Chemical and mineralogical characterization of elbaites from the Alto Quixaba pegmatite, Seridó province, NE Brazil

ANA C.M. FERREIRA[1], VALDEREZ P. FERREIRA[2],
DWIGHT R. SOARES[3] and HUGO S. VILARROEL-LEO[2]

[1]Centro Gemológico do Nordeste, Departamento de Mineração e Geologia, UFCG,
Rua Aprígio Veloso, 882, 58109-170 Campina Grande, PB, Brasil
[2]NEGLABISE, Departamento de Geologia, UFPE,
Avenida Acadêmico Hélio Ramos, s/n – Cidade Universitária, 50740-530 Recife, PE, Brasil
[3]Departamento de Engenharia de Minas, UFPE,
Avenida Acadêmico Hélio Ramos, s/n – Cidade Universitária, 50740-530 Recife, PE, Brasil

ABSTRACT

The Alto Quixaba pegmatite, Seridó region, northeastern Brazil, is a $60°/80°$SW-trending subvertical dike discordantly intruded into biotite schists of the Upper Neoproterozoic Seridó Formation. It has three distinct mineralogical and textural zones, besides a replacement body that cuts the pegmatite at its central portion and in which occur, among other gem minerals, colored elbaites. Elbaites usually occur as prismatic crystals, elongate according to the c-axis, with rounded faces and striations parallel to this axis. Optically, crystals are uniaxial negative with strong pleochroism; refractive index extraordinary axis = 1.619-1.622 and ordinary axis = 1.639-1.643, birefringence between 0.019 and 0.021, average relative density of 3.07, and the following unit cell parameters: ao = 15.845 Å, co = 7.085 Å and V = 1540.476 Å. There is alkali deficiency in the X site of 12-17%. The elbaites are relatively enriched in MnO (1.69 to 2.87%) and ZnO (up to 2.98%).

Key words: elbaite, tourmaline, Seridó pegmatitic province.

INTRODUCTION

Numerous occurrences of elbaite-bearing pegmatites in the Borborema pegmatitic province, northeastern Brazil, have been reported in the last years. The elbaites are found as blue, violet-blue, greenish blue, green and dark green crystals, as well as rare bi- and tricolored zoned crystals, in which cores are deep pink, characteristics that make the Seridó region to become worldwide known as producer of rare gem-quality tourmalines. In spite of this, only few studies on the crystal chemistry of tourmalines of the many pegmatites in the region have been carried out.

One important characteristic of these elbaites is their high Cu contents that are responsible for the hues of blue and green colors, such as those from the Boqueirãozinho and São José da Batalha pegmatites studied by Brandstaetter and Niedermayr (1994) and Rossman et al. (1991).

The objective of this study is to present some of the crystallographic, chemical, and gemological aspects of elbaites from the Alto Quixaba pegmatite, and make some inferences about the origin of tourmaline color.

*Member, Academia Brasileira de Ciências
Correspondence to: Ana Cláudia Mousinho Ferreira
E-mail: a.claudia1@ig.com.br

GEOLOGICAL FRAMEWORK

The studied pegmatite occurs in the Borborema pegmatitic province, part of the Neoproterozoic Seridó tectonostratigraphic terrane, in the Borborema structural province (Almeida et al. 1981). The Seridó terrane is mostly made up of polideformed Neoproterozoic Seridó Group metasedimentary rocks, and discordantly overlies rocks of the Caicó Complex basement and is constituted, from base to top, by the Jucurutu, Equador and Seridó Formations. These sedimentary sequences, metamorphosed in the amphibolite facies, are intruded by a large volume of plutonic, mostly granitic, Neoproterozoic rocks, during the Brasiliano orogenic cycle.

The Borborema pegmatitic province (Paiva 1946), at the eastern and southeastern part of the Seridó terrane, is characterized by a large number (around 1500 occurrences; Silva 1995) of heterogeneous, both simple and complex pegmatite plutons dated between 450 and 510 Ma. Pegmatites lacking economically important minerals consist of K-feldspar, albite, quartz, and muscovite, while mineralized pegmatites contain Nb, Ta, Sn, Be, Li, P, U, and Th-rich minerals, and carry many varieties of quartz and gem-quality minerals. Two major areas of occurrence are described in the province; one of them encompasses beryl-bearing pegmatites and the other one, tourmaline-bearing pegmatites. The Alto Quixaba pegmatite is one of the tourmaline-bearing pegmatites, intrusive into biotite schists of the Seridó Formation, occurring at about 15 km NE of the Frei Martinho town, north of the State of Paraíba, near the boundary with the State of Rio Grande do Norte (Fig. 1).

THE ALTO QUIXABA PEGMATITE

The Alto Quixaba pegmatite is a typical zoned granitic pegmatitic body enriched in lithophile elements, composed of two distinct bodies that are perpendicularly intercrossed. One of them, of major economic importance, is about 15 m long and 6 m of average width. It is N60°W oriented, with average dip of 80°SW, discordant in relation to the

N50°E-host rocks, which dip 75°SE in the local site (Fig. 1).

This pegmatitic pluton presents large mineralogical and textural variations, allowing to the recognition of three main zones (Fig. 2): (a) an external zone composed of K-feldspar, quartz and muscovite, besides black tourmaline that occurs either in massive aggregates or small, brittle crystals of the schorl type; (b) an intermediate zone, a few meters wide, in which microcline, quartz, albite, muscovite, ambligonite and yellowish green beryl occur, besides accessory metallic minerals such as microlite, tantalite to manganotantalite, and blue to greenish blue tourmaline, which usually is opaque, radial, associated with K-feldspar, and less common, with quartz; and (c) an inner zone (nucleus) composed of grayish quartz that, although not well defined, seems to occur as a series of small, narrow and elongate discontinuous segments. The contacts among the three zones are gradational.

There is a subvertical, replacement body intercepting the central part of the pegmatite, a typical replacement body that is usually found in or around complexly-zoned granitic pegmatites. This alteration zone has an average diameter of 1.5 m, at least in the interval of exposure during the present last stage of digging, and show gradational contacts with the unaltered pegmatite. In this alteration zone, the majority of the elbaite tourmaline of different colors occurs, most of them of good gem quality, and always found associated with cleavelandite, lepidolite, bipyramidal light-smoked quartz crystals, which are in some cases cut by green tourmaline, iridescent manganotantalite, and dark green to green microlite, which usually occurs associate with cleavelandite, are also present in this replacement body. Some microlite crystals are translucent, usually showing flat habit, but crystals with typical octahedral forms are also present.

This replacement body clearly represents an enrichment phase of the Alto Quixaba pegmatite, as indicated by the presence of Na, Li, and other elements such as B, Zn, Mg, Mn, Cu, Ti e F, which are incorporated in the elbaite tourmaline, besides
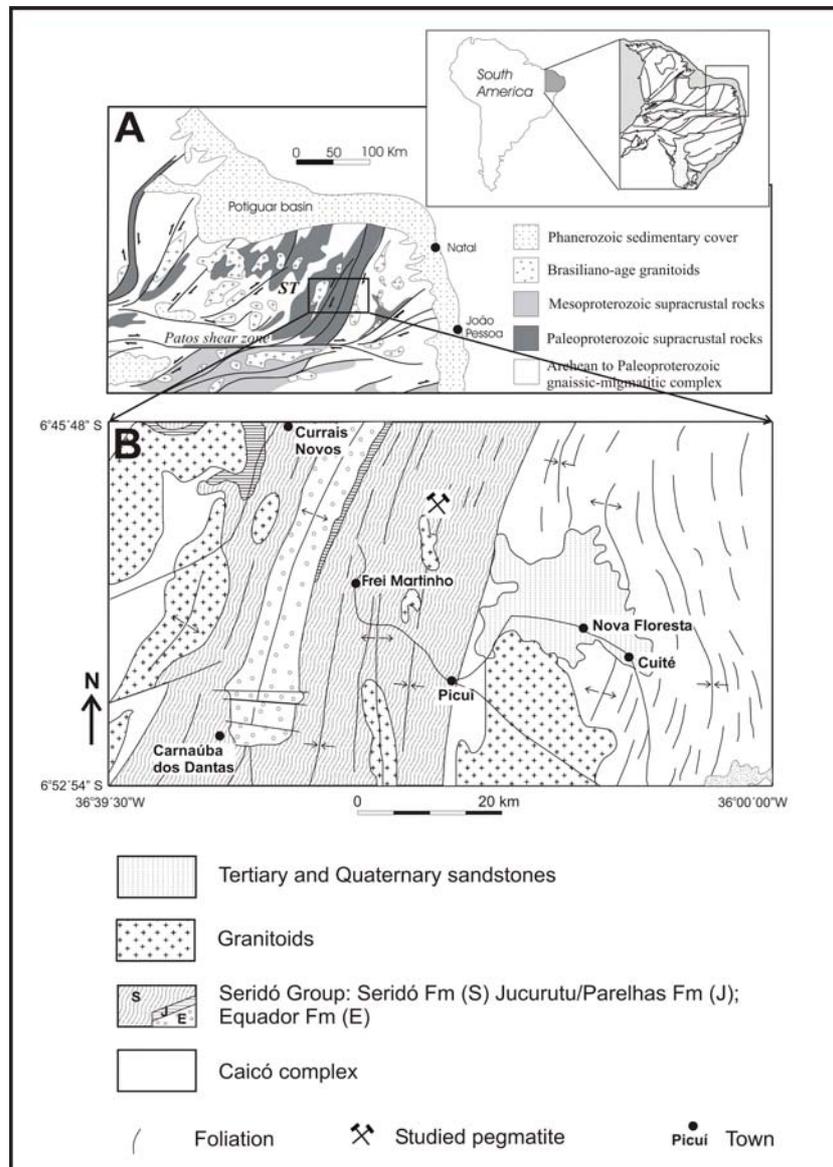
Fig. 1 – Location of the Borborema province in northeastern Brazil (insert of A); (A) geological sketch of the Seridó foldbelt; (B) location of the Alto Quixaba pegmatite, intruded into biotite schists of the Seridó Formation of the Seridó Group. Geological units shown in (B) are from E.F. Jardim de Sá (unpublished data).

some metallic elements in tantalates (A.C.M. Ferreira, unpublished data). This replacement body is texturally and chemically similar to alteration zones described in granitic pegmatitic bodies elsewhere, which are interpreted as representing the final residual water-rich melt rich in silica, alumina, water, halogens, alkali and lithophile elements, and reflect structural and chemical activities during pegmatite crystallization (e.g. Guilbert and Park 1986). The presence of alteration zone coupled with rare miner-
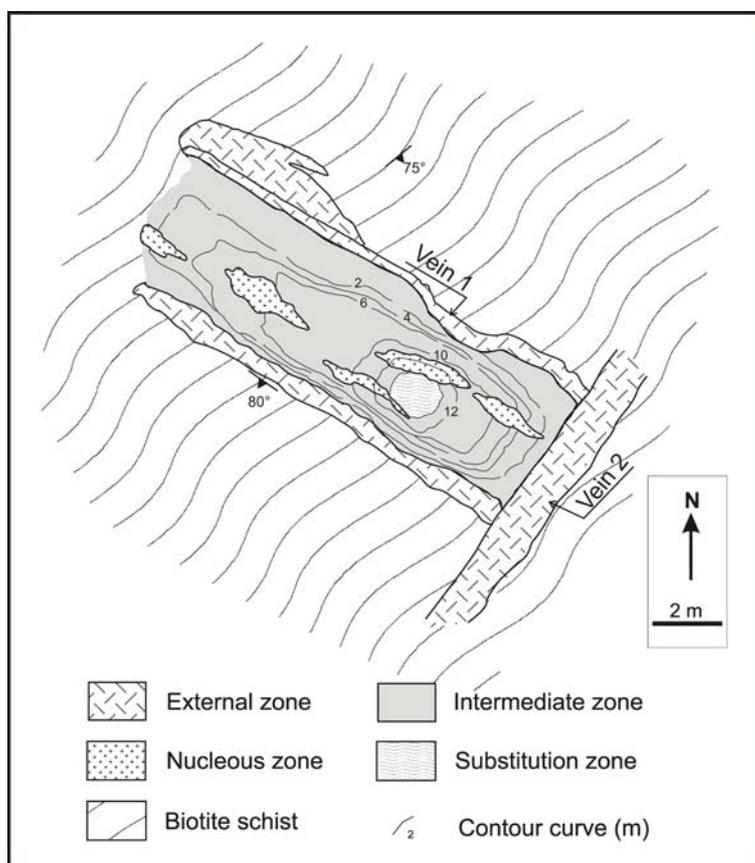
Fig. 2 – Geological sketch of the Alto Quixaba pegmatite showing its textural and mineralogical zonation (A.C.M. Ferreira, unpublished data). Descriptions of each zone are provided in the text.

als such as elbaite, manganotantalite and microlite, among others, define this as a zoned, complex pegmatitic body, according to of Cameron et al. (1949) and Norton (1983) criteria.

SAMPLES AND ANALYTICAL METHODS

Over 80 tourmaline samples, crystals and fragments of a single crystal, many of them of gem quality, have been collected from the Alto Quixaba pegmatite. The size of individual tourmaline crystals varies from few cm up to 6 cm in length. Twenty six gem-quality crystals varying in weigh from 0.35 to 5.4 carats were cut and polished for determination of pleochroism, refractive index and birefringence, at the Gemological Center of Northeast, Federal University of Campina Grande. Refractive indexes have been measured in an Eickhorst refractometer for solids model GEMled. For each sample, 10-15 measurements have been made.

The unit-cell study of selected samples of four different colors was done using powder diagrams obtained in a diffractometer Rigaku Denki, at the Department of Mining Engineering, Federal University of Pernambuco. Radiation used was Cu Kα, a graphite monochromator filter, in the following conditions of operation: 30 mÅ and 40 kV, speed of the goniometer of 4°/minute, and paper of 40 mm/minute, with the diffractometer varying from approximately 10° to 70°.

The cell parameters, calculated using the

method of Ito (Vilarroel-Leo 1971), are displayed in Table I, which also shows representative powder diagrams for blue and green elbaites of the Alto Quixaba pegmatite, as well as the values for an elbaite of the JCPDS (Joint Committee of Powder Diffraction Standard) system, number 21251, for comparison.

Electron microprobe and ICP-AES chemical analyses have been performed in five samples of elbaites of different colors. Chemical analyzes were performed at the University Pierre et Marie Curie, France, using an electronic microprobe CAMECA model SX-50, in the following conditions for all analyzed elements, except for B: 15 kV, 10 nA, 10 μm diameter of the electron bean, and 20 s counting time. A 10 kV voltage and a counting time of 5 s were used for the analyses of B. Reference materials used were: diopside (Si, Mg, Ca), synthetic hematite (Fe), orthoclase (K, Al), pyrophanite (Ti), albite (Na) and boron nitrate (B). Minor elements have been corrected using conventional programs PAP e ZAF. Lithium and other minor elements have been analyzed by ICP-AES at the Saint-Etienne School of Mines, France. Structural formulae were calculated on the basis of 29 oxygens, assuming a complete occupation of 4 anions in the hydroxila site, following the procedures described by Henry and Guidotti (1985). Results are displayed in Tables II and III.

PHYSICAL AND OPTICAL CHARACTERISTICS

The elbaites from the Alto Quixaba pegmatite occur as elongate prismatic crystals, with rounded faces, and typical striations parallel to the c-axis; some crystals are up to 150 g in weigh. They are mainly blue, violet-blue, greenish blue, green and dark green crystals; some of them are translucent when observed perpendicular through the optical c axis. Two major types of zoning are present: (a) perpendicular to the c-axis, with each extremity showing one color (e.g. blue and green), and (b) along the c-axis, giving rise to concentric zoning, in which the core is greenish blue while the rim is green. In this case, tricolor zoning can also be observed, usually with colors ranging from violet through blue and

green, or deep pink core surrounded by a green or blue zone, and a thin pink rim.

They exhibit vitreous luster, no cleavage, and hardness around 7 in the Mohr scale of hardness. Density, determined by the hydrostatic method, varies from 3.05 to 3.10, with an average value of 3.07 ± 0.01, within the range for elbaites studied by Donnay and Barton (1972), who reported densities between 2.84 and 3.10. The studied elbaites have strong pleochroism and uniaxial negative optical character. Measured refractive indexes are

$$\eta_\epsilon = 1.619 - 1.622 \text{ and } \eta_\omega = 1.639 - 1.643,$$

and birefringence (Δ) is between 0.019 and 0.021. These values are in the same range for the elbaites described by Dietrich (1985), who reported values of $\epsilon \sim 1.622$, $\eta \sim 1.641$ and $\Delta \sim 0.019$. Unit-cell dimensions ($ao = 15.845$ Å; $co = 7.085$ Å; $V = 1540.476$ Å) of the studied tourmalines correspond closely to the elbaite reference parameters.

The Kerez effect of cut tourmalines was reported for the first time by Mitchell (1967, in Dietrich 1985) and later studied in detail by Schiffmann (1972, 1975, in Dietrich 1985). Tourmalines that present Kerez effect exhibit two, three or four refractive index bands under a refractrometer. Among the 26 cut tourmalines examined here, the Kerez effect was observed in two dark green crystals that showed two refractive index bands. This is consistent with the observation by Anderson (1980) and Read (1982) that related the Kerez effect to green tourmalines. According to Dietrich (1985), this phenomenon seems to be provoked by overheating of crystal faces during cutting, and the correct refractive index is the largest measured value.

Several cut samples of tourmalines observed under a gemological microscope showed to be free of inclusions. Most samples display only inclusions typical of tourmalines such as channels or fine tubes, known as trinchites (Gübelin 1979); finger prints, which are unoriented thin capillary tubes, usually in nets filled with liquids; biphase inclusions, which are according to Gübelin (1979) two-phase trinchites, and strain or mechanical fractures (A.C.M. Ferreira, unpublished data).

TABLE I
Powder diagram of gem-quality tourmalines from the Alto Quixaba pegmatite.
Data for elbaite of the JCPDS is shown for comparison.

hkl	Green		Blue		Violet blue		Dark green		Elbaite (JCPDS-(21251	
	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
101	6.28	15	6.30	20	6.28	20	6.26	15	6.31	20
111	–	–	–	–	–	–	–	–	5.29	20
021	4.93	25	4.93	15	4.93	35	4.93	15	–	–
300	4.56	10	4.55	10	4.56	5	4.56	5	–	–
211	4.19	25	4.18	30	4.19	30	4.17	20	4.19	25
220	3.95	45	3.95	45	3.95	35	3.95	35	3.96	60
400	3.43	100	3.43	60	3.44	100	3.43	55	3.44	50
131	3.35	10	3.35	15	3.35	10	3.34	10	3.35	16
410	2.99	10	2.99	20	2.99	15	2.98	10	2.994	35
122	2.94	60	2.93	75	2.93	55	2.92	100	2.930	40
051	2.56	55	2.56	100	2.56	50	2.55	30	2.560	100
003	2.37	15	2.37	30	2.37	5	2.36	15	–	–
103	2.33	10	2.33	15	2.33	15	2.32	15	2.333	20
431	2.15	10	2.15	15	2.15	10	2.15	10	2.150	16
521	2.103	15	2.106	20	2.103	15	2.094	15	2.099	20
152	2.027	20	2.030	75	2.027	30	2.027	25	2.025	20
530 700	1.981	< 5	1.981	< 5	1.977	5	1.977	10	1.960	25
342	1.910	55	1.910	30	1.906	20	1.906	30	–	–
522	1.862	5	1.859	10	1.859	5	1.859	10	1.868	25
004	1.767	20	1.767	10	1.770	10	1.770	5	1.776	45
550	1.588	5	1.587	10	1.587	5	1.587	20	–	–
452	1.577	5	1.580	10	1.587	5	1.587	20	1.575	25
641	1.539	5	1.539	< 5	1.540	< 5	–	–	1.537	20

CRYSTAL CHEMISTRY AND STRUCTURE

Tourmaline can be defined as a chemical and structurally complex borosilicate, with a composition, although quite variable, represented by the general formula $XY_3 Z_6(BO_3)_3 (T_6O_{18})W_4$ (Hawthorne 1996), the crystallographic sites being partially or totally occupied. The crystal structure of tourmaline is such that it allows substitution of a variety of ions with respect to both size and charge (Jolliff et al. 1986) in a single site or as coupled substitutions over several sites. The X-structural site is occupied by alkali cations, usually Na^+, Ca^{2+}, K^+, and Mg^{2+}, or even presenting total or partial vacancies. The Y site permits diverse and extensive substitutions, involving monovalent, divalent, trivalent and quadrivalent cations, such as Fe^{2+}, Mg^{2+}, (Al^{3+} + Li^+), Fe^{3+}, Mn^{2+}, Ca^{2+}, Cr^{3+}, Ti^{4+}. The Z site is usually occupied by Al^{3+}. In elbaite, the Y site is predominantly occupied with Al and Li, but may contain Fe^{3+}, Cr^{3+}, V^{3+} or Mg, in dravite predomi-

TABLE II

Electron microprobe analyses of blue and green elbaites from the Alto Quixaba pegmatite, northeastern Brazil. Structural formulae calculated on the basis of 29 oxygens, assuming a complete occupation of 4 anions in the hydroxila site. Li$_2$O contents analyzed by ICP-AES.

Blue elbaite	Crystal 1					
	1	2	3	4	5	6
SiO$_2$	39.08	37.76	38.25	37.62	37.41	37.38
TiO$_2$	0.04	0.04	0.07	0.02	0.06	0.07
Al$_2$O$_3$	38.25	38.49	38.16	38.18	37.67	37.72
FeO	2.85	2.85	2.90	2.95	3.16	3.13
MnO	2.86	2.80	2.88	2.70	2.85	3.12
CaO	0.25	0.33	0.31	0.29	0.27	0.27
MgO	0.00	0.01	0.00	0.02	0.01	0.00
Na$_2$O	2.82	2.56	2.55	2.65	2.59	2.65
K$_2$O	0.00	0.00	0.00	0.00	0.05	0.00
CuO	0.01	0.01	0.00	0.00	0.04	0.04
ZnO	0.41	0.50	0.43	0.45	0.47	0.47
B$_2$O$_3$	11.31	10.93	11.07	10.89	10.83	10.82
Li$_2$O	1.74	1.74	1.74	1.74	1.74	1.74
Total	99.62	98.02	98.36	97.51	97.15	97.41
Si	6.07	5.97	6.02	5.98	5.98	5.97
Ti	0.00	0.00	0.01	0.00	0.01	0.01
Al	7.00	7.17	7.08	7.15	7.10	7.10
Fe	0.37	0.38	0.38	0.39	0.42	0.42
Mn	0.38	0.38	0.38	0.36	0.39	0.42
Ca	0.04	0.06	0.05	0.05	0.05	0.05
Mg	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.85	0.78	0.78	0.82	0.80	0.82
K	0.00	0.00	0.00	0.00	0.01	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.05	0.06	0.05	0.05	0.06	0.06
B	3.03	2.98	3.01	2.99	2.99	2.98
Li	1.08	1.10	1.10	1.11	1.12	1.12
Total	17.79	17.79	17.77	17.80	17.81	17.83
Na	0.85	0.78	0.78	0.82	0.80	0.82
Ca	0.04	0.06	0.05	0.05	0.05	0.05
K	0.00	0.00	0.00	0.00	0.01	0.00
Vac.	0.11	0.16	0.17	0.13	0.14	0.13
Total X	1.00	1.00	1.00	1.00	1.00	1.00
Li	1.08	1.10	1.10	1.11	1.12	1.12
Al(Y)	1.00	1.14	1.08	1.13	1.08	1.07
Fe	0.37	0.38	0.38	0.39	0.42	0.42
Mn	0.38	0.38	0.38	0.36	0.39	0.42
Mg	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.05	0.06	0.05	0.05	0.06	0.06
Ti	0.00	0.00	0.01	0.00	0.01	0.01
Total Y	2.88	3.06	3.00	3.06	3.08	3.09
Al(Z)	6.00	6.00	6.00	6.00	6.00	6.00
Total Z	6.00	6.00	6.00	6.00	6.00	6.00
Si	6.07	5.97	6.02	5.98	5.98	5.97
Al(T)		0.03		0.02	0.02	0.03
Total T						
B	3.03	2.98	3.01	2.99	2.99	2.98
Total B OH+F=4	3.03	2.98	3.01	2.99	2.99	2.98

TABLE II (continuation)

Blue elbaite	Crystal 2					Crystal 3				
	1	2	3	4	5	1	2	3	4	5
SiO_2	36.87	37.20	37.78	37.60	37.14	37.62	37.35	36.74	38.40	37.47
TiO_2	0.05	0.06	0.04	0.05	0.04	0.00	0.00	0.00	0.02	0.01
Al_2O_3	38.65	37.58	38.69	38.84	37.95	37.89	38.45	38.44	38.48	37.00
FeO	3.93	3.76	3.91	3.96	3.80	2.45	2.51	2.70	2.62	2.63
MnO	2.53	2.34	2.44	2.36	2.56	2.26	2.08	1.93	2.10	2.08
CaO	0.25	0.30	0.24	0.21	0.20	0.15	0.19	0.19	0.21	0.12
MgO	0.02	0.03	0.02	0.01	0.02	0.00	0.01	0.01	0.00	0.00
Na_2O	2.48	2.55	2.66	2.64	2.55	2.79	2.63	2.62	2.73	2.83
K_2O	0.00	0.01	0.02	0.00	0.01	0.02	0.01	0.01	0.02	0.01
CuO	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.00
ZnO	0.39	0.43	0.43	0.36	0.48	2.82	2.73	2.95	2.90	2.95
B_2O_3	10.67	10.77	10.94	10.88	10.75	10.89	10.81	10.63	11.12	10.85
Li_2O	1.81	1.81	1.81	1.81	1.81	1.59	1.59	1.59	1.59	1.59
Total	97.65	96.86	98.98	98.72	97.31	98.50	98.36	97.81	100.21	97.54
Si	5.88	5.97	5.94	5.92	5.94	5.98	5.93	5.89	5.99	6.01
Ti	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Al	7.27	7.11	7.17	7.21	7.15	7.10	7.20	7.26	7.08	7.00
Fe	0.52	0.50	0.51	0.52	0.51	0.33	0.33	0.36	0.34	0.35
Mn	0.34	0.32	0.32	0.31	0.35	0.30	0.28	0.26	0.28	0.28
Ca	0.04	0.05	0.04	0.04	0.03	0.03	0.03	0.03	0.04	0.02
Mg	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.77	0.79	0.81	0.81	0.79	0.86	0.81	0.81	0.83	0.88
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.05	0.05	0.05	0.04	0.06	0.33	0.32	0.35	0.33	0.35
B	2.94	2.98	2.97	2.96	2.97	2.99	2.96	2.94	2.99	3.01
Li	1.16	1.17	1.14	1.15	1.16	1.01	1.01	1.02	1.00	1.02
Total	17.82	17.79	17.83	17.82	17.81	17.91	17.88	17.91	17.89	17.91
Na	0.77	0.79	0.81	0.81	0.79	0.86	0.81	0.81	0.83	0.88
Ca	0.04	0.05	0.04	0.04	0.03	0.03	0.03	0.03	0.04	0.02
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Vac.	0.19	0.15	0.15	0.16	0.17	0.11	0.16	0.15	0.13	0.10
Total X	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Li	1.16	1.17	1.14	1.15	1.16	1.01	1.01	1.02	1.00	1.02
Al(Y)	1.15	1.08	1.11	1.13	1.09	1.08	1.13	1.15	1.07	1.00
Fe	0.52	0.50	0.51	0.52	0.51	0.33	0.33	0.36	0.34	0.35
Mn	0.34	0.32	0.32	0.31	0.35	0.30	0.28	0.26	0.28	0.28
Mg	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.05	0.05	0.05	0.04	0.06	0.33	0.32	0.35	0.33	0.35
Ti	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Total Y	3.23	3.14	3.15	3.16	3.17	3.05	3.08	3.14	3.03	3.01
Al(Z)	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Total Z	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Si	5.88	5.97	5.94	5.92	5.94	5.98	5.93	5.89	5.99	6.01
Al(T)	0.12	0.03	0.06	0.08	0.06	0.02	0.07	0.11	0.01	
Total T	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.01
B	2.94	2.98	2.97	2.96	2.97	2.99	2.96	2.94	2.99	3.01
Total B OH+F=4	2.94 2.98	2.97	2.96	2.97	2.99	2.96	2.94	2.99	3.01	

nates Mg, and in schorl, Fe^{2+}. The B site, occupied by B, is of regular triangular coordination, and apparently does not suffer any substitution. The T site is usually filled by Si, but can also accommodate Al. In the W site OH^- can be substituted for F^- or O^{2-} (Foit and Rosenberg 1979, Povondra 1981, Werding and Schreyer 1984, Gallagher 1988, Burt 1989, MacDonald and Hawthorne 1995).

Most natural tourmalines belong to two solid solutions series: schorl-dravite and schorl-elbaite,

TABLE II (continuation)

Green elbaite	Crystal 1				Crystal 2			
	1	2	3	4	1	2	3	4
SiO_2	37.03	37.26	37.37	36.63	37.70	37.79	37.52	37.51
TiO_2	0.11	0.15	0.13	0.10	0.07	0.11	0.07	0.06
Al_2O_3	38.15	38.79	38.87	38.98	37.98	38.09	38.46	38.68
FeO	5.10	5.26	4.65	5.14	2.90	2.81	2.85	2.73
MnO	1.74	1.75	1.63	1.80	1.80	0.96	1.99	2.02
CaO	0.12	0.14	0.16	0.10	0.18	0.15	0.17	0.15
MgO	0.14	0.12	0.11	0.14	0.00	0.00	0.01	0.00
Na_2O	2.66	2.56	2.76	2.58	2.78	2.72	2.90	2.73
K_2O	0.03	0.04	0.02	0.03	0.00	0.00	0.00	0.00
CuO	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00
ZnO	0.25	0.20	0.20	0.27	2.96	3.01	2.96	2.99
B_2O_3	10.72	10.79	10.82	10.60	10.91	10.94	10.86	10.28
Li_2O	1.67	1.67	1.67	1.67	1.67	1.67	1.67	1.67
Total	97.72	98.76	98.39	98.04	98.95	98.25	99.46	98.82
Si	5.91	5.89	5.91	5.84	5.97	5.99	5.92	5.96
Ti	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01
Al	7.18	7.23	7.24	7.32	7.08	7.12	7.15	7.25
Fe	0.68	0.70	0.61	0.69	0.38	0.37	0.38	0.36
Mn	0.24	0.23	0.22	0.24	0.24	0.13	0.27	0.27
Ca	0.02	0.02	0.03	0.02	0.03	0.03	0.03	0.03
Mg	0.03	0.03	0.03	0.03	0.00	0.00	0.00	0.00
Na	0.82	0.78	0.85	0.80	0.85	0.84	0.89	0.84
K	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.03	0.02	0.02	0.03	0.35	0.35	0.34	0.35
B	2.95	2.94	2.95	2.91	2.98	2.99	2.96	2.82
Li	1.07	1.06	1.06	1.07	1.06	1.06	1.06	1.06
Total	17.89	17.88	17.88	17.90	17.89	17.83	17.94	17.89
Na	0.82	0.78	0.85	0.80	0.85	0.84	0.89	0.84
Ca	0.02	0.02	0.03	0.02	0.03	0.03	0.03	0.03
K	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00
Vac.	0.15	0.18	0.12	0.18	0.12	0.14	0.08	0.13
Total X	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Li	1.07	1.06	1.06	1.07	1.06	1.06	1.06	1.06
Al(Y)	1.09	1.12	1.15	1.16	1.05	1.11	1.07	1.21
Fe	0.68	0.70	0.61	0.69	0.38	0.37	0.38	0.36
Mn	0.24	0.23	0.22	0.24	0.24	0.13	0.27	0.27
Mg	0.03	0.03	0.03	0.03	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.03	0.02	0.02	0.03	0.35	0.35	0.34	0.35
Ti	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01
Total Y	3.15	3.18	3.10	3.23	3.08	3.04	3.12	3.27
Al(Z)	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Total Z	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Si	5.91	5.89	5.91	5.84	5.97	5.99	5.92	5.96
Al(T)	0.09	0.11	0.09	0.16	0.03	0.01	0.08	0.04
Total T	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
B	2.95	2.94	2.95	2.91	2.98	2.99	2.96	2.82
Total B OH+F=4	2.95	2.94	2.95	2.91	2.98	2.99	2.96	2.82

with a miscibility gap between dravite and elbaite (Deer et al. 1966). Near complete solid solutions exists between schorl and elbaite (Foit and Rosenberg 1977). Tourmalines are typically described in terms of one of these two series. The compositions of the studied elbaites in terms of Al-Fe-Mg are represented in the Fig. 3 that shows different fields of compositional range of tourmalines from different rock types, as described by Henry and Guidotti (1985). The compositions are very close to the com-
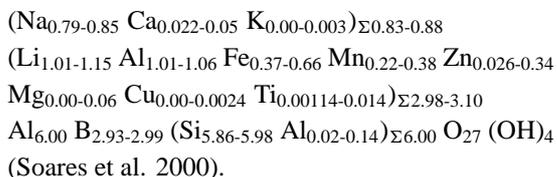
TABLE III

Minor element contents (ppm) obtained by ICP-AES of elbaites from the Alto Quixaba pegmatite, northeastern Brazil (A.C.M. Ferreira, unpublished data).

	blue	Violet blue	Green	Dark green	Greenish blue
Cr	644	897	708	885	825
Ga	170	177	151	173	146
Ni	27.8	20.3	14.1	16.1	15.3
Be	31.2	19.8	12.3	11.4	11.9
V	16.6	8.2	4.2	13.6	4.3
Cu	81.3	47.2	13	31.3	7.3
Li	8069	8407	7369	7736	7734

position of ideal elbaite, falling in the field 1 of the diagram, which is ascribed to tourmalines from Li-rich granitoid pegmatites and aplites.

The cation distribution among the crystallographic sites of the studied tourmalines, calculated on the basis of 29 oxygens indicates that the structural formula can be generically written as:

$(Na_{0.79-0.85} \ Ca_{0.022-0.05} \ K_{0.00-0.003})_{\Sigma 0.83-0.88}$
$(Li_{1.01-1.15} \ Al_{1.01-1.06} \ Fe_{0.37-0.66} \ Mn_{0.22-0.38} \ Zn_{0.026-0.34}$
$Mg_{0.00-0.06} \ Cu_{0.00-0.0024} \ Ti_{0.00114-0.014})_{\Sigma 2.98-3.10}$
$Al_{6.00} \ B_{2.93-2.99} \ (Si_{5.86-5.98} \ Al_{0.02-0.14})_{\Sigma 6.00} \ O_{27} \ (OH)_4$
(Soares et al. 2000).

Both blue and green tourmalines present high occupancy in the X site, compared with the ideal value of 1.00 in elbaite, vacancies ranging from 0.08 to 0.19 apfu. All studied tourmalines are enriched in Al and Li. The occupancy in the Y-site is high, most samples showing excess of cations ($\Sigma Y > 3.00$ apfu), only one sample showing vacancy (total $Y = 2.88$). The excess of electric charge generated by the presence of Al in the Y site is equilibrated with vacancy in the X site, as indicated by slightly positive trend between Al (Y) and vacancy in the X site (Fig. 4a). The presence of Al in the Y site is not due to the substitution for Fe and Mg (Fig. 4b).

However, two coupled substitutions, alkali-defect and proton-loss substitutions, can occur to compensate the charge imbalance due to presence of Al in the Y site, which are more significant than

vacancies in the X site (Foit and Rosenberg 1977). Most natural tourmalines may contain significant amounts of these two components that can be represented in a $(R^+ + R^{2+})$ vs R^{3+} diagram (Fig. 5a) in which R^+ represents the sum of alkalies

$$Na^+ + 2Ca^{2+} + K^+, R^{2+} = Fe^{2+} + Mg^{2+} + Mn^{2+},$$
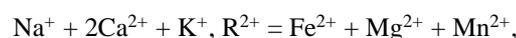
and $R^{3+} = Al^{3+} + 4/3Ti^{4+}$. The substitutions trends proposed by Gallagher (1988) are displayed in the Fig. 5a. The compositions of the studied tourmalines fall away from the loss of protons trend, to the left of the alkali-defect substitution one. Benvenuti et al. (1991) explained this behavior as due to partial occupancy of the Y site by Si and/or presence of additional R^+ cations such as Li. The tourmalines of the Alto Quixaba do not show Si in the Y site (Table II) but significant amounts of Li and Al $(Al + Li > 2$ apfu) and consequent lower Mg contents. Another possibility is that this diagram can not be applied for tourmalines of the schorl-elbaite series. On the other hand, this diagram shows that the compositions are rather homogeneous, which can be related to the decreasing temperature and large degree of evolution as suggested by Manning (1982).

A possible substitution could be of the type $AlNa_{-1}Li_{-1}$ as suggested by the trends roughly parallel to the exchange vectors

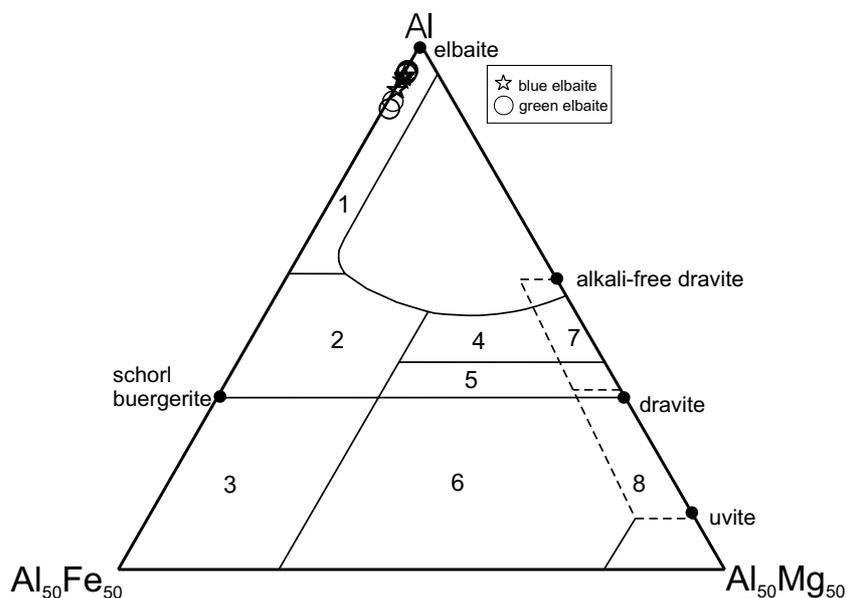$$\{X\}_2 Al_5 O_{13} Na_{-1} Li_{-1} (OH)_{-13} \{Y\}_{-4}$$

Fig. 3 – Al-Fe(t)-Mg diagram showing fields of the compositional range of tourmalines from different rock types proposed by Henry and Guidotti (1985). Field 1 is typical of tourmalines from Li-rich granitoid pegmatites and aplites.
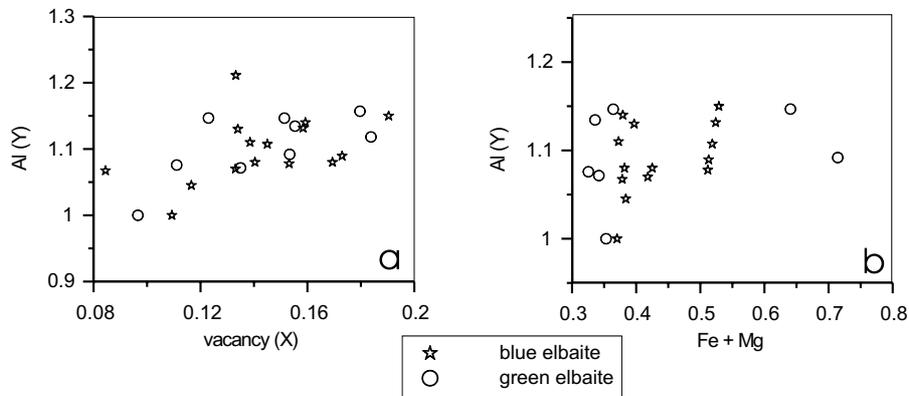

Fig. 4 – (a) Al in the Y site vs. vacancy in the X site of blue and green elbaites; (b) Al in the Y site vs. (Fe + Mg) of blue and green elbaites.

and

$$\{X\}Al_{4.5}O_{12}Na_{-1}Li_{-0.5}(OH)_{-12}\{Y\}_{-4}$$

(Fig.5b), and slightly negative correlation between Al(Y) and (Na + Li). Substitutions that occur in the studied elbaites seem to be more complex than those reported in the literature and it will remain to be better explained.

All samples have high FeO(t), up to 3.96 wt% in the blue tourmalines, and up to 5.26 wt% in the green ones. Blue elbaites tend to have higher Li and Mn contents than the green ones (Fig. 6a, b). MnO contents > 1.5 wt% in tourmalines are relatively rare and usually associated to Na- and Li-bearing pegmatites, in elbaite-schorl tourmalines (Slivko 1961,
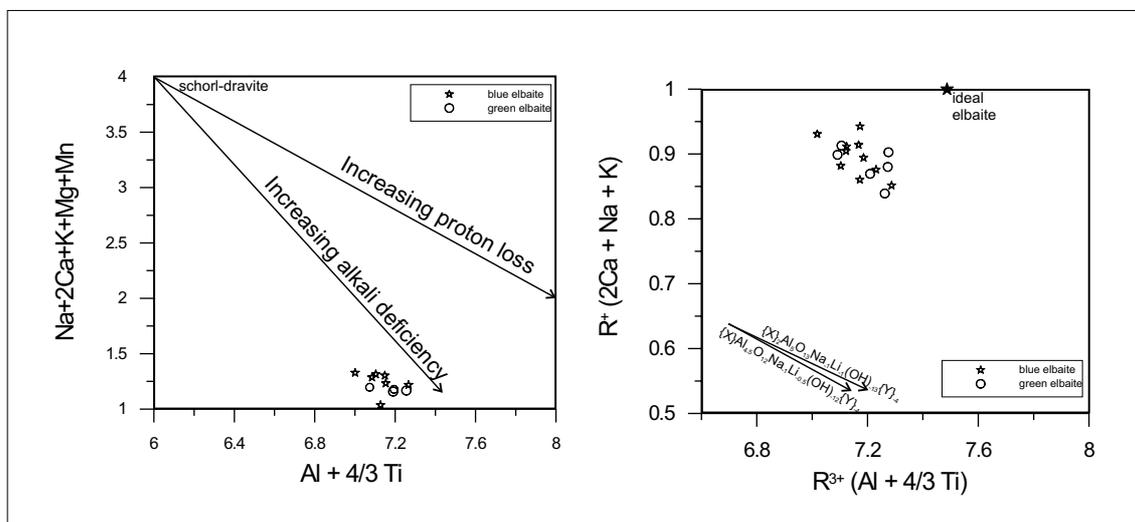
Fig. 5 – (a) R^{3+} (Al + 4/3 Ti) vs. (R^+ + R^{2+}) (Na + 2Ca + K + Mg + Mn) diagram for elbaites of the Alto Quixaba pegmatite. Substitution trends are from Gallagher (1988). (b) R^{3+} (Al + 4/3 Ti) vs. R^+ (Na + 2Ca + K) diagram for elbaites of the Alto Quixaba pegmatite. Substitutions trends are from Gallagher (1988).

Leckebusch 1978, Sahama et al. 1979). Mn contents in the studied tourmalines are high (0.24 − 0.42 apfu; 1.69−2.87% MnO, except for one sample that presents MnO = 0,9%) compared with average contents for blue elbaites, which usually present Mn contents < 0.30 apfu (Selway et al. 1999). Shigley et al. (1986) described tourmalines with up to 8.86% MnO, Gonzalez-Carreño et al. (1988) reported elbaites with up to 6,79% MnO and Burns et al. (1994) with MnO values up to 6.23%. Castañeda et al. (2003) reports tourmalines of the schorl-elbaite series from granitic pegmatites from Minas Gerais State, southeast Brazil, in which MnO is also high, up to 2.32wt%.

The studied elbaites are enriched in Zn, up to 2.98 wt%, a rather high value not commonly reported for other elbaites elsewhere. High ZnO values are reported for other Brazilian elbaites such as dark blue elbaites from other pegmatites of the Seridó region up to 2.43 wt% (D.R. Soares, unpublished data), and from Mina do Cruzeiro pegmatite, State of Minas Gerais, southeast Brazil, in which ZnO content is up to 2.0 wt% (J.C. Mendes, unpublished data).

Studied blue elbaites tend to present higher Cu, Ni, Li and Mn contents than the green ones (Fig. 6a through 6d). Semiquantitative X-ray fluorescence chemical analyses from five tourmalines of different colors indicate TiO_2 (0.1%) in the dark green elbaite, and Bi_2O_3 (from 0.01 to 0.04%) in all but in the blue elbaite (A.C.M. Ferreira, unpublished data).

DISCUSSION AND CONCLUDING REMARKS

Three distinct zones occur in the Alto Quixaba pegmatite, recognized on the basis of mineral assemblage and texture (external, intermediate and core), and a well-developed alteration zone in which one finds among other gem minerals, elbaites of excellent gem-quality of variable blue and green colors and hues. Refractive indexes, birefringence, relative density and parameters of the unit cell for these elbaites are similar to those reported for elbaites elsewhere. These are Mn- and Zn-rich elbaites that present vacancies in the X site from 12 to 17%.

Complex and differentiated pegmatites present tourmalines from the external zones richer in Fe than those from the inner zone, in which tourmalines have much higher Li and Al contents (e.g.
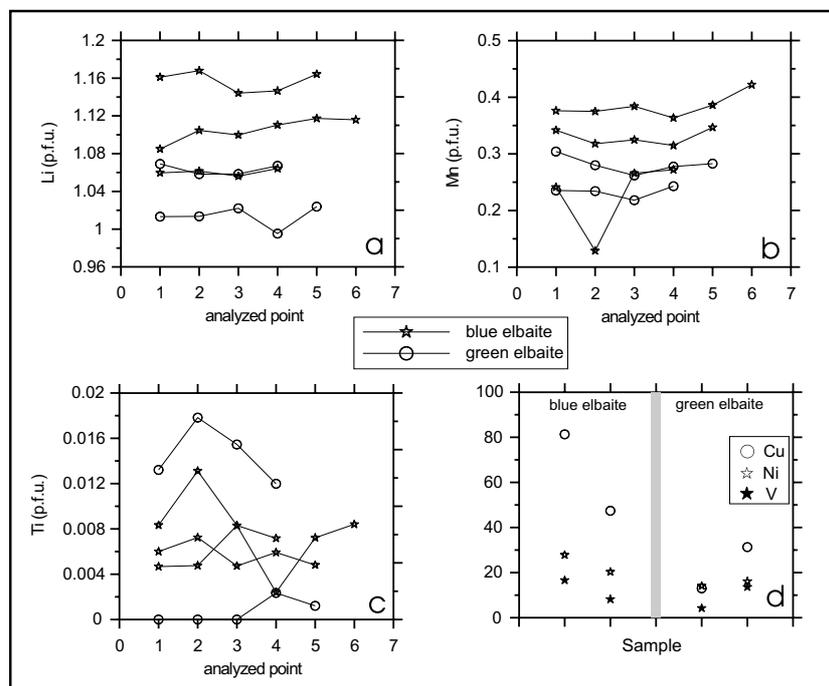
Fig. 6 – Compositional variations of studied blue and green elbaites. (a) through (c): different analyzed points in single grains; Li, Mn, Ti, and Fe obtained by electron microprobe; (d) whole rock; Cu, Ni and V obtained by ICP-AES.

Foord 1977, Jolliff et al. 1986). The Alto Quixaba pegmatite presents similar behavior, as the tourmaline from the external zone is schorl in which FeO contents vary from 12.5 to 13.8 wt% (A.C.M. Ferreira, unpublished data), while the blue and green elbaites from the replacement body in the central zone present FeO contents $< 5.3\%$, and Li_2O varies from 1.59 to 1.81%.

These Li-bearing tourmalines have relatively high Mn contents, in accordance with data reported in the literature (e.g. Sahama et al. 1979), although Mn-rich and Li-poor tourmalines also exist (e.g. Ayuso and Brown 1984). As observed by Dietrich (1985) elbaites contain larger trace element contents than do other tourmalines, probably because the former occur in complex pegmatites. Therefore some trace elements can have higher contents in some tourmalines, such as Zn as observed in the studied elbaites. Generally Zn is more common in green and blue elbaites than in red and yellow ones.

The concentration of major and/or trace elements, besides structural defects (color centers), charge transfer, or a combination of these parameters have been suggested as responsible for the different colors of tourmalines (e.g. Nassau 1978, 1983). On the basis of the concentrations of some known coloring agents such as Fe, Ti, Mg, Mn, Cu, Cr, V, one can infer the possible origin of different colors of tourmalines. Yellowish green to blue-green colors of elbaites from Mina da Batalha pegmatite, in the Borborema pegmatitic province, is attributed to Cu^{2+}, while violet-blue and violet hues are due to Mn (Rossman et al. 1991). The studied elbaites could have their color due to Cu and Mn concentrations, which are higher in the blue elbaites compared to the green ones. Although not a coloring agent, it should be noted that Li contents is also higher in the blue elbaites than in the green ones.

Trace elements, however, can be or not responsible for, or even have some correlation with the

color of tourmalines. Further studies (e.g. absorption spectroscopy) can shed some light on the origin of the different colors and hues of these elbaites.

RESUMO

O pegmatito Alto Quixaba na região do Seridó, nordeste do Brasil, é um corpo subvertical de direção 60°/80°SW intrudindo discordante biotita xistos da Formação Seridó. Apresenta três zonas distintas em termos de mineralogia e textura, além de uma zona de alteração em forma de dique na qual ocorre, entre outros minerais-gema, elbaítas coloridas. As elbaítas ocorrem como cristais prismáticos alongados de acordo com o eixo C, com faces arredondadas e estrias paralelas a esse eixo. Os cristais são uniaxiais negativos e apresentam forte pleocroísmo; índices de refração $n_E = 1,619 - 1,622$ e $n_O = 1.639 - 1.643$, birrefrigência entre 0,019 e 0,021, densidade relativa de 3,07, e os parâmetros seguintes da célula unitária: $a_O = 15,845$ Å, $c_O = 7,085$ Å e V = 1540,476 Å. O sítio X apresenta deficiência em álcalis entre 12 e 17%. As elbaítas são relativamente ricas em MnO (1,69 a 2,87%) e ZnO (até 2,98%).

Palavras-chave: elbaíta, turmalina, província pegmatítica do Seridó.

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