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Chemical Variations in Tourmalines from Pegmatite Occurrences in Chalkidiki Peninsula, Northern Greece

by A. Kassoli-Fournaraki¹

Abstract

Tourmalines from pegmatitic veins crosscutting basic and ultrabasic rocks in the localities of Vavdos and Psakoudia (Chalkidiki peninsula, N. Greece) are examined in terms of their chemistry and conditions of formation. The tourmalines of both areas display optical zoning with considerable chemical variations from core to rim. According to their chemistry they belong to the schorl-dravite solid solution, the Vavdos tourmalines being richer in the dravitic member whereas those from Psakoudia are schorl enriched. Substitutions towards alkali-free or proton deficient members are observed in the tourmalines of both localities being more pronounced in Vavdos where vacancies in alkali sites dominate. A good correlation is also observed between Al_y and $(Mg + Fe)$ indicating a possible substitution of divalent cations by Al.

Al-Fe_(tot)-Mg, Mg-Fe_(tot)-Ca ternary diagrams and FeO/(FeO + MgO) values of the examined tourmalines as well as geological observations seem to exclude a granitic origin of the host pegmatitic veins. A probable origin might be from a pegmatitic residual magma rich in boron which resulted from anatexis of silica-rich sea-floor sediments intruding the ophiolites. The pegmatitic fluids liberated elements from the surrounding rocks which were fixed in the tourmaline structure. Furthermore, differences in the crystallization conditions (rate of crystallization, temperature, pressure and equilibration of the crystallizing material) have resulted in a complicated chemical zoning of the tourmaline grains.

Keywords: pegmatite, tourmaline, chemical zonation, schorl-dravite, Vavdos, Psakoudia, Greece.

Introduction

Tourmaline is a boro-silicate mineral with chemical variability, found in different petrologic environments due to its wide range of stability. Tourmaline provides useful information about the environment and conditions of deposition and hence its significance as a petrogenetic indicator has gained recently more and more attention (e.g. MANNING, 1982; SHIBUE, 1984; SHEARER et al., 1984; TAYLOR and SLACK, 1984; HENRY and GUIDOTTI, 1985; JOLLIFF et al., 1986).

Studies on its crystal-chemistry have contributed in understanding the various substitutional mechanisms in its structure (FORTIER and DONNAY, 1975; FOIT and ROSENBERG, 1977; GALLAGHER, 1988). Furthermore, variability in its crystal-chemistry reflects physical and chemical changes during crystallization of the enclosing rock.

In this study tourmalines from pegmatite veins crosscutting basic and ultrabasic igneous rocks in the Psakoudia and Vavdos areas of Chalkidiki (N. Greece) are examined for the first time in terms of their crystal chemistry and an effort is attempted to explain the conditions of their formation.

Geologic setting and petrography of the pegmatite veins

The examined tourmaline pegmatites occur as veins in the ultrabasic sequence of Vavdos and in the gabbroic bodies of Psakoudia in the Chalkidiki peninsula (Fig. 1). These basic and ultrabasic bodies belong to the latest Middle-earliest Upper Jurassic discontinuous ophiolite sequence (MUSALLAM and JUNG, 1986), which extends from Thessaloniki to Sithonia and is juxtaposed to the

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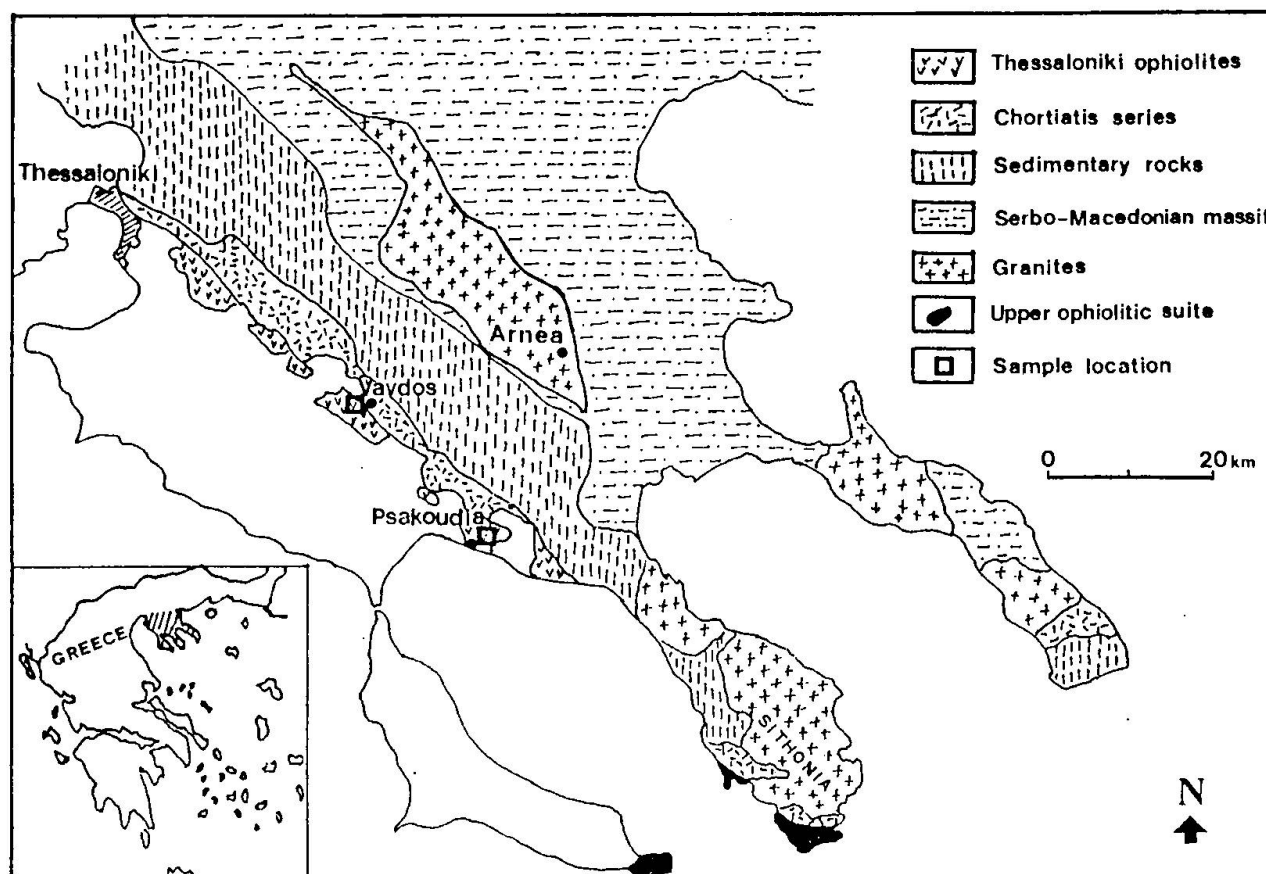


Fig. 1 Geological sketch map of Chalkidiki (simplified after Kockel et al., 1971).

Chortiatis magmatic suite, within the limits of the Circum-Rhodope Belt. The 5 km thick Jurassic Chortiatis magmatic suite occurs at the western border of the Serbomacedonian massif and consists mainly of tonalites-trondhjemites and dioritic petrographic types metamorphosed in the greenschist facies. The juxtaposed ophiolitic sequence displays similar lateral variations and is composed of gabbros, gabbro-norites and peridotites. MUSSALLAM and JUNG (1986) suggest a multi-staged fractional melting of a mafic source for the formation of the salic Chortiatis sequence. They accept an immature island-arc setting for the salic rocks above a NE-dipping subduction zone and they attribute variations in lithology to progressive attenuation of the continental crust. The corresponding variations displayed by the ophiolites are attributed to a change in the plate motion.

The Vavdos pegmatites are composed of quartz, microcline, plagioclase, tourmaline while the Psakoudia ones contain quartz, orthoclase (often kaolinized), plagioclase and tourmaline. Muscovite contributes as a secondary mineral in very minor quantities in the pegmatites of both localities.

Alteration zones between the pegmatite veins and the ultramafic wall rocks have been observed and examined by BURGATH et al. (1980). The reactions included transformation of quartz, microcline, plagioclase, olivine and orthopyroxene, and formation of tourmaline, phlogopite (now vermiculite), clino-amphibole and talc. According to the above authors the pegmatite veins with their contact rims in some cases provided possibilities for the emplacement of magnesite deposits along their selvages.

Morphology and optical zoning of the examined tourmalines

The investigated tourmalines occur as black sub-hedral elongated grains and as skeletal crystals. The Vavdos tourmalines have a grain size ranging in length from some mm up to around 3 cm; these last megacrystals display a diameter of about 1.5 cm in transverse sections. Those in Psakoudia pegmatites show grains with dimensions much smaller, from some mm up to 1 cm. The skeletal type of formation in this last locality is the most frequent.

The skeletal growth of crystals in both localities may be attributed to rapid crystallization.

Almost all the examined tourmaline grains display a concentric optical zoning which is generally distinguished into two broad zones of varying extent and shape. Colors range from olive-green cores with brown-green rims for the Vavdos tourmalines, to blue-green cores with green rims for the Psakoudia ones. The color change from core to rim involves sharp optical discontinuities for the grains of both areas. In Vavdos, tourmaline grains are sometimes cored with K-feldspar or quartz.

Crystal-chemistry of tourmaline

The general formula of tourmaline can be written as $XY_3Z_6Si_6B_3O_{27}(OH, O, F)_4$.

The polyhedral X site is usually occupied by Na. Variable amounts of Ca, K and Mg are also found. The Z octahedral site is occupied mainly by Al while the larger Y octahedral site by Mg, Fe^{2+} , Fe^{3+} , Mn, Cr, Li etc.

The principal end-members are:

| | |
|--------------|--|
| elbaite | $Na(Li, Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$ |
| schorl | $Na_3Fe^{2+}Al_6(BO_3)_3Si_6O_{18}(OH)_4$ |
| dravite | $NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$ |
| buergerite | $NaFe^{3+}_3Al_6(BO_3)_3Si_6O_{21}F$ |
| tsilaisite | $NaMn_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$ |
| ferridravite | $NaMg_3Fe^{3+}_6(BO_3)_3Si_6O_{18}(OH)_4$ |
| uvite | $CaMg_3(MgAl_5)(BO_3)_3Si_6O_{18}(OH)_4$ |
| liddicoatite | $Ca(Li, Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$ |

The most frequent miscibility series are those of schorl-dravite and schorl-elbaite. However, between dravite and elbaite there is a miscibility gap (DEER et al., 1962).

Generally, tourmaline withstands extensive substitutions. FOIT and ROSENBERG (1977) suggested two types for the schorl-dravite series: a dehydroxylation-type substitution $(OH)^- + R^{2+} = R^{3+} + O^{2-}$ and an alkali-defect type substitution $Na^+ + R^{2+} = R^{3+}$, resulting in proton-deficient and alkali-deficient end-members respectively. According to the above authors the proton-loss type is more common than the alkali-deficient one.

Analytical procedures and chemical results

Step scanning analysis of optically zoned tourmaline grains from the pegmatites of the two areas was carried out in a CAMECA CAMEBAX probe, using an energy dispersive spectrometer, at the department of Geology, University of Manchester, England. Operating conditions were 15 kV accelerating potential and 3 nA beam current. All analyses were made using 100 second counting times. Natural minerals or pure metals were used as standards. Elements concentrations have been calculated with a ZAF-4/FLS software.

Considerable composition variation occurs for FeO, MgO, CaO, Al_2O_3 and MnO between the two areas.

The results of the averaged analyses on six representative tourmaline crystals are presented in Table 1 for the Vavdos tourmalines and Table 2 for the Psakoudia ones (the detailed analyses are available from the author on request). Boron can not be detected by the electron probe microanalyzer. A theoretical calculation of boron contents may be obtained on the assumption that the atomic number of boron is half of the atomic number of silicon.

Cations were calculated on the basis of 31 oxygens assuming three B atoms and four hydroxyl anions, so that the recalculation was actually made on the basis of 24.5 oxygen atoms. Fe was considered to be present as Fe^{2+} , though a small amount of Fe^{3+} was determined by Mössbauer spectra (work in preparation). The further variations of the elements inside cores and rims are illustrated in Figs. 3 and 4.

In the site filling a model equal to that of FOIT and ROSENBERG (1977), and HENRY and GUIDOTTI (1985) was followed with 6 Al atoms in the octahedral Z site. As regards Si distribution the model of GALLAGHER (1988) was adopted considering originally 6 Si in the tetrahedral site but in cases that Si was less, excess Al over 6 was used to complete the T site. The remaining Al was used in the octahedral Y site. In cases that Si was exceeding 6 atoms, the remaining amount after filling the T site was placed in the Y site (this is not so clearly seen in the two Tables since Si value in each analysis represents average composition).

The above model of site filling assumes that Al substitutes for Si in the studied tourmalines. An opposite opinion has been expressed by JOLLIFF et al. (1986) who support a full occupation of the tetrahedral site by Si, suggesting a normalization of the probe analyses to 6 Si.

| | Grain PVa | | Grain PVb | | Grain PVC | |
|--------------------------------|-----------|---------|-----------|---------|-----------|---------|
| | core (4) | rim (4) | core (6) | rim (6) | core (3) | rim (3) |
| SiO ₂ | 37.22 | 36.67 | 37.70 | 37.40 | 37.31 | 37.46 |
| TiO ₂ | 0.29 | 0.51 | 0.33 | 0.48 | 0.47 | 0.60 |
| Al ₂ O ₃ | 33.90 | 34.00 | 36.45 | 35.76 | 35.82 | 35.88 |
| FeO* | 7.90 | 8.05 | 6.81 | 6.63 | 6.79 | 6.56 |
| MnO | 0.06 | 0.07 | 0.03 | 0.03 | 0.03 | 0.00 |
| MgO | 5.06 | 5.13 | 4.61 | 4.95 | 4.89 | 5.38 |
| NiO | 0.10 | 0.09 | 0.04 | 0.07 | 0.05 | 0.00 |
| Cr ₂ O ₃ | n.d.** | n.d. | 0.04 | 0.04 | 0.00 | 0.08 |
| CaO | 0.24 | 0.52 | 0.09 | 0.20 | 0.20 | 0.16 |
| Na ₂ O | 2.09 | 2.13 | 1.74 | 1.91 | 1.99 | 2.48 |
| K ₂ O | 0.03 | 0.05 | 0.04 | 0.03 | 0.03 | 0.09 |
| Total | 86.89 | 87.22 | 87.88 | 87.50 | 87.58 | 88.69 |

Cations on the basis of 24.5 oxygens.

| | | | | | | |
|--------------------|-------|-------|-------|-------|-------|-------|
| Si _T | 6.000 | 5.935 | 5.964 | 5.948 | 5.941 | 5.902 |
| Al _T | - | 0.065 | 0.036 | 0.052 | 0.059 | 0.098 |
| Al _Z | 6.000 | 6.000 | 6.000 | 6.000 | 6.000 | 6.000 |
| Al _Y | 0.464 | 0.421 | 0.762 | 0.651 | 0.663 | 0.566 |
| Fe | 1.069 | 1.089 | 0.901 | 0.882 | 0.905 | 0.865 |
| Mn | 0.008 | 0.009 | 0.004 | 0.004 | 0.004 | 0.000 |
| Mg | 1.221 | 1.238 | 1.088 | 1.172 | 1.161 | 1.263 |
| Ti | 0.035 | 0.062 | 0.040 | 0.071 | 0.056 | 0.071 |
| Ni | 0.010 | 0.012 | 0.006 | 0.009 | 0.006 | 0.001 |
| Cr | - | - | 0.005 | 0.005 | 0.000 | 0.010 |
| Si _Y | 0.025 | - | - | - | - | - |
| Y _{total} | 2.832 | 2.831 | 2.806 | 2.792 | 2.795 | 2.776 |
| Ca | 0.042 | 0.091 | 0.015 | 0.034 | 0.035 | 0.026 |
| Na | 0.656 | 0.668 | 0.534 | 0.591 | 0.615 | 0.757 |
| K | 0.006 | 0.010 | 0.007 | 0.006 | 0.011 | 0.017 |
| X _{total} | 0.704 | 0.769 | 0.556 | 0.631 | 0.661 | 0.800 |

Each analysis represents the average of the number of spots analyzed given in the parenthesis.

* Total iron as FeO

**n.d.=not determined

Tab. 1 Microprobe analyses of colored zones of Vavdos tourmalines.

| | Grain PSa | | Grain PSb | | Grain PSc | |
|--------------------------------|-----------|---------|-----------|---------|-----------|---------|
| | core (5) | rim (5) | core (2) | rim (2) | core (3) | rim (3) |
| SiO ₂ | 35.80 | 35.68 | 36.23 | 35.34 | 36.82 | 36.00 |
| TiO ₂ | 0.07 | 0.71 | 0.61 | 1.02 | 0.04 | 0.18 |
| Al ₂ O ₃ | 33.40 | 31.43 | 33.22 | 30.88 | 33.99 | 33.11 |
| FeO* | 11.91 | 11.26 | 11.92 | 12.75 | 10.73 | 11.50 |
| MnO | 0.31 | 0.28 | 0.26 | 0.33 | 0.10 | 0.24 |
| MgO | 3.00 | 4.42 | 3.44 | 3.47 | 3.45 | 3.26 |
| CaO | 0.56 | 0.81 | 0.47 | 0.84 | 0.19 | 0.58 |
| Na ₂ O | 2.00 | 2.14 | 1.98 | 2.10 | 1.91 | 2.04 |
| K ₂ O | 0.03 | 0.05 | 0.05 | 0.08 | 0.02 | 0.03 |
| Total | 87.03 | 86.78 | 88.18 | 86.81 | 87.25 | 86.94 |

Cations on the basis of 24.5 oxygens.

| | | | | | | |
|--------------------|-------|-------|-------|-------|-------|-------|
| Si _T | 5.927 | 5.939 | 5.922 | 5.935 | 5.998 | 5.955 |
| Al _T | 0.073 | 0.061 | 0.078 | 0.065 | 0.002 | 0.045 |
| Al _Z | 6.000 | 6.000 | 6.000 | 6.000 | 6.000 | 6.000 |
| Al _Y | 0.443 | 0.105 | 0.323 | 0.046 | 0.538 | 0.411 |
| Fe | 1.648 | 1.567 | 1.629 | 1.792 | 1.464 | 1.591 |
| Mn | 0.043 | 0.040 | 0.036 | 0.047 | 0.007 | 0.033 |
| Mg | 0.740 | 1.095 | 0.839 | 0.868 | 0.840 | 0.803 |
| Ti | 0.025 | 0.089 | 0.073 | 0.129 | 0.005 | 0.023 |
| Si _Y | - | - | - | - | - | - |
| Y _{total} | 2.899 | 2.896 | 2.900 | 2.882 | 2.854 | 2.861 |
| Ca | 0.100 | 0.144 | 0.083 | 0.152 | 0.033 | 0.103 |
| Na | 0.643 | 0.692 | 0.627 | 0.684 | 0.605 | 0.656 |
| K | 0.006 | 0.011 | 0.010 | 0.017 | 0.004 | 0.005 |
| X _{total} | 0.749 | 0.847 | 0.720 | 0.853 | 0.642 | 0.764 |

Each analysis represents the average of the number of spots analyzed given in the parenthesis.

*Total iron as FeO.

Tab. 2 Microprobe analyses of colored zones of Psakoudia tourmalines.

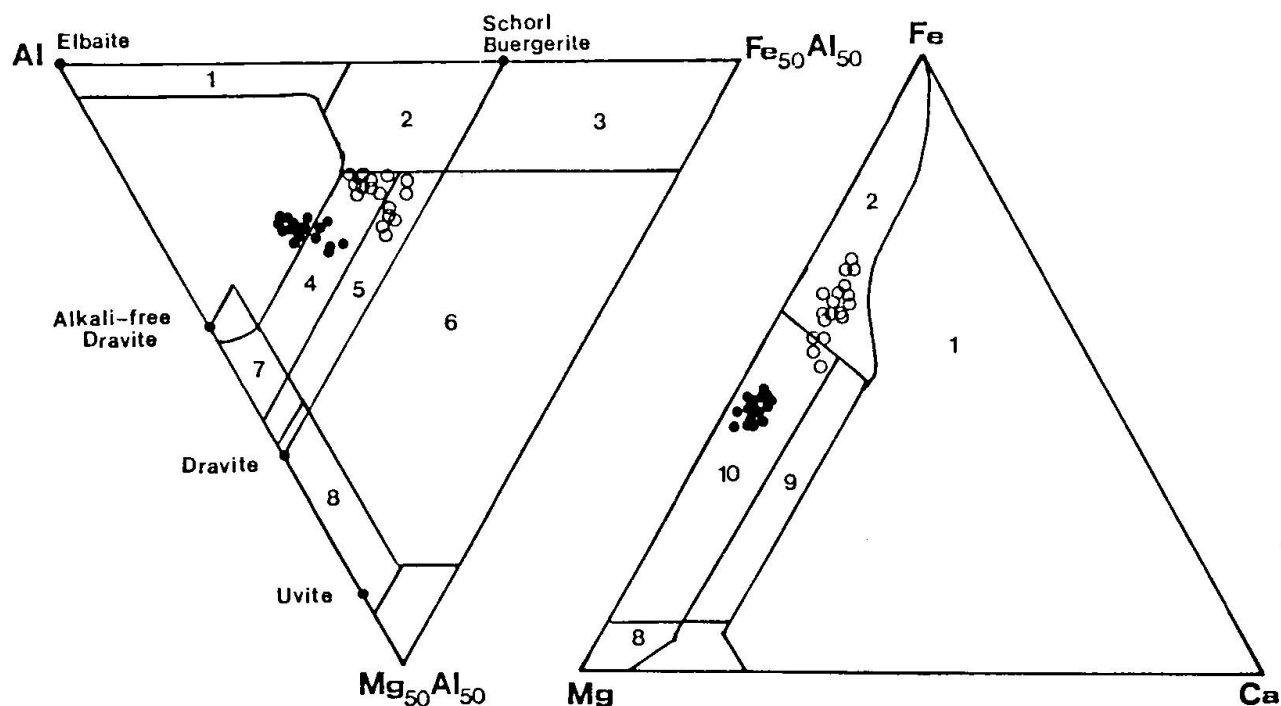


Fig. 2 Al-Fe_(tot)-Mg and Mg-Fe_(tot)-Ca diagrams (in molecular proportions) for tourmalines from Vavdos and Psakoudia pegmatites (after HENRY and GUIDOTTI, 1985 and PLIMER and LEES, 1988).

(1) Li-rich granitoid pegmatites and aplites, (2) Li-poor granitoids and their associated pegmatites and aplites, (3) Fe³⁺-rich quartz-tourmaline rocks (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) Fe³⁺-rich quartz-tourmaline rocks, calc silicate rocks and metapelites, (7) Low-Ca metaultramafics and Cr, V-rich metasediments, (8) Metacarbonates and metapyroxenites, (9) Ca-rich metapelites and (10) Ca-poor metapelites, metapsammities and quartz-tourmaline rocks.

- Vavdos tourmalines
- Psakoudia tourmalines

Cores and rims were plotted with the same symbols since it was difficult to distinguish between them due to great overlapping.

From Tables 1 and 2 results that the examined tourmalines of both areas belong to the schorl-dravite solid solution, the Vavdos tourmalines being richer in the dravitic member (Mg > Fe) whereas the Psakoudia ones schorl richer (Fe > Mg). The higher values in MnO of the Psakoudia tourmalines are commensurated with the higher FeO amounts.

FeO/FeO + MgO ranges from 0.55 to 0.61 for the Vavdos tourmalines and from 0.72 to 0.80 for the Psakoudia ones.

Correlation of tourmaline chemistry versus the host rock type

HENRY and GUIDOTTI's (1985) Al-Fe_(tot)-Mg and Mg-Fe_(tot)-Ca ternary diagrams were used to verify the type of the rock in which the tourmalines were formed (Fig. 2). The higher Al₂O₃ and MgO values of the Vavdos tourmalines in contradiction to the higher FeO and CaO values of the Psakoudia ones may reflect Al, Mg and Fe

phases respectively in their environment of formation.

Furthermore, cores appear enriched in Al comparing to rims, with small enrichment in Vavdos samples and larger enrichment in Psakoudia ones. It is also noticeable that in the Al-Fe-Mg diagram the majority of Vavdos tourmaline plots occur in the elbaite-dravite field where, as it is known, there is a miscibility gap (DONNAY and BARTON, 1972).

Concerning the type of rock where the tourmalines were formed we notice that the Psakoudia tourmalines plot in the fields of Li-poor granitoids (field 2) and in those of metapelites and metapsammities coexisting or not with an Al-saturating phase (fields 4 and 5). The Vavdos tourmalines plot in the field of Ca-poor metapelites, metapsammities and quartz-tourmaline rocks (field 10) and partly in the field of metapelites and metapsammities coexisting with an Al-saturating phase (field 4). Part of the Vavdos tourmalines, as mentioned before, plot in the elbaite-dravite field.

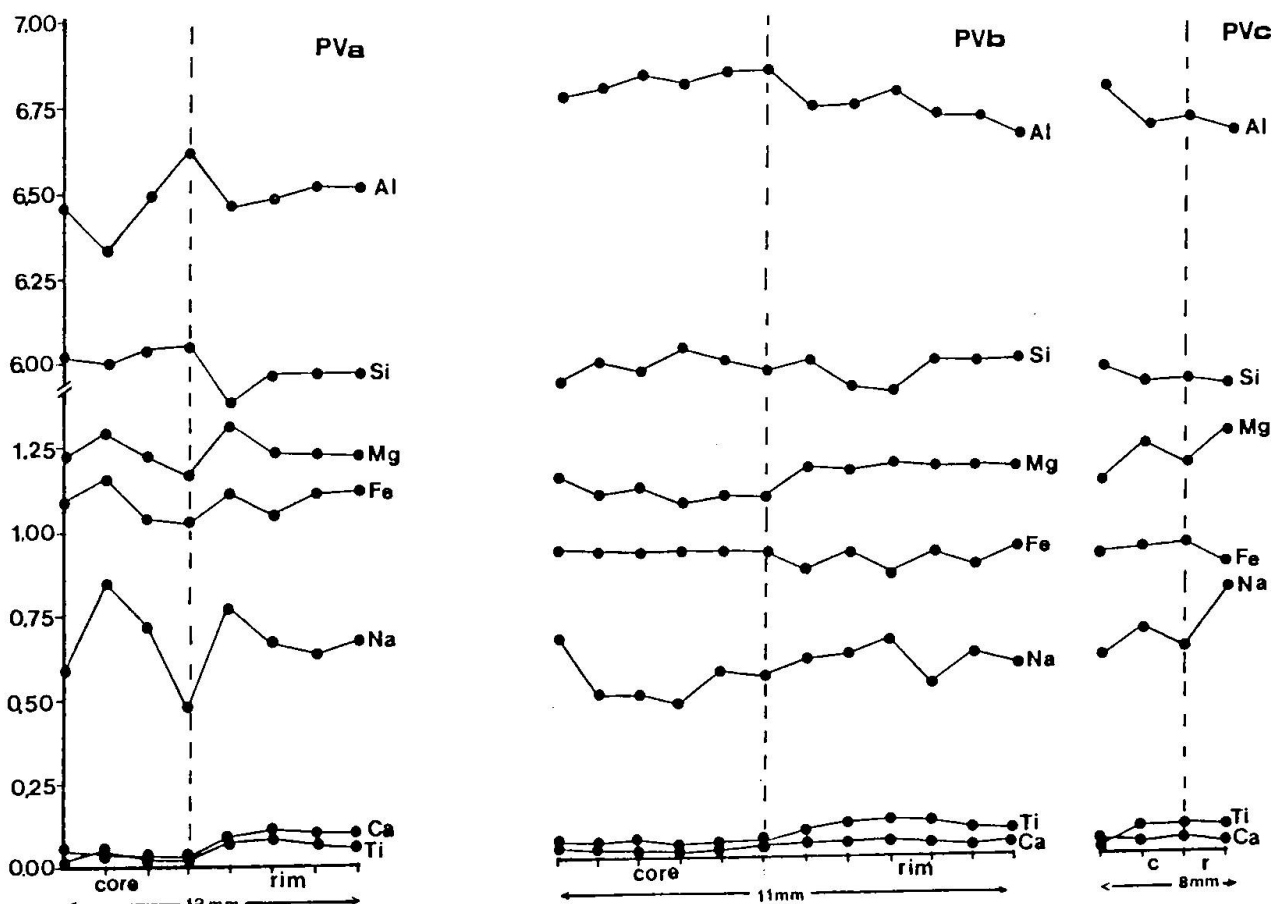


Fig. 3 Compositional variation in three tourmaline grains from Vavdos pegmatites.

According to the above correlation of tourmaline chemistry versus the host type, a granitic origin of the pegmatites in discussion seems to be excluded.

Chemical zoning

Chemical zoning displays peculiarities not only between the tourmalines of the two areas but even between the tourmalines of the same area and sometimes between grains of the same thin section, indicating different environmental conditions of growing for each case.

In general, the tourmalines of both areas display chemically discontinuous core-to-rim zoning patterns. There is a distinct change during transition from core to rim for nearly all the elements, corresponding to optical zoning. Furthermore characteristic chemical discontinuities are revealed inside core zones and rim zones, which are not optically discernible (Figs. 3 and 4). These discontinuities based on the analysed points of each crystal under the same analytical conditions seem to be characterized by abrupt changes in nearly all the elements. The main irregularities are those expressed by Na for the Vavdos tourmalines and by Al, Mg and Na for the Psakoudia ones.

Considering the tourmaline composition from each area separately we distinguish the following (Figs. 3 and 4):

In the core to rim compositional profiles from three grains of Vavdos pegmatites (Fig. 3) the cations show differences from grain to grain, even in the same section (grains PVb and PVc). Only Ca and Ti display a possible constant core to rim increase. If we ignore the irregularities inside core and rim zones, there is a general trend for Al_y and Si to increase from the center to the outer parts of the core and decrease in the rim. Nearly opposite trends are expressed by Fe and Mg, though the case is not so for Fe in grain PVc. Also in grain PVa for any abrupt decrease of Al and Si (both in core and rim) there is a corresponding increase in Mg, Fe and Na. Similar trends are noticed for the same cations of PVC except for Fe, whereas PVb does not show such relations. This means that the environmental conditions of formation were nearly equal for PVa and PVC and different for PVb.

Figure 4 presents the core to rim compositional profiles for three grains from Psakoudia pegmatites. As in Vavdos, there is again an increase for Ti and Ca from core to rim but there are differences for the rest of the cations. There

is a general trend for Al to decrease from core to rim in all three grains (although inside cores and inside rims there exist further irregularities) but the other cations show differences from grain to grain. Fe values are lower in core and higher in rim for grains PSb and PSc while for PSa the opposite happens. Mg increases from core to rim in PSa and PSb while it decreases in PSc. Na displays many irregularities while Si seems to be more enriched in rim for grains PSa and PSb and more depleted for PSc. Finally, in all three grains there is a general negative correlation between Al-Si and Fe-Mg.

Variations in chemistry for the tourmalines of both areas do not seem to explain the color variation in the zoned tourmaline grains.

Site occupancy and coupled substitutions

The total number of cations in the Y site (Tab. 1 and 2) implies vacancies in this octahedral site.

Al of the Y site correlates quite well with (Mg + Fe). This correlation is revealed in Figs. 5 and 6 where the core-to-rim relation of Al_Y versus (Fe + Mg) of the tourmalines from Vavdos and Psakoudia is presented. GALLAGHER (1988) pointed out that there is indeed a good correlation between these two parameters indicating that Al_Y is controlled by the calculated Si deficiency and consequently Si is substituted by Al despite theoretical objections. As it results from Figs. 5 and 6, Al_Y and (Mg + Fe) correlate well indicating that there is a possible substitution of divalent cations by Al in the investigated tourmalines and that Al_Y is independent of the normalization scheme.

The positive charge which results from Al → Fe, Mg substitutions is balanced by the two coupled substitutions, alkali-defect and proton-loss. FOIT and ROSENBERG (1977) refer that proton-loss substitution is more important.

The alkali-defect and proton-loss substitutions in tourmalines from Vavdos and Psakoudia,

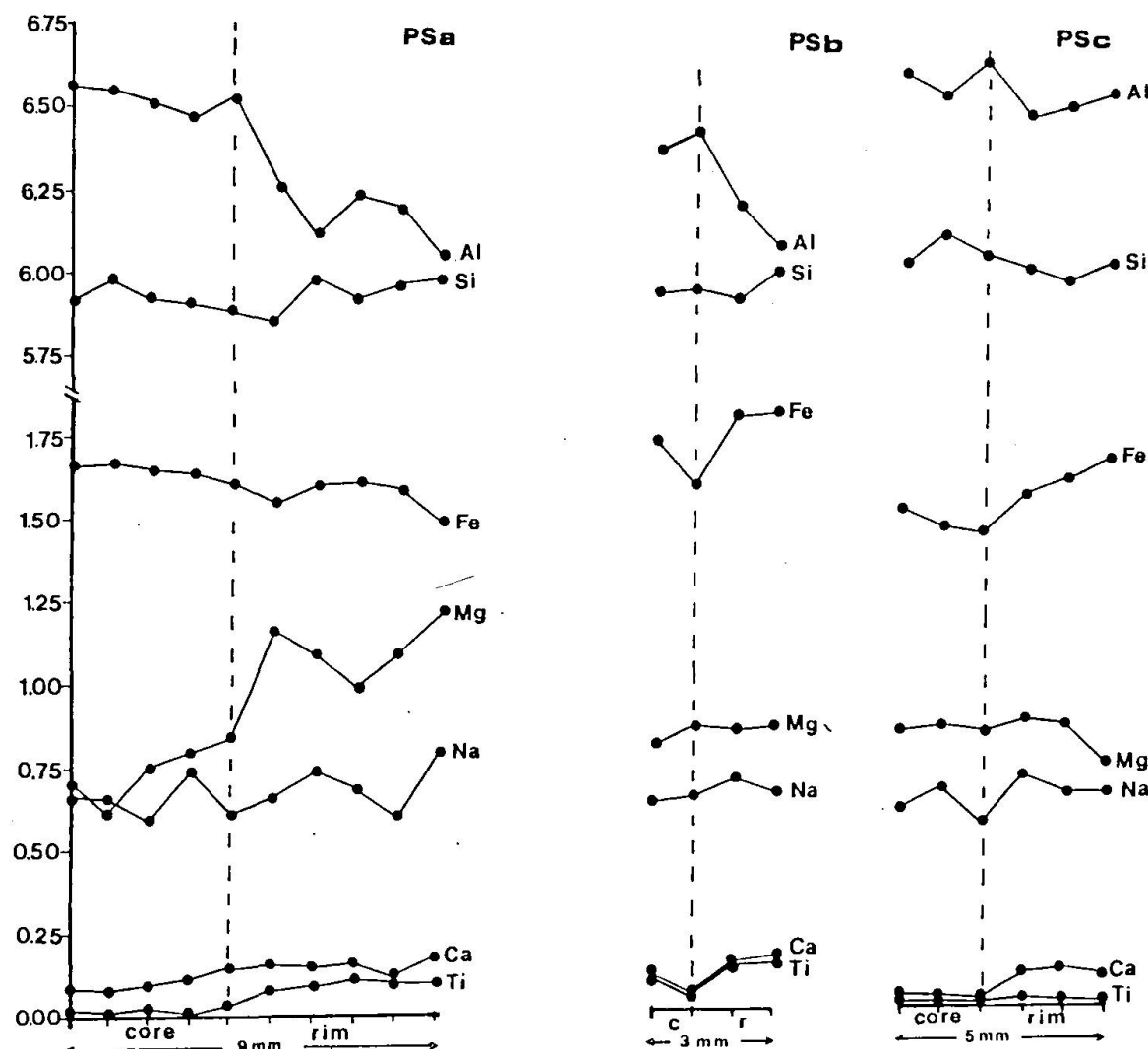


Fig. 4 Compositional variation in three tourmaline grains from Psakoudia pegmatites.

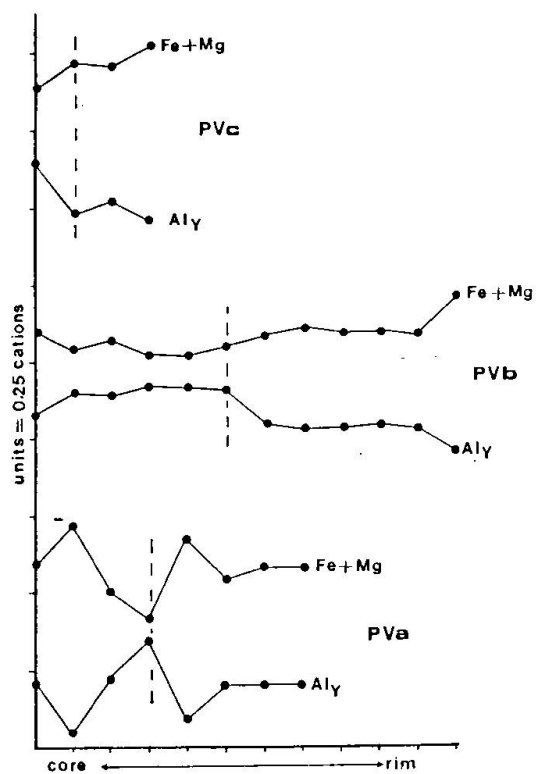


Fig. 5 Al_v versus $Fe + Mg$ for the three core-to-rim analyzed tourmaline grains from Vavdos pegmatites.

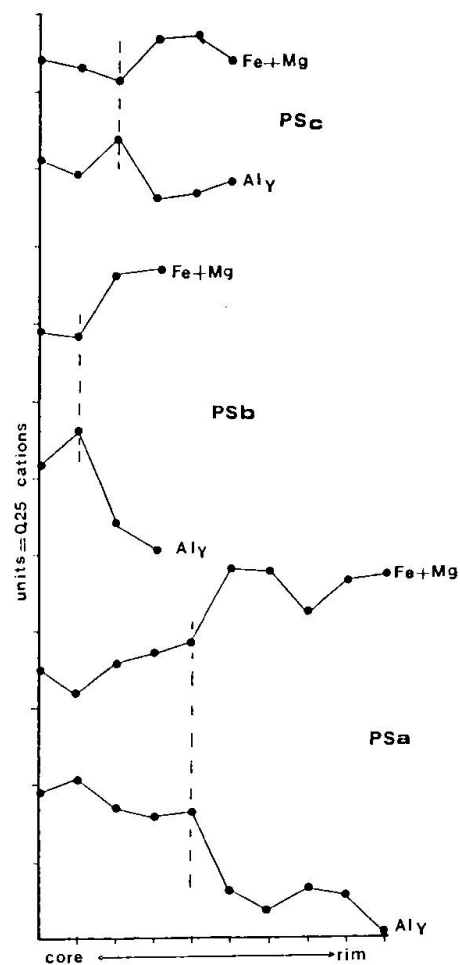


Fig. 6 Al_v versus $Fe + Mg$ for the three core-to-rim analyzed tourmaline grains from Psakoudia pegmatites.

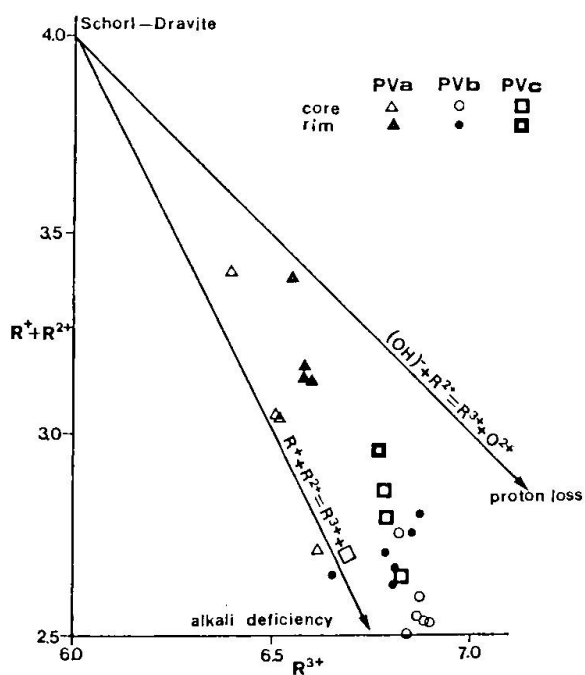


Fig. 7 Alkali-defect versus proton-loss substitution in Vavdos tourmaline grains.

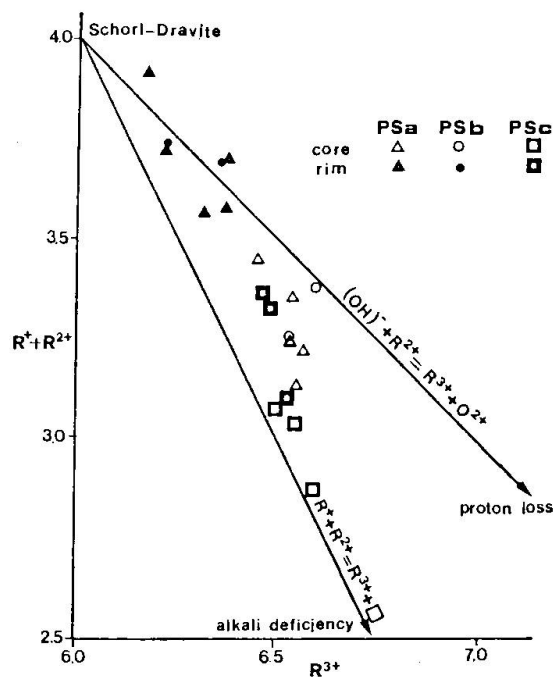
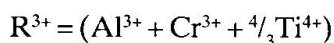
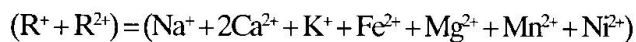


Fig. 8 Alkali-defect versus proton-loss substitution in Psakoudia tourmaline grains.

indicating the existence of considerable coupled substitutions, are illustrated in Figs. 7 and 8. These substitutions are expressed according to the relation of the monovalent and divalent cations versus the trivalent ones as following:



The coupled substitutions are much more pronounced in Vavdos tourmalines (Figs. 7 and 8). There is also a slight trend for cores to present a greater degree of the two substitutions than the rims. Furthermore, in Vavdos tourmalines alkali-free defect dominates distinctly. May be these tourmalines were formed in an environment enriched in water. In Psakoudia tourmalines proton-loss substitution seems as frequent as alkali-defect. So in contrast to FOIT and ROSENBERG'S (1977) suggestion, alkali-defect in the examined tourmalines, seems to be equally important as proton-loss substitution.

The greater degree of Al substitution for Mg and Fe of the Vavdos tourmalines, compared to that of Psakoudia, corresponds with their higher Al contents which reflect an Al enrichment in the corresponding host rock.

As regards other substitutions in zoning diagrams, Figs. 3 and 4 reveal a mostly positive correlation of Ti and Ca from core to rim for the tourmalines of both areas. STAATZ et al. (1955) suggested that Na in tourmaline was independent of bulk chemical control in the Brown Derby pegmatite, Colorado. Besides, GALLAGHER (1987, 1988) did not observe any correlation of Na with respect to other elements within SE Ireland tourmalines, or with respect to bulk chemistry indicating that Na contents depend on charge-balance considerations. Yet, a general positive correlation was noticed between Na and Mg for nearly all the examined tourmaline grains of Vavdos and Psakoudia.

Petrogenesis and discussion

It is already well-known that the crystal-chemistry of tourmaline is a significant factor that influences the compositional trends of this mineral. Furthermore, tourmaline composition may provide important information about the type of rock where this mineral was formed, as well as about the possible conditions and processes of crystallization. There are many examples in literature where tourmaline composition is used as an effective indicator of the genetic history of host rock formation (e.g. POWER, 1968; MANN-

ING, 1982; HENRY and GUIDOTTI, 1985; JOLLIFF et al., 1986; LOTTERMOSER and PLIMER, 1987).

The origin of the Vavdos and Psakoudia tourmaline-bearing pegmatitic veins is a matter of question in the present study. Their distance from the granitic intrusions of Arnea and Sithonia in Chalkidiki peninsula is quite great to justify a genetic relation; no mineralogical correlations with these granitic bodies were found. Besides, from the up to now literature data, radiometric dating on the occurrences of the broader area gave an age of 172 ± 5 m.y. for a hornblende gabbro in the Thessaloniki ophiolitic sequence, and K/Ar-muscovite model ages of 155.6 ± 1.1 m.y., 154.2 ± 2.5 m.y. and 125.3 ± 1.4 m.y. for a tourmaline pegmatite in this ophiolite (from BURGATH et al., 1980; MUSSALAM and JUNG, 1986). So the 52 m.y. age of the Sithonia granite rejects any genetic relationship with the pegmatites in discussion. Unfortunately radiometric dating of the Arnea granite is still not available. The possibility of these pegmatites to represent late-stage formations of the neighbouring Chortiatiss magmatic suite was also rejected since the formation of the Chortiatiss suite preceded the emplacement of the associated ophiolites (MUSSALAM and JUNG, 1986). A probable origin of the present tourmaline pegmatitic veins might be attributed to a pegmatitic residual magma rich in fluids and especially in boron, which intruded the ophiolite suite during or after its tectonic emplacement on the continental margin. The source or the magma might be related to sea-floor sediments rich in silica like sandstones and pelites which suffered anatexis during their subduction into deeper zones. The pegmatitic fluids liberated elements from the surrounding rocks which inserted the structure of tourmalines.

The above assumption is supported also by the chemistry of the tourmalines: According to HENRY and GUIDOTTI'S (1985) $Al-Fe_{(tot)}-Mg$ and $Mg-Fe_{(tot)}-Ca$ ternary diagrams (Fig. 2), a metapelitic or metapsammitic origin was mainly obtained. Besides, data from the literature refer that enrichment in the dravite or schorl member of the schorl-dravite series in pegmatites and aplites is a result of magmatic differentiation. Relatively Mg-rich tourmalines have been found to combine with early stage of magmatic differentiation whereas late differentiates are the most schorl-rich (POWER, 1968; NEIVA, 1974; MANNING, 1982). This does not seem to be the case for the pegmatitic tourmalines in this study. Differences in chemistry as well as schorl enrichment for the Psakoudia tourmalines and dravite enrichment for the Vavdos ones, are not attributed to real magmatic differentiation but to

differences of crystallization conditions as well as to the influence of the surrounding rock. Besides, no significant variation in Mg and Fe was observed from cores to rims in the tourmalines of Vavdos; as regards the Psakoudia tourmalines Fe and Mg display increase from core to rim in the two grains while the opposite happens in the third one.

The $\text{FeO}/(\text{FeO} + \text{MgO})$ ratio of tourmalines shows an average of 0.58 and 0.76 for Vavdos and Psakoudia correspondingly. These values are lower compared to the 0.86 from Portuguese granites (NEIVA, 1974) and 0.91 from English granites (POWER, 1968). ETHIER and CAMPBELL (1977) give a range of 0.45–0.67 for Proterozoic sediments of British Columbia.

If we accept that the pegmatite occurrences of the two localities originate from the same fluid, then the conditions of crystallization must have been different for the tourmalines of each case. Fe and Mg are cations with high field strength and are favoured in high temperature conditions, while cations with lower field strength as Li display their maximum concentrations at lower temperatures. Though Li cannot be determined by electron microprobe analysis it is assumed to be present in considerable amounts in the Al-rich tourmalines, due to its coupling with Al in the Y site (HENRY and GUIDOTTI, 1985). Since Al has a high field strength fitting easily the Y-site it seems that in the couple (Li + Al) the field strength of Li is the governing factor (JOLLIFF et al., 1986). Taking into account that the Vavdos tourmalines are richer in the elbaite component (Fig. 2) we accept that the Psakoudia tourmalines were formed at higher temperatures than the Vavdos ones.

Furthermore, differences in the crystallization conditions result even for the tourmaline grains within the same pegmatitic body or within the same hand specimen. As Figs. 5 and 6 reveal there is an important substitution of Al for Fe^{2+} + Mg in the Y site, corresponding to a general progressive evolution of the pegmatites. On the other hand careful examination of the above figures shows that even in the same pegmatitic occurrence the tourmaline grains were not formed in the same time. Changes in the Fe and Mg from cores to rims reveal that some cores were formed from the silicic fluid of the pegmatite before being contaminated by the country rocks. Some other cores were formed after the country rock contamination of the pegmatite fluid.

The situation is more complex for the rims where the variation of the elements represents successive enrichment and depletion dependent on the country rock contamination and varying

conditions of temperature, pressure, chemical composition and equilibration of the crystallizing material as well.

Consequently, a complex history of formation of the examined tourmalines is deduced and a combination of various factors seems to have acted during their growth.

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