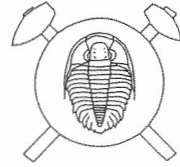


Chemistry of tourmalines in some pegmatites of São José da Safira Area, Minas Gerais, Brazil

Chemické složení turmalínu v pegmatitech v oblasti São José da Safira, Minas Gerais, Brazílie (Czech summary)



(6 text-figs.)

ESSAÏD BILAL¹ - JULIO CÉSAR-MENDES² - JOSÉ MARQUES CORREIA-NEVES³
- MOHAMED NASRAOUI¹ - KAZUO-FUZIKAWA⁴

¹Ecole des Mines de Saint-Etienne. 158, cours Fauriel, 42023 Saint-Etienne cedex 2, France

²Universidade Federal de Ouro Preto, DEGEO. Morro do Cruzeiro S/N°, 35400-000, Ouro Preto, MG, Brazil

³Universidade Federal de Minas Gerais, IGC. Av. Antônio Carlos, 6627, Pampulha, 31270-901 Belo Horizonte, MG, Brazil

⁴Comissão Nacional de Energia Nuclear (CNEN)/Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) Av. Antônio Carlos 6627, Pampulha 31270-901 Belo Horizonte, MG, Brasil

The tourmaline group minerals (schorl to elbaite) typically occur in the Li-bearing pegmatites from the São José da Safira region (the Oriental Pegmatitic Province (OPP) in Minas Gerais State, Brazil). The Fe/Mn ratios of the tourmalines are compared to those measured in columbite-tantalite and garnet and decrease northward continuously from the beryl-bearing pegmatites to the spodumene-bearing ones. The Fe/Mn ratio has been used as a qualitative index of fractionation which seems to reflect the regional zoning of the pegmatites around a hidden granite body. The Fe/Mn ratio values correlate negatively with the Na and Li contents. The REE, Nb, Co and Zn contents are controlled by the mineral assemblages.

Key words: tourmaline, behierite, columbite-tantalite, Brazil, Minas Gerais, Li-bearing pegmatite, fractionation.

Introduction

In the São José da Safira region, eastern centre of the Oriental Pegmatitic Province (OPP) in Minas Gerais State (Brazil), many of zoned Li-bearing pegmatites crop out. However, parent granites have not yet been found within the area. Minerals of the tourmaline group, compositionally varying from schorl to elbaite, occur in all pegmatites. Schorl always occurs close to the country rock and to elbaite is found in the late metasomatic bodies.

This paper aims to highlight the importance of mineral assemblages in the control of the chemical compositions of the studied tourmalines. The tourmaline composition from various pegmatites has been found to correlate with the spatial distribution of the pegmatite bodies in São José da Safira region around a hidden granite body.

Geological setting

This region is represented by Neoproterozoic mobile belts associated with the Brasiliano orogeny (600-480 Ma). These mobile belts reworked the early Proterozoic basement and the late proterozoic supracrustal sequences of the Rio Doce group. Several rare elements and gem minerals-bearing pegmatites are emplaced in the supracrustal sequences. These pegmatites were locally folded. Two main deformation phases, developed under low pressure amphibolite facies conditions (500 °C < T < 600 °C and P = 4 kbars), have been characterised in this region (Bilal et al. 1997). The first deformation (D1) was responsible for penetrative foliation (solid state) N10°-30° W/middle to high angle and mineral lineation of host rocks and the peg-

matite borders. It controlled magmatic foliation the syn-tectonic pegmatites. The second deformation was characterised by a cleavage crenulation, boudinage and normal faults. It was associated to an extensional phase. The pegmatitic melt has been emplaced along this penetrative foliation D1, and it seems that the emplacement took place as follows: the simple pegmatites of the region at the onset of the deformation and the most evolved Li-bearing ones at the fading out of this tectonic event.

Pegmatites bodies

A few hundred pegmatite bodies occur in São José da Safira area (Fig. 1). The most mineralised and Li-bearing bodies show outcropping lengths ranging from 150 m up to 1300 m and widths ranging from 10 m up to 60 m. They are subvertical bodies striking N10-20° W. The pegmatites outcropping at different topographic levels, range from 150 m up to 1100 m in the Serra do Cruzeiro, are intrusive either into quartzites (the Cruzeiro pegmatites) or into staurolite-garnet schists and paragneisses belonging to Rio Doce group.

The internal structure is very similar in all of them (Table 1). They show not only consistent mineral assemblages but an internal zoning around the quartz core, too.

Tourmaline crystals, up to several cm in size, have been collected. They are distributed according to the following internal zoning:

(1) the border and the wall zones (always black tourmalines); (2) the intermediate zones (black, green, blue and pink tourmalines); or even (3) the pockets (always green, blue and pink to red tourmalines).

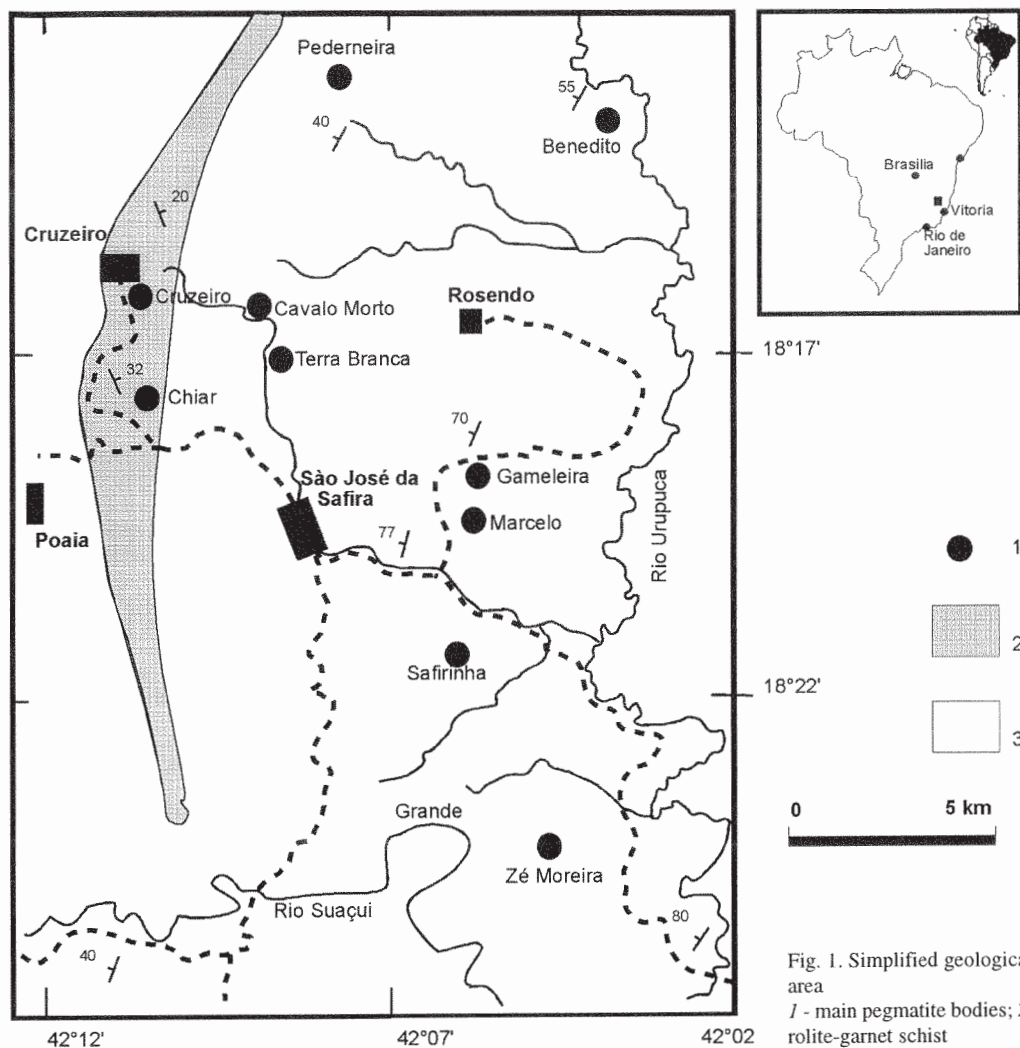


Fig. 1. Simplified geological map of the São José da Safira area
 1 - main pegmatite bodies; 2 - quartzite; 3 - gneiss and staurolite-garnet schist

The black tourmalines (schorl) are associated with quartz, locally biotite, muscovite, (K, Na)-feldspar, garnet (almandine-spessartite), columbite-tantalite ($Nb > Ta$) and prismatic beryl. Elbaite is found within the metasomatic bodies together with albite (cleavelandite), quartz, amblygonite, spodumene, Li-rich violet micas, tabular morganite, tantalite-columbite ($Ta > Nb$) and spessartite garnet (Bilal et al. 1994, César-Mendes et al. 1994).

The Rb/Cs, K/Rb and K/Cs ratios and Na_2O contents of the micas and K-feldspars as well as the Fe/Mn ratios of columbite-tantalite, micas and garnets from rare-ele-

ments bearing-pegmatites in São José da Safira area decrease continuously from the Zé Moreira beryl-bearing pegmatite to those of Cruzeiro spodumene-bearing pegmatites. These latter ones are the most differentiated within the region and show a high fractionation as indicated by low Na_2O content within the latest crystallised K-feldspars and low K/Cs ratios of micas. The rare-elements-bearing pegmatites in the São José da Safira area reflect compositional variations during the regional evolution and point to a zoning around a so far hidden granite body.

Table 1. Main characteristics of pegmatites within the São José da Safira region

Pegmatite	Type	Mineralogy
1) Zé Moreira, Cavalo Morto	1) beryl pegmatite	quartz, K-feldspar, biotite, muscovite, albite, tourmaline, garnet, beryl, and columbite-tantalite ($Nb > Ta$)
2) Benedito, Pederneira	2) beryl spodumene pegmatite	quartz, K-feldspar, muscovite, Li-bearing micas, albite, gem quality-tourmalines, behierite, garnet, beryl, spodumene, amblygonite, columbite-tantalite ($Nb = Ta$), cassiterite and apatite
3) Cruzeiro	3) spodumene pegmatite	quartz, K-feldspar, muscovite, Li-bearing micas, albite, gem quality elbaite, behierite, garnet, (blue and pink) beryl, spodumene, amblygonite, columbite-tantalite ($Nb < Ta$), cassiterite and apatite

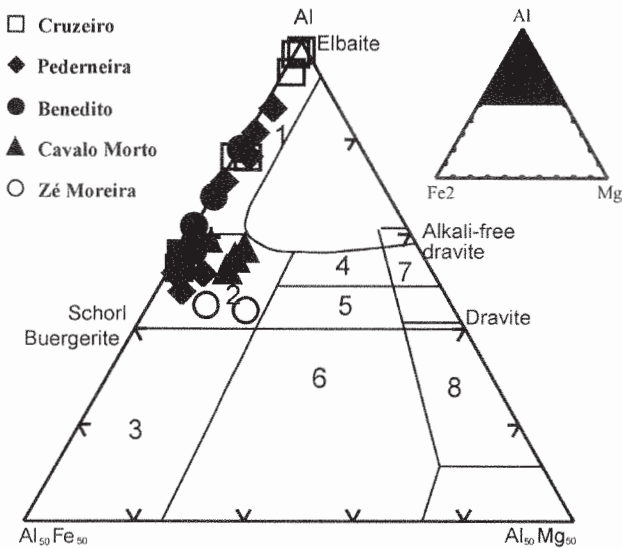


Fig. 2. Al-Fe(tot)-Mg diagram (in molar proportions) for tourmalines from some of the pegmatites of São José da Safira area. Fields after Henry - Guidotti (1985)

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 metapsammities coexisting with an Al-saturating phase; 5 - metapelites and metapsammities 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; 8 - metacarbonates and metapyroxenites

Tourmaline chemistry

The general formula for the tourmaline can be written as follows: $XY_3Z_6[(BO_3)_3Si_6O_{18}(OH,F)_{1+3}]$, where X(Na + Ca); Y(Mg,Fe²⁺,Al,Li,Ti,Mn) and Z(Fe³⁺,Cr³⁺,Al). All analysed tourmalines belong to the schorl-elbaite series (Fig. 2), suggesting the effect of two coupled substitutions (Foit - Rosenberg 1977) involving dehydroxylation and alkalis-defect.

The infrared spectra of these tourmaline samples, in the principal hydroxyl-stretching region (Fig. 3), show clearly defined absorption peaks at 3474-3489 cm⁻¹ and 3373 cm⁻¹.

As described below the latter most intense absorption peaks and the Y-site cations, almost only Fe and Al in analysed samples (Table 2), seem to be correlated. Thus the possible associations in these tourmalines samples of São José da Safira are Fe²⁺-Al-OH, Al-Al-OH, Fe²⁺-Al-Li and Al-Al-Li. We have already assigned band 3633 cm⁻¹ to configuration Fe²⁺-Al-OH. The 3555 cm⁻¹ band is also assigned the Al-Al-OH and both 3480 cm⁻¹ and 3373 cm⁻¹ bands must correspond to associations Fe²⁺-Al-Li and Al-Al-Li. The infrared spectra of these samples in the principal hydroxyl-stretching region are strikingly different and

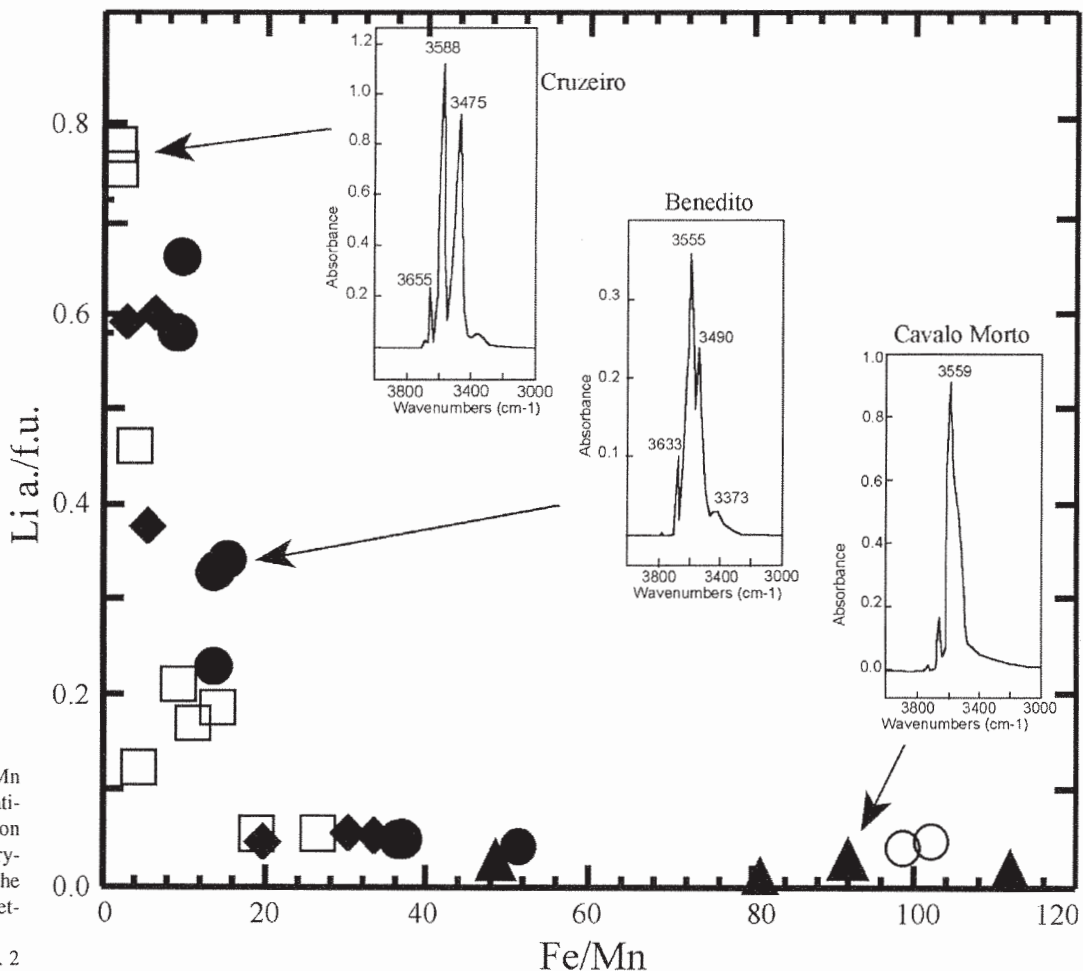


Fig. 3. Variation of Fe/Mn with Li a./f.u. and variation of infrared absorption spectra of tourmaline crystals with Li a./f.u. in the principal hydroxyl-stretching region. Used symbols as in Fig. 2

Table 2. Representative chemical composition of tourmaline from São José da Safira region

Sample	ZM	CAT2	CA4A	BET9	BE8C	PedA	PedB	CHT4	CHT5	CR4B	CR1
SiO ₂	34.19	35.31	36.35	35.03	37.07	36.99	36.77	34.66	36.19	36.31	37.31
TiO ₂	0.34	0.32	0.30	0.06	0.01	0.28	0.09	0.15	0.12	0.11	0.01
Al ₂ O ₃	33.43	34.52	35.62	34.25	36.65	36.28	35.96	34.65	40.43	36.92	42.85
FeO	10.79	10.40	10.07	8.61	6.38	6.14	5.04	11.95	2.87	6.87	0.15
MnO	0.12	0.09	0.12	0.61	0.71	0.91	0.95	0.73	0.56	1.39	0.32
MgO	1.81	1.91	1.83	0.05	0.01	0.31	0.12	0.15	0.22	0.01	0.01
CaO	0.11	0.12	0.11	0.10	0.11	0.21	0.22	0.06	0.37	0.16	0.85
Na ₂ O	1.61	1.85	1.87	1.97	3.27	2.96	2.76	2.02	2.09	2.57	2.29
K ₂ O	0.05	0.06	0.05	0.04	0.02	0.05	0.46	0.05	0.03	0.04	0.06
Li ₂ O	0.04	0.03	0.02	0.48	0.90	0.91	0.57	0.17	0.23	0.67	1.31
Total	82.49	84.61	86.34	81.2	85.13	85.04	82.94	84.59	83.11	85.05	85.16
Si	5.915	5.934	5.961	6.065	6.054	6.047	6.136	5.895	5.905	5.969	5.836
Al(T)	0.085	0.066	0.039	0.000	0.000	0.000	0.000	0.105	0.095	0.031	0.164
Al(Z)	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Al(Y)	0.811	0.832	0.879	0.983	1.049	0.984	1.067	0.940	1.769	1.147	1.894
Ti	0.044	0.040	0.037	0.008	0.001	0.034	0.011	0.019	0.015	0.014	0.001
Fe ²⁺	1.561	1.462	1.381	1.247	0.871	0.839	0.703	1.700	0.392	0.944	0.020
Mn	0.017	0.013	0.017	0.089	0.098	0.126	0.134	0.105	0.077	0.194	0.042
Mg	0.467	0.479	0.447	0.013	0.002	0.076	0.030	0.038	0.054	0.002	0.002
Li	0.028	0.020	0.013	0.334	0.591	0.598	0.383	0.116	0.151	0.443	0.824
Y total	2.928	2.846	2.774	2.674	2.612	2.657	2.328	2.918	2.458	2.744	2.783
Ca	0.020	0.022	0.019	0.019	0.019	0.037	0.039	0.011	0.065	0.028	0.142
Na	0.540	0.603	0.595	0.661	1.035	0.938	0.893	0.666	0.661	0.819	0.695
K	0.011	0.013	0.010	0.009	0.004	0.010	0.098	0.011	0.006	0.008	0.012
X total	0.571	0.638	0.624	0.689	1.058	0.985	1.030	0.688	0.732	0.855	0.849
Zn ppm	636	539	850	2188	1322	2467	325	262	2100	732	107
Co ppm	8.47	8.59	12.4	9.29	5.95	15.9	4.08	2.71	10.5	8.92	0.43
Y ppm	0.26	6.21	0.37	0.1	0	0.201	0.128	0.29	0.35	0.35	0.39
Sm ppm	0	0	0.53	0	0	2.58	1.48	0	0	0.27	0.27
La ppm	0.31	0.27	0.51	0.27	0.8	0.765	2.32	1.49	0.72	2.94	2.64
Ce ppm	0.97	5.1	0.65	1.41	0	5	2.61	4.2	2.15	2.15	3.48
Yb ppm	0.54	1.35	0.5	0.56	0.2	0.521	0.31	0.2	0.4	0.06	0.08
Nb ppm	2.02	2.68	2.08	15.1	12.0	7.2	5.05	3.15	6.7	2.96	1.9
Th ppm	0	0.83	0.41	0	0	0	0	0	0	2.38	0.73
Nd ppm	0.69	1.98	2.61	1.48	0	0	0	1.9	2.02	2.05	1.52
Eu ppm	0.25	0.39	0.1	0.31	0	0	0	0.3	0.3	0.01	0.02

Determined by electron microprobe, model Camebax SX50. Trace elements and REE determined by ICP-AES and INAA. Boron was not analysed and electron microprobe analyses were normalised to 24.5 O atoms.

Pegmatite sample codes: ZM: Zé Moreira; CAT2 and CA4A: Cavallo Morto; BET9 and BE8C: Benedito; PedA and Ped B: Pedreira; CHT4 and CHT5: Chiar and CR4B and CR1: Cruzeiro.

variation of the Y-site (Fig. 4) indicating $2R^{2+} = (Al(Y) + Li^+)$ as the principal substitution mechanism. The same result was reported by Jolliff et al. (1986) for Bob Ingersoll tourmaline. This mechanism seems to be dependent on the Li a./f.u. content of the tourmaline. In this case we can make use of the infrared spectra to characterise the different tourmaline types of the schorl-elbaite series.

The Fe/Mn ratio of the tourmalines show the same trend as those measured in columbite-tantalite and garnets. All of them decrease northward continuously from the Zé Moreira pegmatite (SE in Fig. 1) to those of Cruzeiro. The Fe/Mn ratio has been used as a qualitative index of fractionation reflecting not only the regional degree of evolution of the pegmatites but also the internal evolution of these bodies. The Fe/Mn ratio correlate negatively with the Li contents (Fig. 3). The Co, Zn and Nb contents begin to increase (Fig. 5) but with the setting up the columbite-tantalite, behierite and garnet crystallisation these values de-

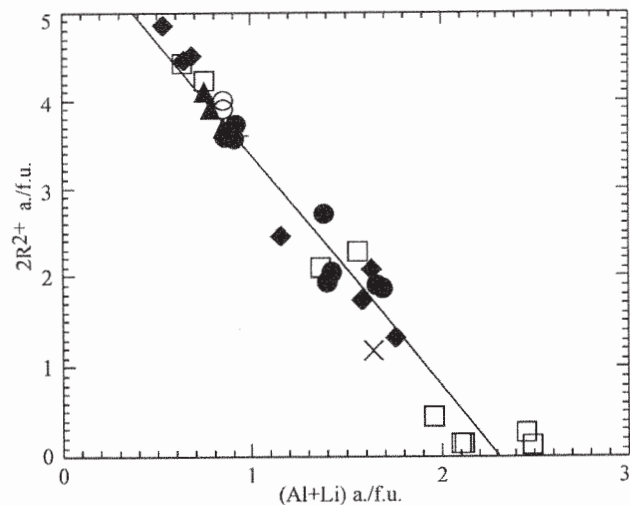


Fig. 4. Variation of $2R^{2+}$ with $Al(Y) + Li$ a./f.u. in tourmaline from some of the different types of pegmatites of the São José da Safira area. Used symbols as in Fig. 2.

crease. The same trends have been observed in Bob Ingersoll tourmaline by Jolliff et al. (1986), but these authors have proposed another mechanism based on the fractionation of these elements between coexisting silicate melt and aqueous fluid. The minor and trace elements are essential components of accessory minerals or strongly partitioned into others minerals that occur in the pegmatite.

The LREE contents increase but HREE contents in tourmaline do not show a definite trend (Fig. 6). The abundance and distribution of REE are mainly controlled by the mineral assemblages. Apatite and garnet fractionation strongly affect the HREE distribution in tourmaline.

Conditions of crystallisation

The crystallisation fluid which has been trapped within the primary fluid inclusions in green tourmaline of Cruzeiro pegmatite is essentially composed by H₂O, CH₄ and N₂ (Fuzikawa et al. 1996). The H₂O, CH₄ and N₂ were con-

firmed by Raman spectroscopy. The total homogenisation temperatures of these inclusions range from 300 up to 400 °C. Minimum pressure estimates range from 0.6 up to 1.1 kbar. Mineral assemblages in pegmatites of São José da Safira indicate that the tourmalines were crystallised under temperature 360 °C to 570 °C and pressure 1.1 kbars to 3 kbars (Bilal et al. 1997).

Conclusion

The tourmaline composition variations observed in São José da Safira region reflect not only compositional variations during the regional evolution of the pegmatites, but also the internal evolution within the pegmatites themselves. The Fe/Mn ratio determined in tourmalines decreases from the Zé Moreira beryl-bearing pegmatite outcropping southward to the Cruzeiro spodumene-bearing pegmatites along with the increase of the pegmatite evolution. A systematic chemical trend seems to suggest a petrogenetic linkage among the most evolved pegmatites of this region.

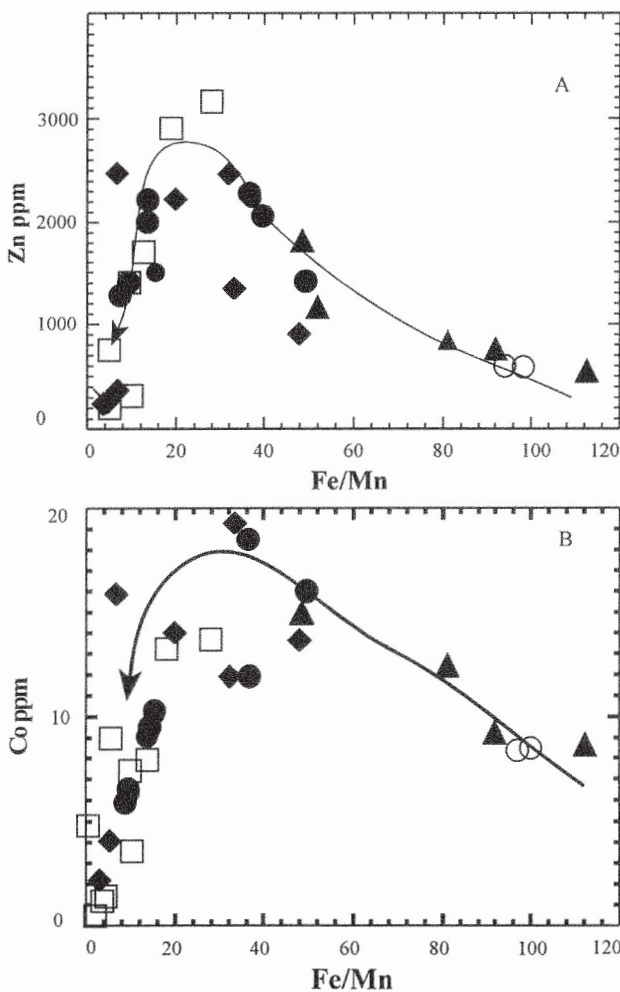


Fig. 5. Plot of concentration of Zn (ppm) and Co (ppm) versus Fe/Mn in tourmaline from some of the different types of pegmatites of the São José da Safira area
Used symbols as in Fig. 2

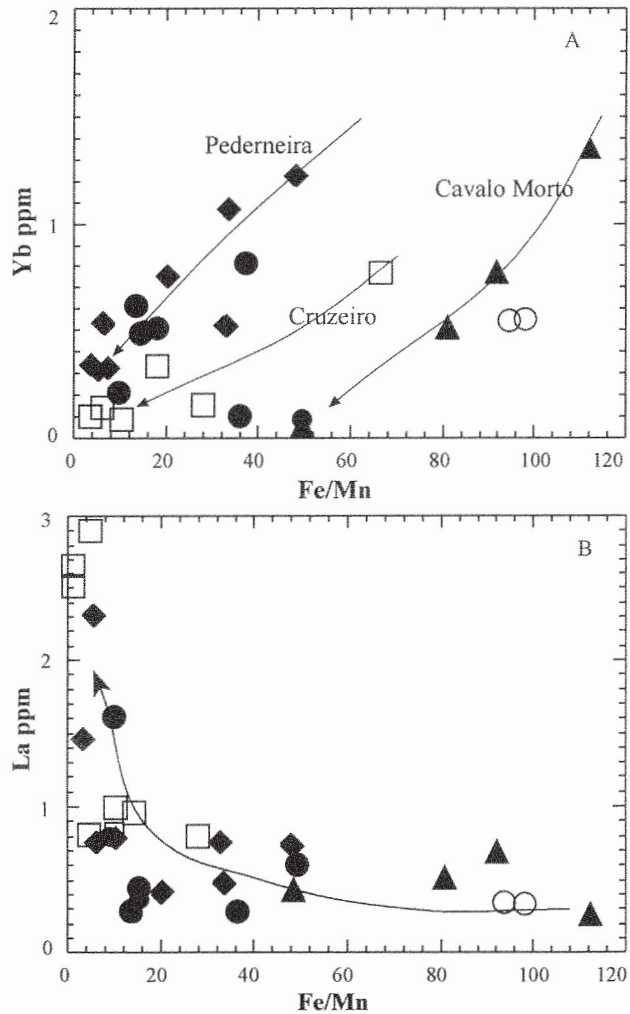


Fig. 6. Variation of Yb (ppm) and La (ppm) with Fe/Mn in tourmaline from some of the different types of pegmatites of the São José da Safira area
Used symbols as in Fig. 2

This interpretation is corroborated by the variation of the composition of columbite-tantalite and garnets evolving from ferrocolumbite ($Nb > Ta$) in the Zé Moreira pegmatite to true mangano-tantalite ($Nb < Ta$) found in Cruzeiro pegmatites.

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Chemické složení turmalínu v pegmatitech v oblasti São José da Safira, Minas Gerais, Brazílie

Minerály ze skupiny turmalínu (skoryl-elbait) se vyskytují v Li-pegmatitech v oblasti São José da Safira (pegmatitová provincie Oriental), Minas Gerais, Brazílie. Poměry Fe/Mn v turmalínu jsou srovnatelné s Fe/Mn poměry v columbit-tantalitu a granátech a postupně se snižují od berylových pegmatitů ke spodumenovým. Poměr Fe/Mn byl také zvolen jako kvalitativní index stupně frakcionace, který, jak se zdá, odráží regionální zónalnost pegmatitů kolem skrytého granitového tělesa. Obsahy Na a Li koreluji negativně s poměrem Fe/Mn. Obsahy REE, Nb, Co a Zn jsou ovlivňovány minerální asociací turmalínu.