

ZONED TOURMALINE FROM PEGMATITE BODIES OF ROMANIA

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Abstract

Microprobe analyses have been used in order to make a geochemical characterization of zoned tourmaline crystals from pegmatites of Carpathian Province (Romania); the analyses have been carried out on both core and rim of tourmaline grains. The geochemical approach shows that tourmaline belong to schorl-dravite solid solution series, with a higher amount of schorl molecule in the core of the grain. The chemical evolution from the core toward the rim of the tourmaline reveals three types of reactions in the process of tourmaline crystallization: deprotonation, uvite exchange and the reaction that generates an alkali-deficiency. The amount of Na (especially) and Ca in the fluid from which tourmaline crystallized controls the degree of occupancy of R1 structural positions. Tourmaline grains have the chemical features of tourmalines from Li-poor granitoids and associated pegmatites and aplites.

Key words: zoned tourmaline, major elements, pegmatite, microprobe, Romania

Introduction

This scientific approach deals with a geochemical characterization of zoned tourmaline developed in the rim band of some pegmatite bodies from Romania.

Tourmaline is one of the specific accessory minerals of granite pegmatites of Romania, its presence proving a volatile-rich (B, F, OH) environment of crystallization at some moments of pegmatites genesis. Tourmaline crystals develop in all bands of the

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zoned pegmatite bodies and associate mostly with quartz and feldspars, sometimes with muscovite; in the rim band of pegmatite bodies, tourmaline associates with garnet and biotite.

Site description

The pegmatite occurrences of Romania are associated with no exception to medium- and high-grade metamorphic rocks of Romanian Carpathians (Eastern, Southern and Western Carpathians). Early studies carried out on pegmatites revealed that they are spatially and genetically related to gneisses, migmatic gneisses, leptynites, migmatites (arterites, nebulites, agmatites) and gneissic or massive granitoids. Starting from the tectonic, structural and metalogenetic criteria, *Mârza* (1980) groups the granitic pegmatites of Romania in a so-called Carpathian Province; some studies emphasize that pegmatites have an anatectic origin, while others consider pegmatites as magmatic.



Fig. 1 Geological sketch of the Carpathian Province, showing the location of pegmatite subunits (modified from *Mârza*, 1985): 1-Preluca subunit; 2-Rodna subunit; 3-Gilău subunit; 4-Getic subunit. a-granitoids; b-low-grade metamorphic rocks; c-medium-grade metamorphic rocks.

The subunits of Carpathian Province are: Preluca and Rodna subunits (Eastern Carpathians), Getic subunit (Southern Carpathians) and Gilău-Muntele Mare subunit (Western Carpathians) (fig. 1); beyond these units, pegmatite bodies have been described as detached occurrences (i.e. Mănăstireni area – Western Carpathians; Almăjului Mts. area and the northern part of Mehedinți Mts. area – Southern Carpathians etc.).

In Preluca subunit, the pegmatite bodies are associated to the Răzoare (paragneisses with almandine and cyanite, limestones, dolomites with tremolite) and Preluca (paragneisses and micaschists with staurolite and cyanite) medium-grade metamorphic groups. The mineralogy of pegmatites consists of quartz, potassium feldspars (orthoclase, microcline), plagioclases (albite-oligoclase), muscovite and, rarely, biotite, tourmaline, garnets (almandine-spessartine), apatite.

The pegmatites of Rodna subunit are hosted by the medium-grade metamorphic rocks of Rebra group (paragneisses, micaschists). The pegmatites are made up of potassium feldspars (orthoclase, microcline), plagioclases (albite-oligoclase), muscovite and biotite; as subordinate minerals, tourmaline, garnets (almandine-spessartine terms), apatite and pyrite have been identified.

The Getic subunit is the most extent and the most important of the pegmatite subunits. The pegmatite bodies are associated to Getic metamorphic formations, especially to the Sebeș-Lotru group (granitoids, migmatites, gneisses and micaschists with almandine, cyanite, staurolite, sillimanite, as well as amphibolites). Mineralogically, pegmatites belong to the following types: ceramic, micaferous and pegmatites with niobo-tantalates. In this pegmatite subunit develops the largest pegmatite body of Romania (3500×100m), the pegmatite of Cataracte (potassium feldspars, sodium feldspars, quartz, muscovite, biotite and, rarely, garnets, tourmaline, apatite, beryl).

The pegmatite bodies of Gilău-Muntele Mare subunit are associated to: Someș medium-grade metamorphic group (granitoids, migmatites, leptynites, gneisses and micaschists) – Someșul Rece-Iara Valley pegmatite district; Baia de Arieș medium-grade metamorphic series (micaschists with almandine, staurolite, cyanite, as well as gneisses, amphibolites) – Geamăna-Măzăratu pegmatite district. The pegmatite mineralogy is simple and quite similar to the mineralogy of pegmatites from the others subunits: potassium feldspars, sodium feldspars, quartz, muscovite, subsequently tourmaline, molybdenite, ilmenite and rare-metals.

Materials and techniques

The geochemical approach of tourmalines lies on 24 analyses of major elements performed on samples from pegmatites of Getic (Cataracte), Preluca (Răzoare) and Gilău (Crișeni) subunits. The analyses have been carried out on zoned tourmaline crystals using a Cameca SX 50 microprobe (beam energy: 15kV; beam intensity: 10nA).

Zoned tourmaline crystals analyzed by mean of the microprobe have been selected using a polarizing microscope. Under polarized light, the color of zoned tourmaline grain changes from the rim (dark green), to the core (bluish).

In order to find out the pattern of chemical changes undergone by the tourmaline grains from the rim toward the core, four samples of tourmaline from each of the three occurrences have been analyzed. The microprobe analyses have been performed on both rim and core of the grain.

Results

Table 1 shows the average values of major elements content in respect of the grain zoning. The results of table 1 reveal that the content of TiO₂, Fe₂O₃, MgO, CaO, Na₂O increases from the core, toward the rim. On the contrary, the content of FeO, MnO as well as that of Al₂O₃ (except samples of Cataracte – Getic subunit) decreases in the same direction. The amount of Fe₂O₃ has been calculated using the method presented by *Cavarretta and Puxeddu* (1990), that includes the recalculation of ferrous and ferric iron in order to produce full T and R3 site occupancy.

Tab. 1. Average values of major elements contents in zoned tourmalines

	CC	CR	RC	RR	GC	GR
SiO ₂	35.34	35.55	35.10	35.05	35.44	34.97
TiO ₂	0.28	0.29	0.50	0.67	0.08	0.12
Al ₂ O ₃	34.76	34.89	34.37	34.05	37.24	33.47
Fe ₂ O ₃	3.78	4.31	4.15	4.27	3.19	3.92
FeO	7.03	5.22	5.77	5.36	9.22	6.62
MnO	0.10	0.07	0.07	0.06	0.15	0.03
MgO	2.91	3.85	3.83	4.18	1.77	4.00
CaO	0.16	0.31	0.36	0.44	0.29	0.44
K ₂ O	0.01	0.03	0.04	0.05	0.06	0.05
Na ₂ O	1.73	2.15	2.00	2.02	1.78	2.23
Structural formula on the basis of 24.5 oxygen atoms						
Si	5.813	5.781	5.759	5.751	5.676	5.794
AlT	0.187	0.219	0.241	0.249	0.324	0.206
Ti	0.035	0.035	0.062	0.083	0.010	0.015
Fe ³⁺	0.468	0.528	0.513	0.527	0.384	0.488
AlR3	5.498	5.437	5.426	5.390	5.606	5.497
Fe ²⁺	0.966	0.709	0.792	0.735	1.234	0.917

Mn	0.014	0.010	0.010	0.008	0.020	0.004
Mg	0.713	0.933	0.936	1.022	0.422	0.987
AlR2	1.053	1.030	0.978	0.944	1.099	0.832
R2	2.746	2.682	2.716	2.708	2.776	2.739
Ca	0.028	0.054	0.063	0.077	0.050	0.078
K	0.002	0.006	0.008	0.010	0.012	0.011
Na	0.550	0.676	0.634	0.641	0.551	0.714
R1	0.580	0.736	0.706	0.728	0.613	0.803

CC, CR – Cataracte core/rim (Getic subunit); RC, RR – Răzoare core/rim (Preluca subunit); GC, GR – Crișeni core/rim (Gilău subunit). Each result represents the average values of 4 analyses.

In order to make a more accurate geochemical characterization of zoned tourmaline the structural formula on the basis of 24.5 oxygen atoms has been performed (table 1). As shown in this table, vacancies in R2 site (0.224-0.318) as well as in R1 site (0.197-0.420) are revealed. Moreover, vacancies in R2 site are smaller in the core of tourmaline crystal than in its rim, while vacancies in R1 site are smaller in rims, than in the core of the grain.

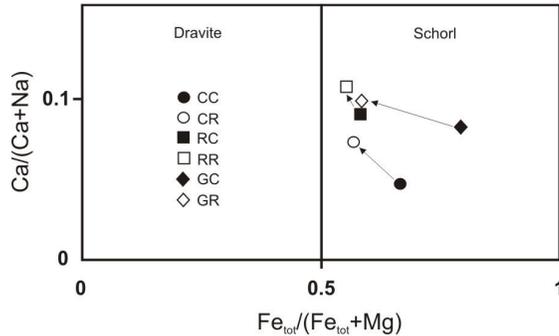


Fig. 2 Ca/(Ca+Na) vs. $Fe_{tot}/(Fe_{tot}+Mg)$ for zoned tourmaline of pegmatites from Romania. Fields as in Béziat *et al.* (1997). CC, CR, RC, RR, GC, GR as in table 1.

The chemical composition of either the core or the rim of zoned tourmaline is that of schorl term as reported in figure 2. However the tendency toward an enrichment of the rim in dravite molecule can be observed.

The diagram of figure 3 shows the plot of $(R1 + R2)$ vs. $R3$ (e.g. Gallagher, 1988) values of zoned tourmaline, wherein $R1 = (Na + Ca)$, $R2 = (Fe_{tot} + Mg + Mn)$ and $R3 = (Al + 1.33Ti)$.

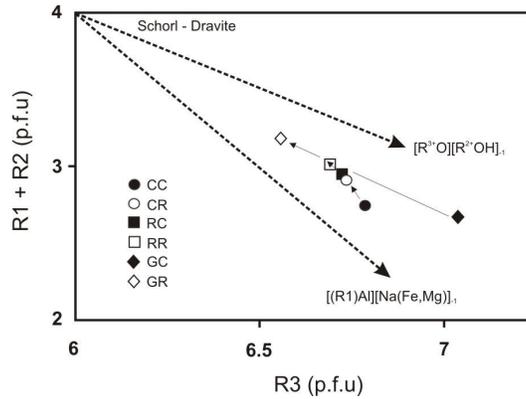


Fig. 3 (R1+R2) vs. R3 for zoned tourmaline of pegmatites from Romania. Fields as in *Gallagher (1988)*. CC, CR, RC, RR, GC, GR as in table 1.

On this diagram, the samples of pegmatite tourmaline plot in between vectors of the exchange $[R^{3+}O][R^{2+}OH]_{-1}$ (deprotonation reaction) and $[(R^1)Al][Na(Mg,Fe)]_{-1}$ that generates an alkali-deficient composition. The (R1+R2)/R3 ratio increases from the core of the tourmaline grain toward the rim; this direction suggests the change of the chemical features of zoned tourmalines in respect of uvite exchange vector: $[Ca(Fe,Mg)][NaAl]_{-1}$.

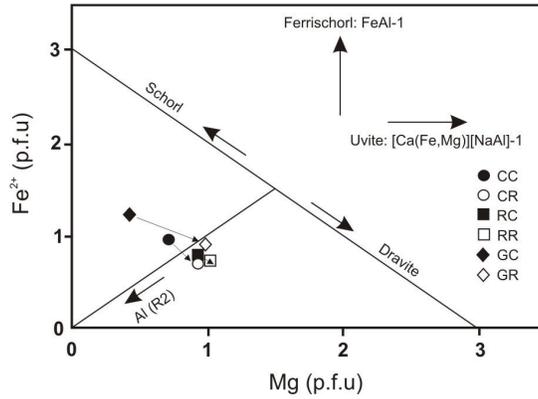


Fig. 4 Fe^{2+} vs. Mg for zoned tourmaline of pegmatites from Romania. Fields as in *London and Manning (1995)*. CC, CR, RC, RR, GC, GR as in table 1.

The plot of Fe^{2+} and Mg values in diagram of figure 4 reveals that the core of tourmaline grain is richer in Fe^{2+} , the participation of this element decreasing toward the rim of the crystal throughout a schorl-dravite substitution.

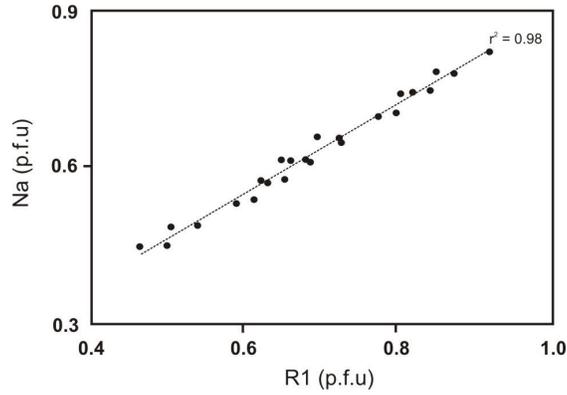


Fig. 5 Na vs. R1 for zoned tourmaline of pegmatites from Romania.

Diagram of figure 5 shows a strong positive correlation between the participation of Na in the structural formula and the sum of cations in R1 structural position; a quite evident positive correlation between Ca and the sum of cations in R1 structural position has been observed too.

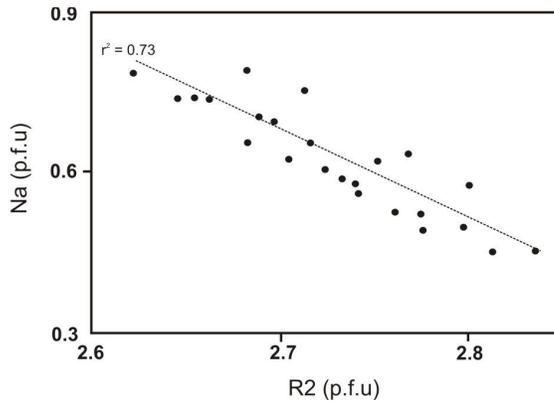


Fig. 6 Na vs. R2 for zoned tourmaline of pegmatites from Romania.

On the other hand, the plot of Na and R2 (sum of cations in R2 structural position) values is reported to diagram of figure 6 and reveals a negative correlation.

The plot of the average composition of zoned tourmaline in Fe_{tot} -Mg-Ca ternary diagram of *Henry and Guidotti* (1985) (figure 7) falls within the Li-poor granitoids and associated pegmatites and aplites field; the display of tourmaline samples shows also that they belong to schorl-dravite solid solution series.

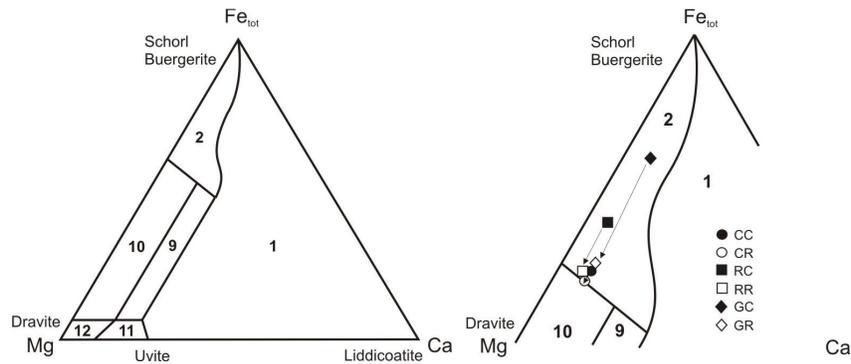


Fig. 7 Fe_{tot} -Mg-Ca for zoned tourmaline of pegmatites from Romania. Fields as in *Henry and Guidotti* (1985): 1-Li-rich granitoids and aplites; 2-Li-poor granitoids and associated pegmatites and aplites; 9-Ca-rich metapelites, metapsammites, calc-silicate rocks; 10-Ca-poor metapelites, metapsammites and quartz-tourmaline rocks; 11-metacarbonate rocks; 12-metaultramafic rocks. CC, CR, RC, RR, GC, GR as in table 1.

Discussion and conclusion

Microprobe analyses reveal that zoned tourmaline of pegmatite from the three subunits of the Carpathian Province are intermediate between the end-members of schorl-dravite solid solution series.

The composition of both core and rim of the tourmaline crystals is that of the schorl term; however, the amount of schorl molecule is larger in the core of the grain than in its rim, showing an evolution of the chemical composition of the fluid that generated tourmaline toward a Mg-enriched one. In the same direction in which the content of Mg increases, the content of Fe^{2+} decreases, suggesting a schorl-dravite substitution.

The evolution of $(R1+R2)/R3$ ratio between the core and the rim of zoned tourmaline shows the development of three type of reactions in the process of tourmaline crystallization: reaction of deprotonation, reaction of uvite exchange and reaction that generates an alkali-deficiency.

The degree of occupancy of R1 structural position is related to the amount of Na especially and Ca in the fluid from which tourmaline crystallized; the participation of K in R1 position seems to be rather constant.

The substitution of some divalent cations by Al in R2 structural positions, coupled with loss of Na from R1 sites for charge balance reasons correspond to an alkali-deficient substitution; the quite negative correlation between Na and the charge of R2 structural position supports the assumption of such a substitution.

However, the deficiency in R2 sites could be only apparent as *Foit and Rosenberg* (1977) stressed; these authors believe that some amount of divalent cations that actually penetrate the R1 site, are in fact erroneously attributed to R2 site.

Further indications of the chemical evolution of zoned tourmalines from pegmatites of Carpathian Province are given by the Fe_{tot} -Mg-Ca ternary diagram of *Henry and Guidotti* (1985). The trend of the tourmaline composition is parallel to Fe_{tot} -Mg side which means that pegmatite tourmaline belongs to schorl-dravite solid solution series. Moreover, while the core of tourmaline grains has the chemical features of tourmalines from Li-poor granitoids and associated pegmatites and aplites, the rim of tourmaline samples has chemical features near to tourmaline from Ca-poor metapelites, metapsammites and quartz-tourmaline rocks.

References

- Béziat, D., Bourges, F., Debat, P., Lancelot, M. P., Lompo, M., Martin, F., Nikiéma, S., Tollon, F., 1997. Tourmaline and associated gold deposits in Birimian greenstone belts from Burkina Faso. Abstracts of Tourmaline 1997 - International Symposium on Tourmaline, Brno, 5-6.
- Cavarretta, G., Puxeddu, M., 1990. Schorl-Dravite-Ferridravite Tourmalines Deposited by Hydrothermal Magmatic Fluids during Early Evolution of the Larderello Geothermal Field, Italy. *Econ. Geology*, **85**, 1236-1251.
- Foit, F., F.Jr., Rosenberg, P., E., 1977. Coupled substitutions in the tourmaline group. *Contr. Mineralogy Petrology*, **62**, 109-127.
- Gallagher, V., 1988. Coupled substitutions in schorl-dravite tourmaline. New evidence from SE Ireland. *Mineralogical Magazine*, **52**, 637-650.
- Hawthorne, F., C., MacDonald, D., J., Burns, P., C., 1993. Reassignment of cation site occupancies in tourmaline: Al-Mg disorder in the crystal structure of dravite. *Am. Mineralogist*, **78**, 265-270.
- Henry, D., J., Guidotti, C., V., 1985. Tourmaline as a petrogenetic indicator mineral: An example from the staurolite-grade metapelites of NW Maine. *Am. Mineralogist*, **70**, 1-15.
- Hughes, J., M., Ertl, A., Dyar, M., D., Grew, E., S., Shearer, C., K., Yates, M., G., Guidotti, C., V., 2000. Tetrahedrally coordinated boron in a tourmaline: boron-rich olenite from Stoffhütte, Koralpe, Austria. *Can. Mineralogist*, **38**, 861-868.
- London, D., Manning, D., A., C., 1995. Chemical variation and significance of tourmaline from Southwest England. *Econ. Geol.*, **90**, 495-519.
- Mârza, I., 1985. Genesis of ore deposits of magmatic origin, vol. 2 (In Romanian), Publishing House Dacia, Cluj-Napoca, 331p.