R^+ + R^{2+} = R^{3+}$ + vacancies.

In general, the $(R^+ + R^{2+})/R^{3+}$ value in the tourmaline from the country rock is higher than that of the tourmaline from the pegmatitic bodies (Figs. 4a, b), which reflects the higher Al contents of the latter. In contrast to the suggestions of Foit & Rosenberg (1977), substitutions involving alkali deficiency are more common than those implying proton loss. Such substitutions are partly controlled by bulk chemical environment, H_2O-rich systems favoring alkali-defect substitution (Gallagher 1988). Tourmaline from pegmatites (2), (3) and (4) shows a higher degree of

TABLE 4. TRACE-ELEMENT CONCENTRATION OF TOURMALINE FROM THE DIFFERENT TYPES OF PEGMATITE AND THEIR TOURMALINIZED COUNTRY-ROCK

*Peg. type	(T1)	(T1)	(T3)	(T3)	(T4)	(T4)	(T4)CR	(T4)CR	(T6)	(T6)	(T7)CR	(T7)CR
Li	70	47	52	42	22	54	50	95	29	29	460	380
Sc	0.5	10.71	-	-	16	5	6	4.8	5	5	5.4	8.8
Cr	3	10	-	-	3	3	131	109	3	3	112	121
Co	5	8	-	-	7	2	25	15	12	14	19	20
Zn	1700	986	-	-	663	1258	1054	1581	1173	1479	561	357
As	<3.4	<3.4	-	-	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	5	3.4
Se	<5	<5	-	-	<5	<5	<5	<5	<5	<5	<5	<5
Rb	25	34	-	-	25	25	51	34	25	25	68	68
Mo	8.5	8.5	-	-	8.5	8.5	8.5	8.5	8.5	12	8.5	8.5
Ag	8.5	8.5	-	-	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Sn	21	22	9	27	12	51	20	36	15	26	32	32
Cs	1.7	1.7	-	-	0.8	3.4	8.5	3.4	1.7	3.4	29	39
Hf	0.4	0.4	-	-	0.4	0.4	5.8	2.7	0.4	0.4	5	4.9
Ta	1.7	1.7	-	-	<1.7	<1.7	5	1.7	<1.7	5	1.7	<1.7
W	<5	<5	-	-	<5	<5	<5	<5	<5	<5	<5	12
Th	0.42	0.42	-	-	0.42	0.42	18.7	17	0.42	0.85	10.54	10.71
U	0.42	0.42	-	-	1.2	0.42	7	2.9	0.42	0.42	1.7	2.4
La	0.42	0.42	-	-	1.02	1.02	45.2	41.5	0.42	0.85	57.8	61.2
Ce	3.4	3.4	-	-	3.4	3.4	86.7	74.8	3.4	3.4	34	36
Nd	6.8	6.8	-	-	6.8	6.8	35.7	28.9	6.8	6.8	15.3	20.4
Sm	0.08	0.08	-	-	0.34	0.17	6.46	5.44	0.08	0.08	4.25	4.93
Eu	0.17	0.17	-	-	0.17	0.17	0.85	0.85	0.17	1.02	1.19	1.19
Tb	<0.85	<0.85	-	-	<0.85	<0.85	0.85	<0.85	<0.85	<0.85	<0.85	<0.85
Yb	0,1	0,1	-	-	0,7	0,1	0,5	0,5	0,1	0,1	0,5	0,8
Lu	0.04	0.04	-	-	0.29	0.04	0.85	0.12	0.04	0.04	0.15	0.29
Lacn/Ybcn	1.6	1.6	-	-	0.5	3.9	34.4	31.6	1.6	3.2	23.0	14.2

CR: country-rock. values in ppm. Lacn/Ybcn: ratio of chondrite-normalized concentrations. * numbers of the legend as in Table 1. All data, except Li and Sn, have been corrected with the Fe_{EM}/Fe_{NA} factor.

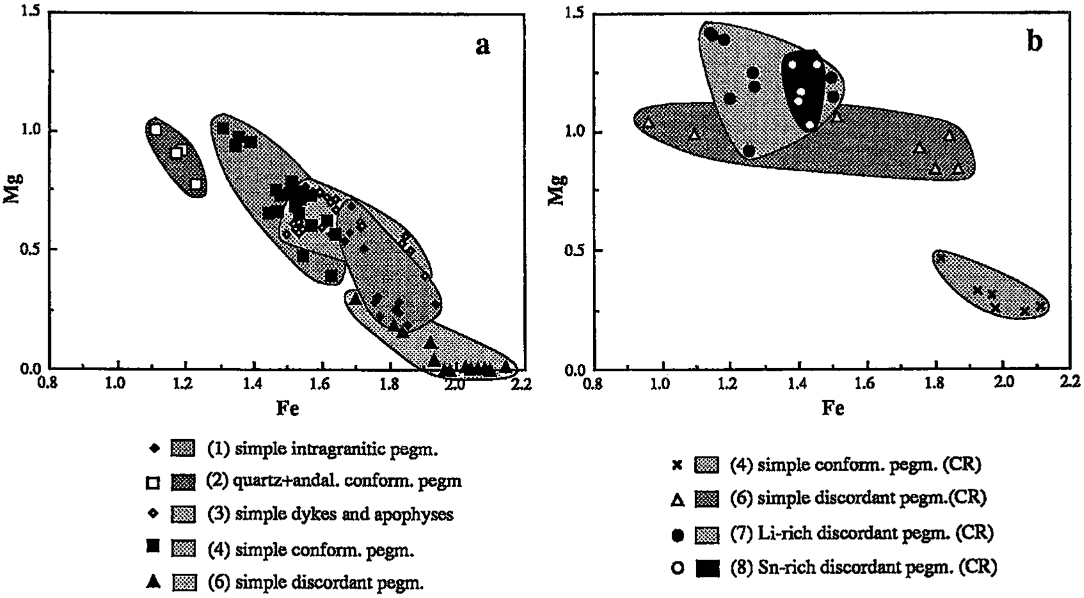

FIG. 3. Plot of concentration of Fe *versus* that of Mg in tourmaline from some of the different types of pegmatite (a) and their tourmalinized country-rock (CR) (b). Values are expressed in atoms per formula unit (numbers as in Table 1).

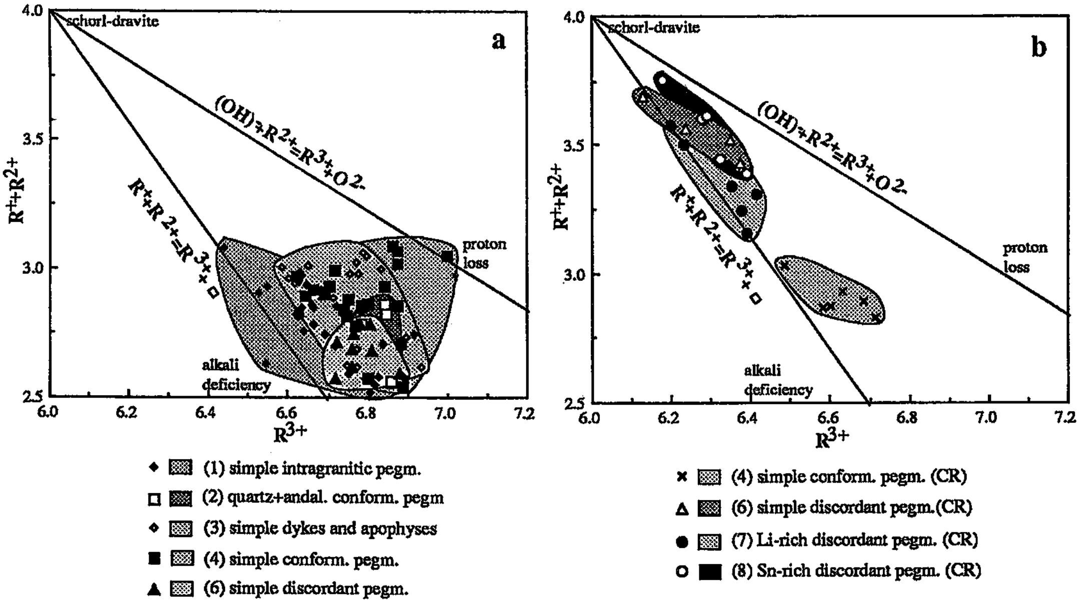

FIG. 4. (R^+ + R^{2+}) *versus* R^{3+} variation in tourmaline from some of the different types of pegmatite (a) and their tourmalinized country-rock (CR) (b). The variation can be related to alkali-defect and proton-loss substitutions in tourmaline. The lines represent compositions between unsubstituted schorl–dravite and the fully substituted end-members (proton-loss and alkali-defect end-members). Diagram modified from Manning (1982) (numbers in the legend as in Table 1).

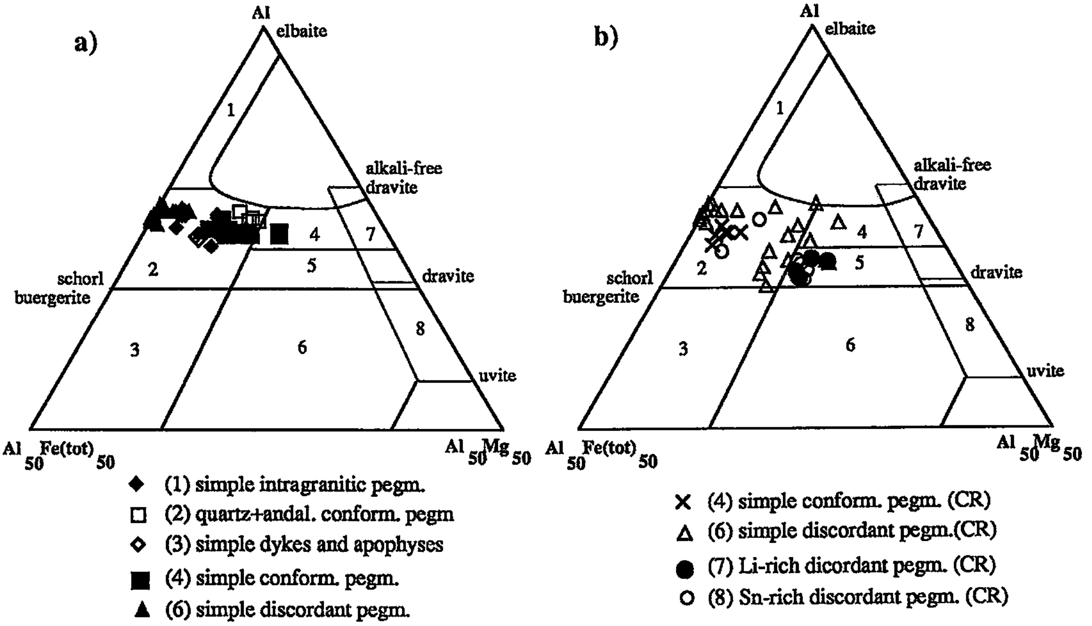

FIG. 5. Al–Fe(tot)–Mg diagram (in molar proportions) for tourmaline from a) some of the pegmatite types and b) their tourmalinized country-rock (CR), with fields after Henry & Guidotti (1985). 1: Li-rich granitic pegmatites and aplites, 2: Li-poor granitic rocks and associated pegmatites and aplites, 3: Fe-rich quartz–tourmaline (hydrothermally altered granites), 4: metapelites and metapsammites coexisting with an Al-saturating phase, 5: metapelites and metapsammites not coexisting with an Al-saturating phase, 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 (numbers in the legend as in Table 1).

proton-loss substitutions, suggesting that its development was mainly buffered by alkalis instead of H_2O. On the contrary, tourmaline from pegmatites (1) and (6) presents a greater degree of alkali-deficient substitutions, which would indicate a higher availability of water in the system. Tourmaline from the country rock shows a greater degree of alkali-defect substitutions, likewise reflecting growth of these crystals of tourmaline in a H_2O-rich environment during metasomatism of the wallrock schist.

Nevertheless, in calculations on the basis of 24.5 oxygen atoms, the relative importance of alkali-defect substitution is exaggerated. A way to allow for proton-loss substitution is to normalize cation contents to 6Si, but then the degree of proton-loss substitution is exaggerated. Normalizations based on 24.5 atoms of oxygen and to 6 atoms of Si represent extreme positions not found in natural tourmalines (Gallagher 1988). On the other hand, the content of ferric iron in the tourmaline would not change the distribution in Figure 4, as according to Henry & Guidotti (1985), where tourmaline compositions plot above the line schorl–dravite in the Al–Fe–Mg diagram (Fig. 5), the amount of Fe^{3+} is very low.

In the Al–Fe–Mg and Ca–Fe–Mg diagrams (Henry & Guidotti 1985), most of the tourmaline samples plot in field 2 (Figs. 5, 6), which corresponds to tourmaline from Li-poor granitic rocks and their associated aplites and pegmatites, whereas the rest of the suite plot in the metapelite and metapsammite fields.

The total concentrations of *REE* in all tourmaline samples, particularly those within the bodies of pegmatite, are low (Table 4). In terms of *REE* distribution, the tourmaline of the country rock has a moderately fractionated pattern (chondrite-normalized La/Yb between 14.2 and 34.4), with a monotonic decrease from La to Yb, followed by an upturn to Lu; the tourmaline taken from pegmatitic samples shows a highly fractionated pattern (chondrite-normalized La/Yb between 0.6 and 3.9), with a scatter of the values.

The tourmaline from pegmatitic samples is also poorer in other trace elements, so that tourmaline from the country rock shows higher contents in Cr, Rb, Hf, Th and U (Table 4). It is also notable that the tourmaline in the country rock adjacent to the Li-rich pegmatites (7) shows a relative enrichment in Li (380–460 ppm), Rb (68 ppm) and Cs (29–39 ppm).

Most of the tourmaline prisms are zoned concentrically about the *c* axis. This zoning and the shape of the crystals reflect the ease of growth in the *c* direction (Jolliff *et al.* 1986). The zoning is chromatic and com-

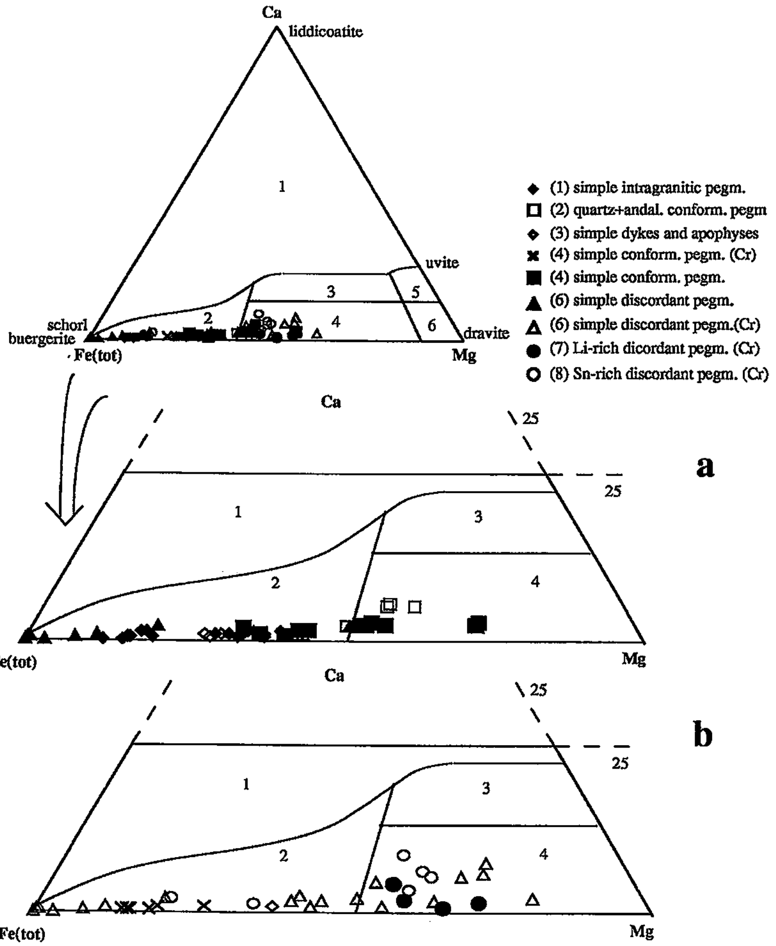

FIG. 6. Ca–Fe(tot)–Mg (in molar proportions) for tourmaline from a) some of the pegmatite types and b) their tourmalinized country-rock (CR), with fields after Henry & Guidotti (1985). 1: Li-rich granitic pegmatites and aplites, 2: Li-poor granitoids and associated pegmatites and aplites, 3: Ca-rich metapelites, metapsammites, and calc-silicate rocks, 4: Ca-poor metapelites, metapsammites, and quartz–tourmaline rocks, 5: metacarbonates, and 6: meta-ultramafic rocks (numbers in the legend as in Table 1).

positional, with a slight tendency to enrichment in Mg in the core relative to the rim, observed in all groups (Fig. 7). A relation between composition and color has not been established, as there are zones with the same color and different composition, whereas crystals with similar contents show different colorations. These differences could reflect small variations in the ratio Fe^{2+}/Fe^{3+}.

Finally, results of the unit-cell determinations are listed in Table 5. Values of *a versus c* are plotted in Figure 8. The tourmaline samples plot near the schorl–dravite reference line (Donnay & Barton 1972), near the schorl end-member, in agreement with the chemical data.

DISCUSSION

The observed compositional variations indicate the importance of coupled substitutions (alkali-defect and proton-loss substitutions), which are more extensive in tourmaline from pegmatites than from the country rocks (Fig. 4). This variation could be explained by the greater availability of Fe and Mg in the country-rock environment. Manning (1982) found that the extent of such coupled substitutions becomes greater with decreasing temperature, *i.e.*, with an increase in the degree of fractionation. However, all the tourmaline samples taken from pegmatite bodies show a similar extent of these coupled substitutions (Fig. 4a); their

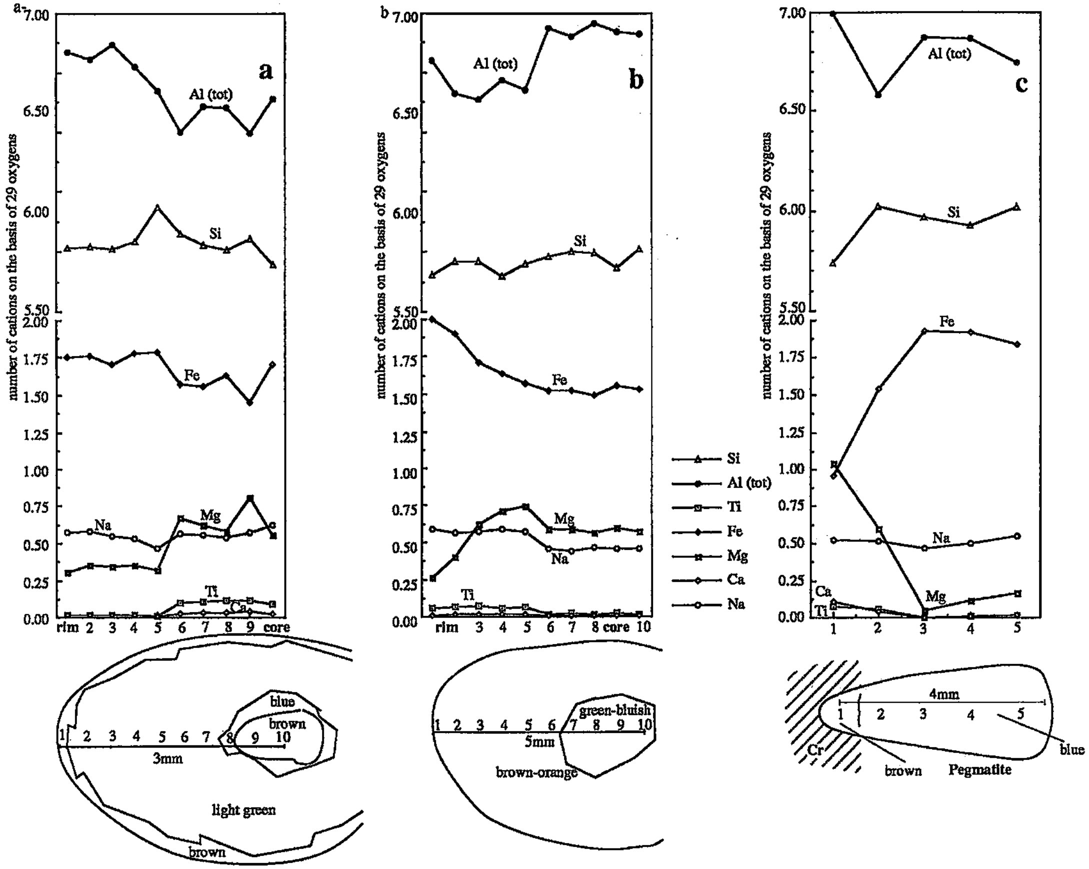

FIG. 7. Detailed compositional variation of zoned crystals of tourmaline occurring in or near a) enclosed pegmatite (1), b) apophyses within aplitic and pegmatitic facies (3), and c) simple discordant pegmatite (6) (CR: country rock).

extent is thus not a useful tool to monitor differences in degree of fractionation. Moreover, the tourmaline occurring in the country rock near simple conformable pegmatites (4) shows a greater extent of such substitutions relative to that in the schists near the simple discordant pegmatites (6), the Li-rich pegmatites (7), and the Sn-rich dykes (8) (Fig. 4b). Thus, differences in the conditions of crystallization, such as the rate of crystallization and in the composition of the original melts, also could affect the extent of these substitutions.

Tourmaline in the pegmatites has, in general, a higher Fe/Mg value than that found in the country rock (Fig. 3). Among the tourmaline samples from pegmatites (Fig. 3a), the richest in Fe and the poorest in Mg occurs in the simple discordant pegmatites (6), followed by the intragranitic pegmatites (1) and the apophyses with aplitic and pegmatitic facies (3). Tourmaline from the simple comformable pegmatites (4) shows a lower content in Fe; finally, the richest in Mg is that associated to the quartz–andalusite dykes (2). At a particular set of pressure–temperature conditions, the compositional evolution of the pegmatite-forming melt–fluid system is closely related to the stability of a given composition of tourmaline. Thus, based on ionic size and charge (Tauson 1965), lithium-bearing tourmaline would be expected to be more stable at lower temperatures than Fe-rich tourmaline, which in turn will be more stable than Mg-rich tourmaline. Previous investigators (Neiva 1974, Manning 1982, Jolliff *et al.* 1986) agree with the fact that tourmaline associated to the earliest stages of differentiation is richer in Mg than that crystallizing in the later stages. In addition, zoned crystals in our suite tend to show a rim enriched in Fe relative to Mg, compared to the core. It thus seems that the sequence obtained for the Fe/Mg value in tourmaline from pegmatites could be used as a tool to establish the

TABLE 5. UNIT-CELL DIMENSIONS OF REPRESENTATIVE TOURMALINE SAMPLES FROM THE PEGMATITES OF THE FREGENEDA AREA AND THEIR TOURMALINIZED COUNTRY-ROCK

Tipo peg.*	a(Å)	c(Å)	V(Å³)	c/a
(T1)	15,992(2)	7,166(1)	1587,4(4)	0,448
(T1)	15,957(4)	7,156(3)	1578,2(9)	0,449
(T2)	15,950(1)	7,169(1)	1579,7(3)	0,449
(T3)	15,960(1)	7,154(0)	1578,3(2)	0,448
(T3)	15,956(2)	7,157(1)	1578,0(4)	0,449
(T3)	15,957(1)	7,152(1)	1577,3(2)	0,448
(T3)	15,961(1)	7,170(2)	1582,2(5)	0,449
(T3)	15,971(1)	7,153(1)	1580,4(2)	0,448
(T4)	15,959(1)	7,158(0)	1579,1(2)	0,449
(T4)	15,954(1)	7,151(1)	1576,6(3)	0,448
(T4)	15,959(1)	7,155(0)	1578,3(2)	0,448
(T4)	15,968(1)	7,156(1)	1580,3(4)	0,448
(T4)	15,954(1)	7,152(0)	1576,6(2)	0,448
(T4)	15,953(1)	7,178(1)	1582,2(3)	0,450
(T4)	15,958(1)	7,161(1)	1579,4(3)	0,449
(T4)(CR)	15,967(1)	7,153(0)	1579,5(2)	0,448
(T7)(CR)	15,955(3)	7,175(2)	1582,0(6)	0,450
(T7)(CR)	15,976(2)	7,175(2)	1586,1(5)	0,449
(T7)(CR)	15,958(2)	7,175(1)	1582,5(4)	0,450
(T7)(CR)	15,953(4)	7,167(2)	1579,8(7)	0,449
(T7)(CR)	15,961(2)	7,152(1)	1578,1(3)	0,448
(T7)(CR)	15,969(5)	7,159(3)	1581,2(9)	0,448

(* numbers of pegmatite types as in Table 1)(CR: country rock) .

sequence of crystallization for the pegmatite bodies. According to this ratio, the most evolved tourmaline-bearing pegmatites would be the simple discordant pegmatites (6), followed by the intragranitic pegmatites (1) and the apophyses with aplitic and pegmatitic facies (3). Finally, the simple comformable pegmatites (4) and the quartz–andalusite dykes (2) seem to be the least evolved pegmatites. This sequence agrees with that obtained from the K/Rb ratio in micas and K-feldspar from these pegmatites (Roda *et al.* 1993). In the pegmatites of the Fregeneda area, therefore, tourmaline associated with the early stages of crystallization is richer in Mg than that growing later, which is richer in Fe.

Concentrations of *REE* are uniformly lower for tourmaline in the pegmatites compared to tourmaline in the country rocks. This may mean that the *REE* abundances and distributions in tourmaline are predominantly controlled by the paragenetic conditions, that is, the *REE* content in tourmaline reflects the *REE* content of the medium where the tourmaline crystallized (Jolliff *et al.* 1987, King *et al.* 1988). Therefore, the high concentrations of *REE* in tourmaline from the country rocks may be inherited from the schists in which they grew. This inheritance could cause the similarity in shape between the patterns for tourmaline of the country rock and those of the metasedimentary rocks of the Schist–Metagraywacke Complex.

Tourmaline from the country rock near the Li-rich pegmatites shows evidence of enrichment in Li, Rb and Cs, as a result of the interaction of a fluid derived from

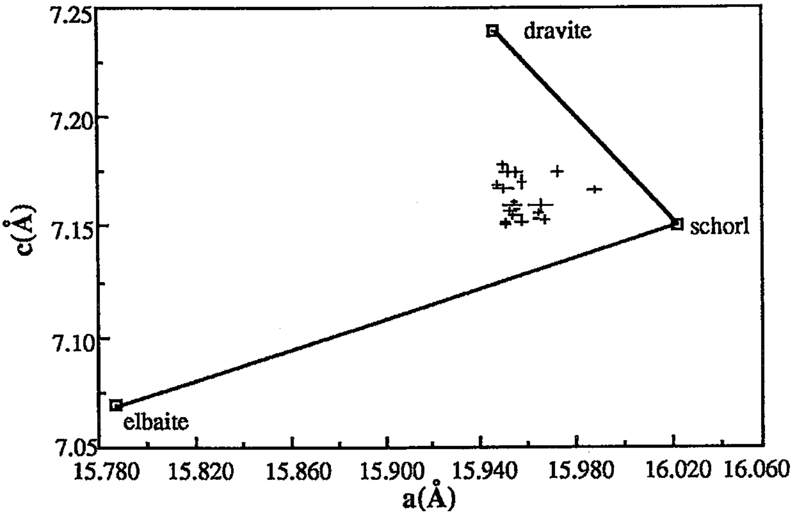

FIG. 8. Unit-cell dimensions of tourmaline samples representative of the different types of pegmatite and their tourmalinized country-rock. Reference lines from Donnay & Barton (1972), modified from Epprecht (1953).

the crystallizing melt and the country rock. Tourmalinization of the schists is strong only in a halo approximately 20 cm wide around these pegmatite bodies; beyond 50 cm, tourmalinization is not developed.

Finally, the tourmaline compositions plot in the field of Li-poor granitic and associated rocks, on the Al–Fe–Mg and Ca–Fe–Mg diagrams. Note that the pegmatites that contain tourmaline are spatially related to the Li-rich Lumbrales granite, which contain from 170 to 230 ppm of Li (García Garzón & Locutura 1981). This apparent contradiction suggests that, on one hand, the composition of tourmaline may be influenced by the chemical environment, achieving mixed petrogenetic affinities, and, on the other hand, the geochemical conditions existing during the formation of the granite and its associated pegmatites are complex and not completely understood.

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