Accessory minerals

Prof. RNDr. Milan Novák, CSc.
R. Čopjaková, R. Škoda)

Tourmaline group

Thesis:

1. **Crystal structure and chemical composition**
2. **Classification of tourmalines**
3. **Tourmaline from distinct geological environments**

1. Crystal structure and chemical composition

- **Minerals of tourmaline group (chiefly dravite and schorl) are the most abundant minerals with substantial amount of B in rocks of Earth crust. This is controlled by high stability field in PTX-conditions and high mechanical and chemical refractority.**

- **Refraktory properties, presence of tourmaline in many rocks with highly variable chemical composition and crystal structure are the main reasons why tourmaline is one of the most examined mineral in last decades.**

1. Crystal structure and chemical composition

- **Tourmaline belongs to cyklosilicates, trigonal, space group *R*3*m*. Acentric structure controls polar development of crystals and pyroelektric and piezoelectric properties.**

General formula:

X Y3 Z6 T6 O18 (BO3)3 V3 W

***X* = Na*, Ca, □, K**
***Y* = Mg, Fe2+, Li, Al, Fe3+, Mn, Zn, Cr3+, V3+, Ti4+, (□)**
***Z* = Al, Mg, Fe3+, Cr3+, V3+**
***T* = Si, Al, B**
***B* = B**
***V* = OH, O**
***W* = OH, F, O**
Additional minor elements: Cu, Pb, Ni, Sr, Ba, Bi, Cl.

1. Crystal structure and chemical composition

- **Substitutions:**

- **monovalent:**

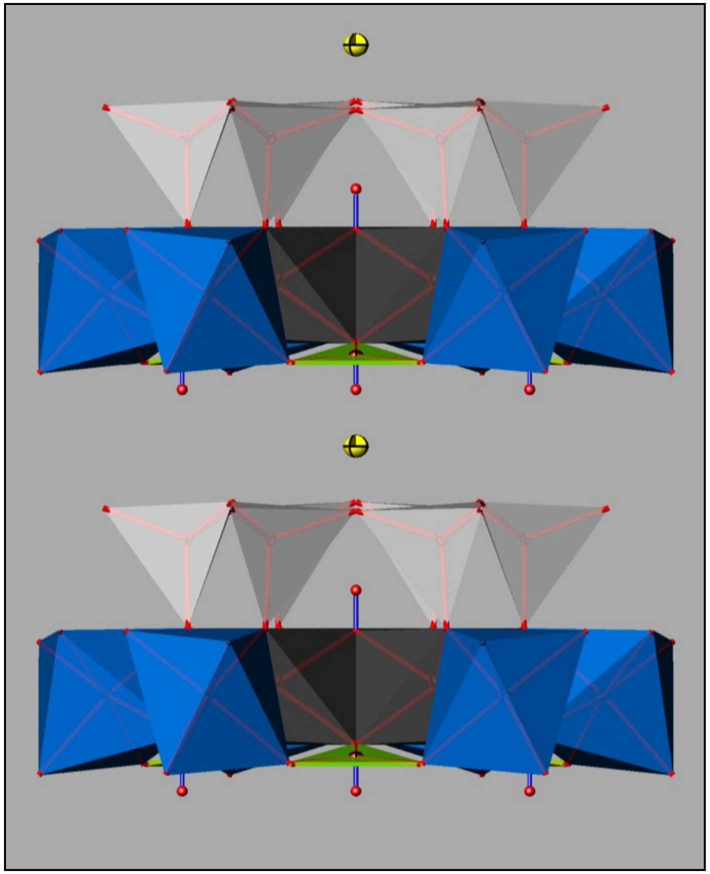
  $^{Y}\mathrm{Mg} = {}^{Y}\mathrm{Fe2+}$
  $^{W}\mathrm{OH} = {}^{W}\mathrm{F}$
  $^{Z}\mathrm{Al} = {}^{Z}\mathrm{Fe3+}$
  $^{X}\mathrm{Na} = {}^{X}\mathrm{K}$

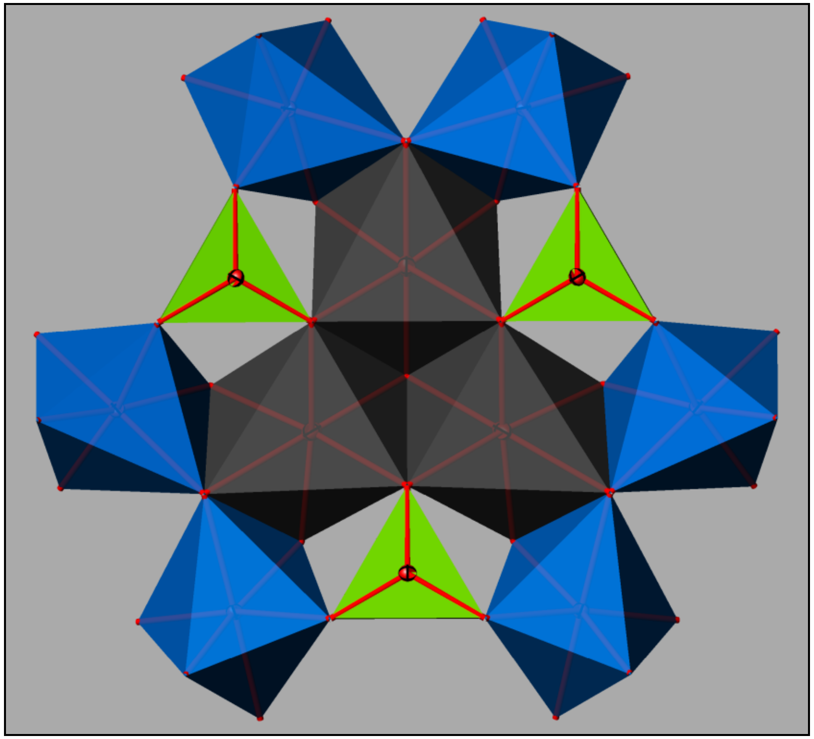
- **heterovalent:**

  $2{}^{Y}\mathrm{Fe2+} = {}^{Y}\mathrm{Li} + {}^{Y}\mathrm{Al}$
  $^{X}\mathrm{Na} + {}^{Y}\mathrm{Al} = {}^{X}\mathrm{Ca} + {}^{Y}\mathrm{Mg}$
  $^{X}\mathrm{Na} + {}^{Y}\mathrm{Mg} = {}^{X}\square + {}^{Y}\mathrm{Al}$
  $^{Y}\mathrm{Mg} + {}^{V}\mathrm{OH} = {}^{Y}\mathrm{Al} + {}^{V}\mathrm{O}$
  $^{X}\square + {}^{Y}\mathrm{Al} + {}^{W}\mathrm{OH} = {}^{X}\mathrm{Ca} + {}^{Y}\mathrm{Mg} + {}^{W}\mathrm{O}$
  $2{}^{Y}\mathrm{Mg} + {}^{Z}\mathrm{Al} + {}^{W}\mathrm{OH} = 2{}^{Y}\mathrm{Al} + {}^{Z}\mathrm{Mg} + {}^{W}\mathrm{O}$

- **heterovalent substitutions predominate. The last substitution leads to change in order/disorder (sites *Y* and *Z)*.**

1. Crystal structure and chemical composition





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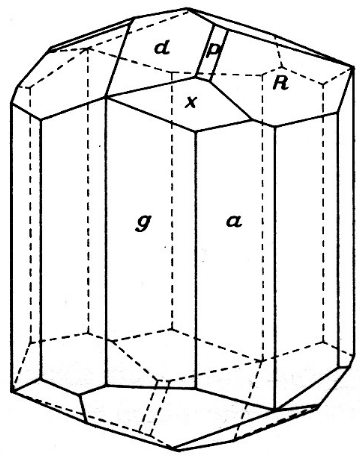
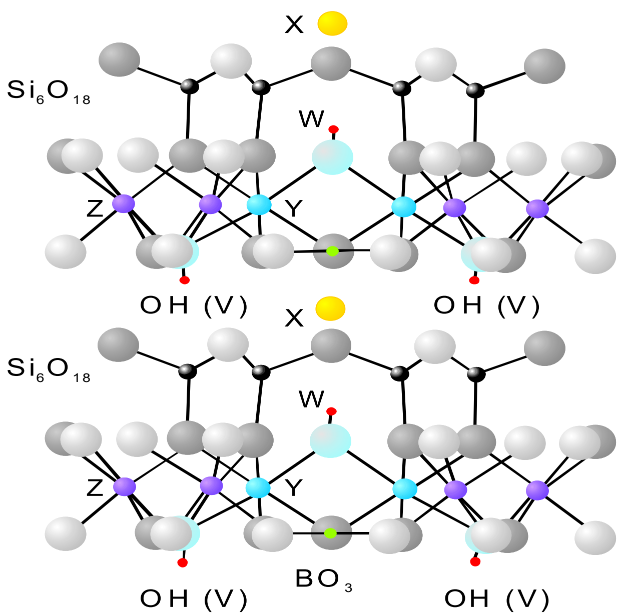
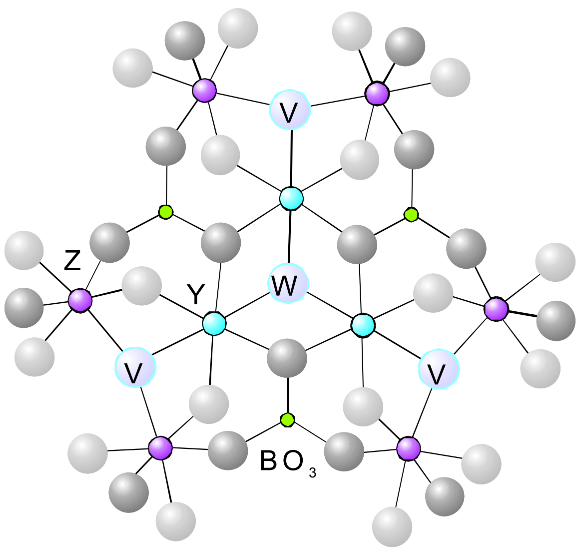
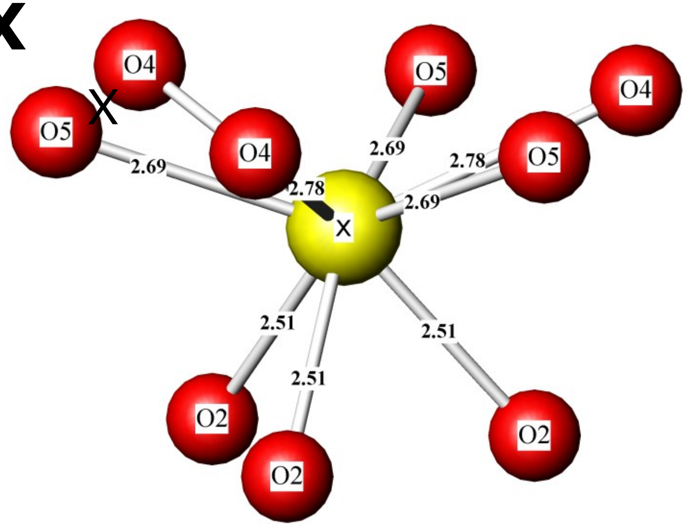






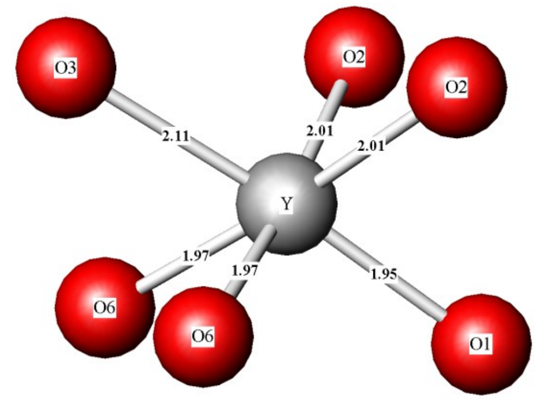
1. Crystal structure and chemical composition

X



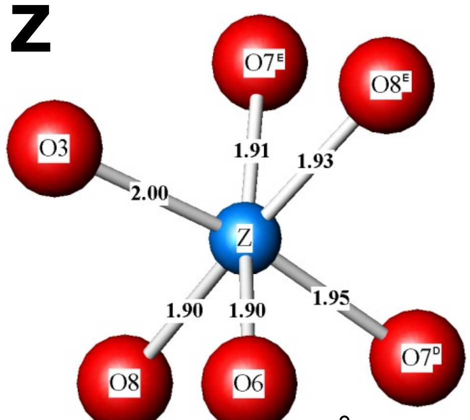
X-O = 2.51-2.78 Å

Y



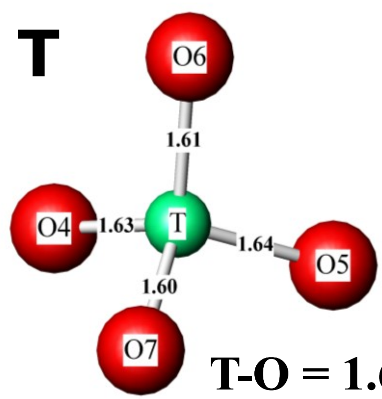
Y-O = 1.95-2.11 Å

Z

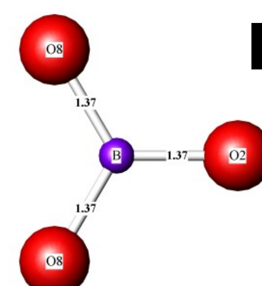


Z-O = 1.90-2.00 Å

T



T-O = 1.60-1.64 Å



B

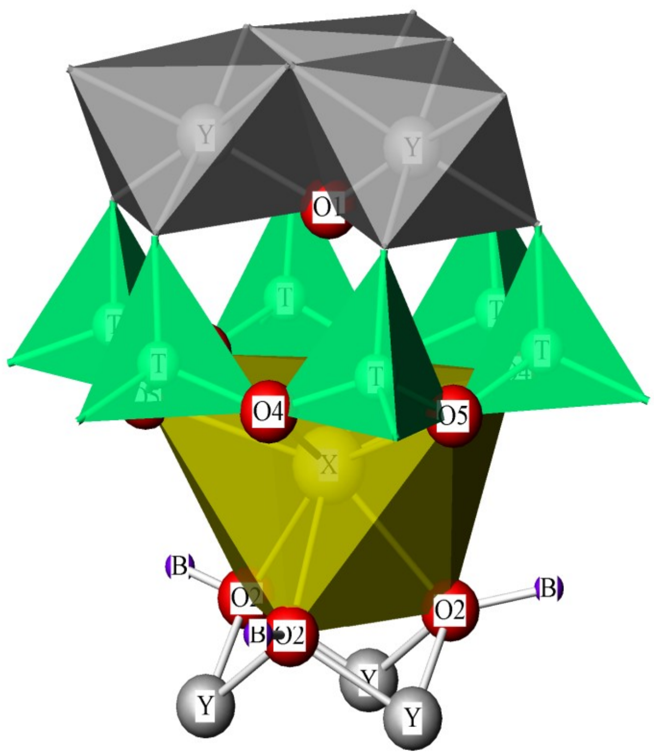
1. Crystal structure and chemical composition

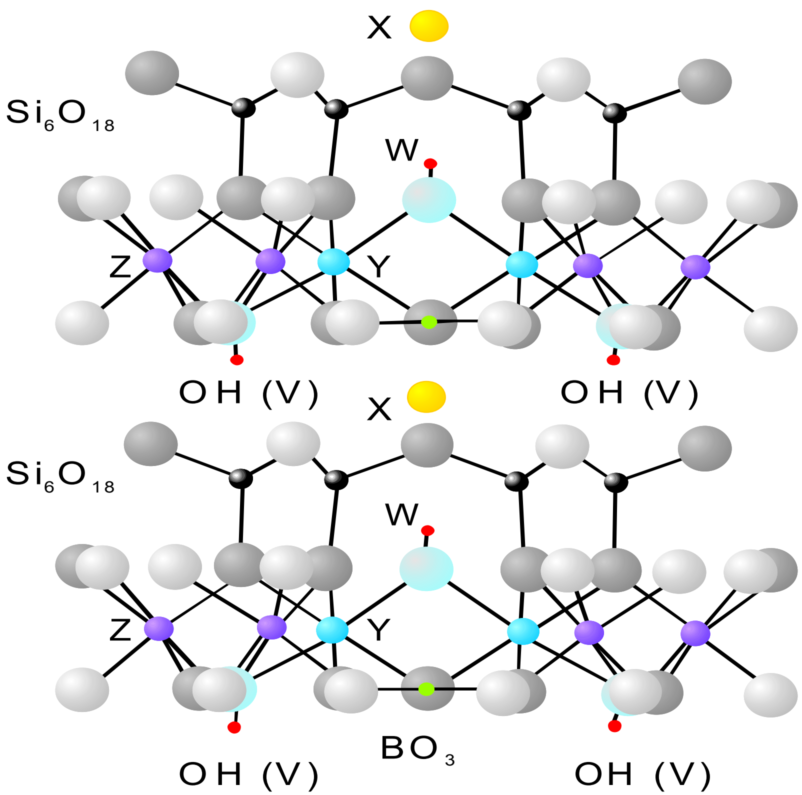
- **Crystal structure (e.g., short-range order) has essential infuence on chemical composition of tourmaline along with commonly considered chemical composition of parental medium (melt, hydrothermal fluids), chemical composition of associated minerals and P-T-X conditions. See occupation of *W*-site bymonovalent or divalent element.**

a) monovalent F or OH (see fig. 2 and 3) in the W-site implies the most suitable configurations in the *Y* – site are 3Mg or Al + 2Mg. accordingly divalent O *Y* - 3Al or 2Al + Mg.

b) If monovalent F (but not OH) is in W-site X-site prefers Na. But only up to Ca (> ~0,2 *apfu*).

1. Crystal structure and chemical composition





1. Crystal structure and chemical composition

- **Analogically occupation on *V-site* (OH nebo O) controls configuration of cationts in the *Z-site*.**

- **In nature, the following conmpositions are most common controlled by crystal structure:**

- **dravite-schorl**

  $Na_{0,5}\square_{0,5} (Mg,Fe^{2+})_2 Al Al_6 (BO_3)_3 Si_6O_{18} (OH)_3 (OH)_{0,5} O_{0,5}$
- **elbaite**

  $Na_{0,5}\square_{0,5} Li Al_2 Al_6 (BO_3)_3 Si_6O_{18} (OH)_3 (OH)_{0,5} O_{0,5}$

2. Classification of tourmalines

- **The latest Classification of the tourmaline group minerals was approved by the CNMMN of IMA in 2008.**

- **The Subcommission for classification of the tourmaline group minerals was established at the Commission for New Minerals and Mineral Classification of the IMA at 2002, and currently this commission involves:**

  M. Novák - Masaryk University, Brno – chairman

  D. Henry – University of Louisiana, Baton Rouge – vicechairman

  Members:

  B. Dutrow - University of Louisiana, Baton Rouge

  A. Ertl – University of Vienna

  F.C. Hawthorne – University of Manitoba, Winnipeg

  F. Pezzotta – Museum of Natural History, Milano

  P. Uher – Komensky University, Bratislava

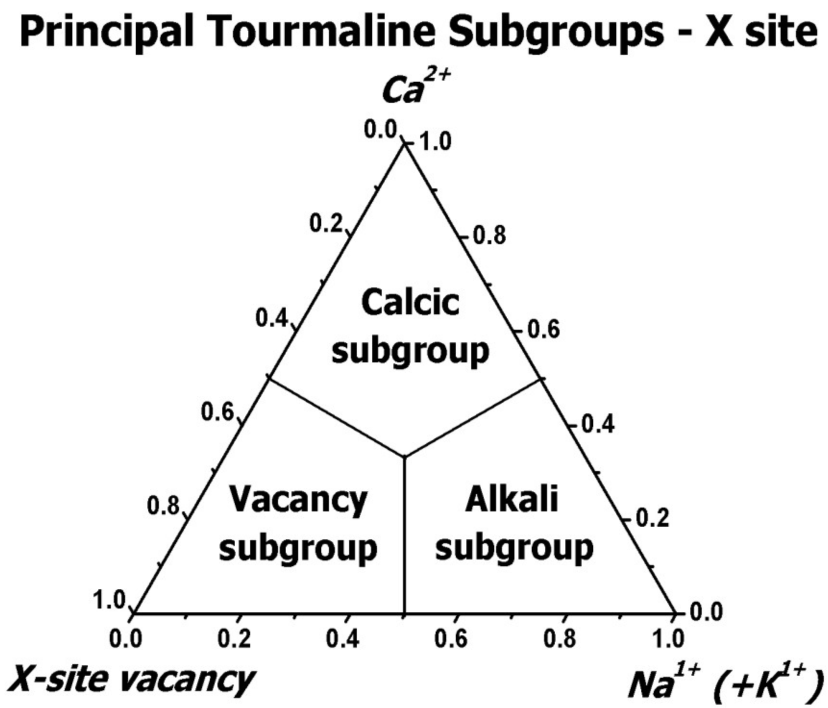
2. Classification of tourmalines

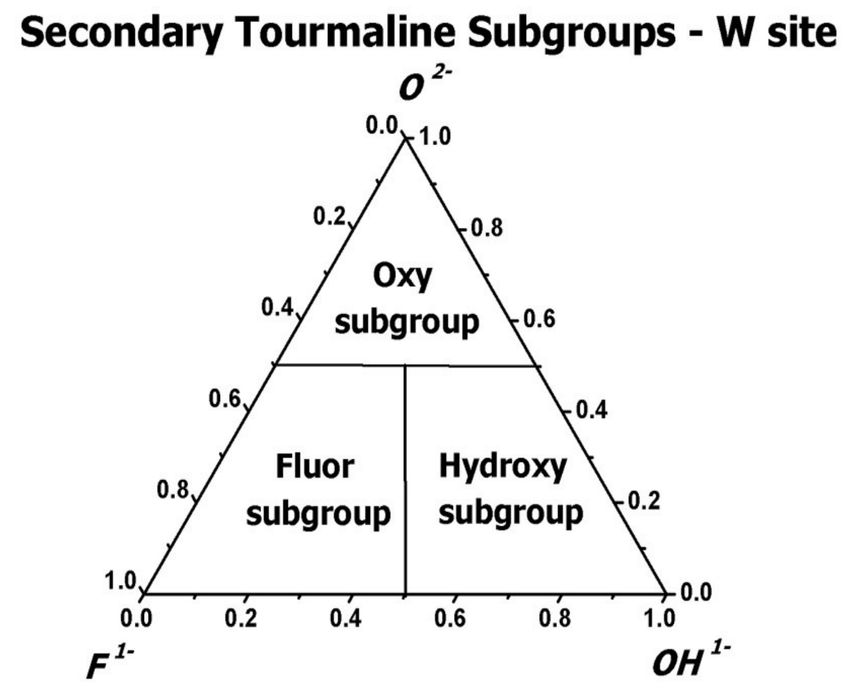
- **Complications:**
- **commonly undetermined B, H, Li, F, Fe^{2+} a Fe^{3+} on electron microprobe.**
- ***X-site*: Na – Ca – □ (see amphibols)**
- ***W-site*: OH – F – O (problematic)**
- ***V-site*: OH – O (problematic)**
- ***Y-site*: Mg – Fe2+ – (Li+Al) – Al**
- ***Z-site*: Al – Fe3+ – Cr – V**

2. Classification of tourmalines

General formula	*X*	*Y3*	*Z6*	*T6 O18*	*(BO3)3*	*V3*	*W*
Elbaite	**Na**	$Li_{1.5}\ Al_{1.5}$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Schorl	**Na**	$Fe^{2+}{}_3$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Dravite	**Na**	Mg_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Olenite	**Na**	Al_3	Al_6	Si_6O_{18}	$(BO_3)_3$	$(O)_3$	(OH)
Chromdravite	**Na**	Mg_3	Cr_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Vanaddravite	**Na**	Mg_3	V_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Buergerite	**Na**	$Fe^{3+}{}_3$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(O)_3$	F
Povondraite	**Na**	$Fe^{3+}{}_3$	$Fe^{3+}{}_4Mg_2$	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	O
Liddicoatite	**Ca**	Li_2Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	F
Uvite	**Ca**	Mg_3	$MgAl_5$	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	F
Hydroxyferuvite	**Ca**	$Fe^{2+}{}_3$	$MgAl_5$	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Rossmanite	❑	$LiAl_2$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Foitite	❑	$Fe^{2+}{}_2Al$	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)
Magnesiofoitite	❑	Mg_2Al	Al_6	Si_6O_{18}	$(BO_3)_3$	$(OH)_3$	(OH)

2. Classification of tourmalines





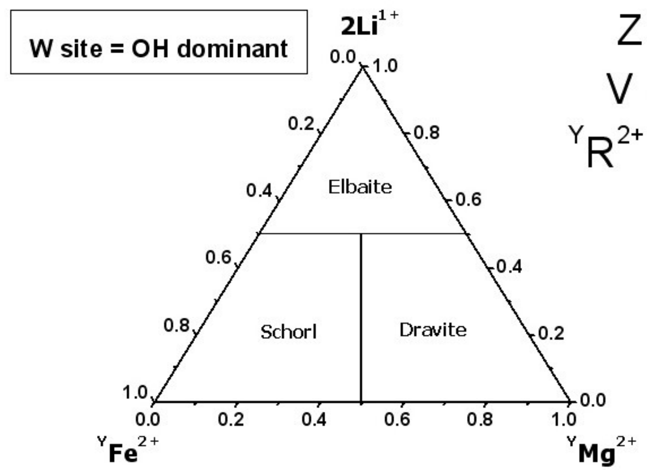
2. Classification of tourmalines

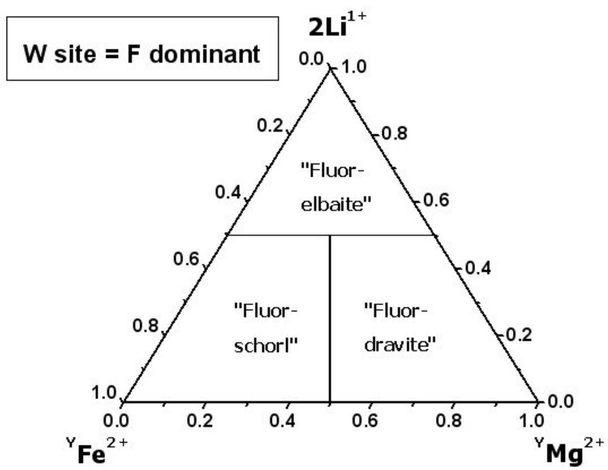
Alkali subgroup

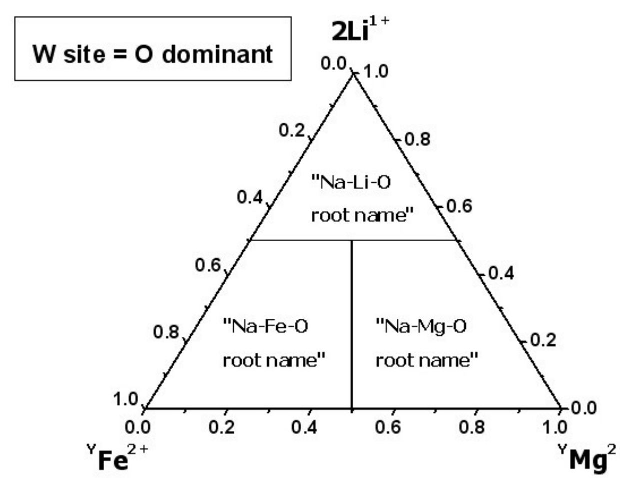
Z site = Al dominant

V site = OH dominant

$^{Y}R^{2+}$ = Fe^{2+} or Mg dominant







Formula calculations

- **Based on general formula but due absence of information about light-elements contents in most analyses - complicated.**
- **If all elements determined (very rare example), from general formula.**
- **Data from electron microprobe – Si, Ti, Al, Fetot, Mg, Mn, Ca, Na, K, F, Cr, V, Zn), several distinct approaches exist (Henry and Dutrow 1996, Dutrow and Henry 2000).**

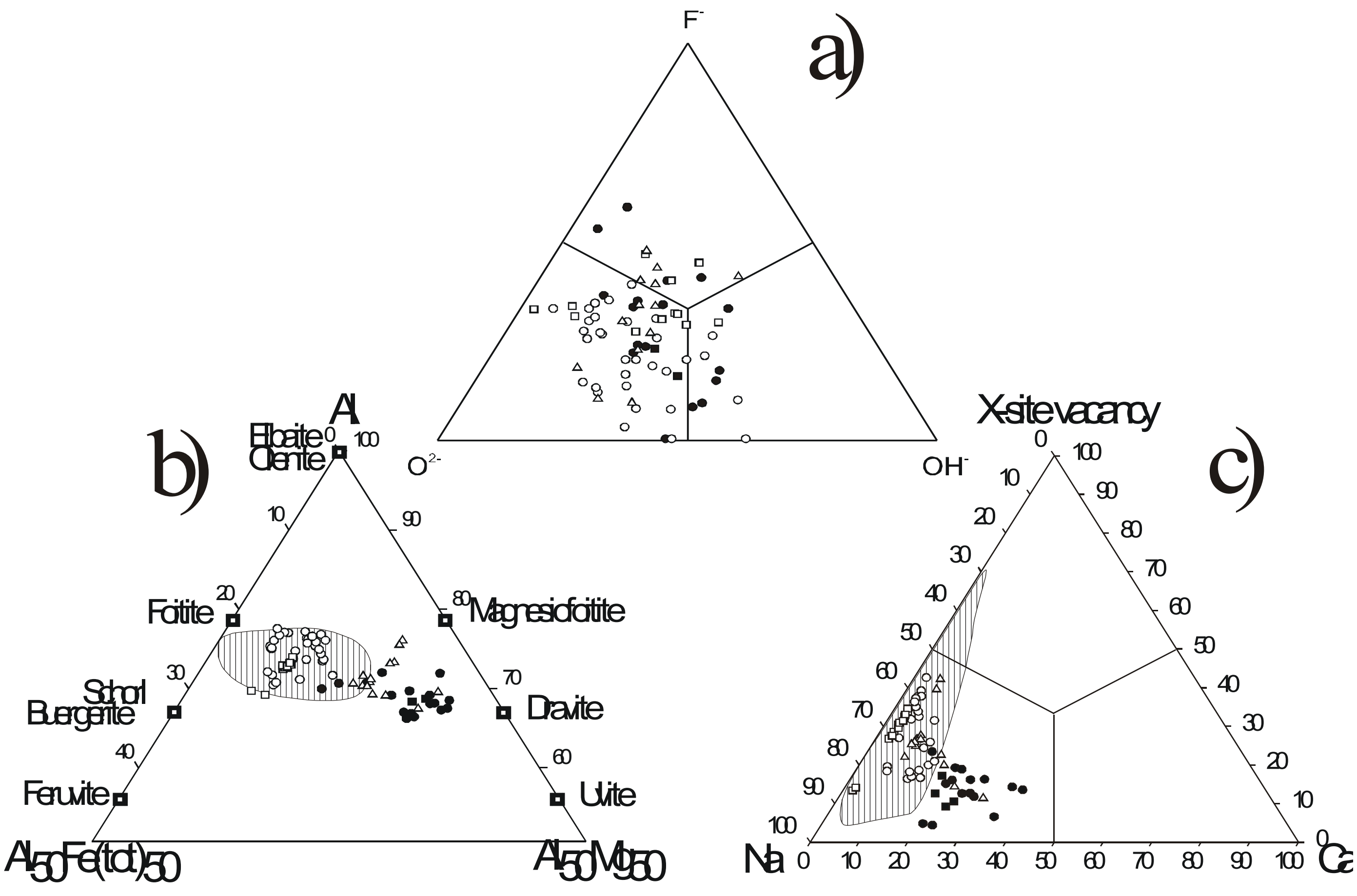
Formula calculations

- **Normalization on 6 Si *apfu*. Simplification but easy and potential errors are recognizeable. For geochemical studies sufficient.**

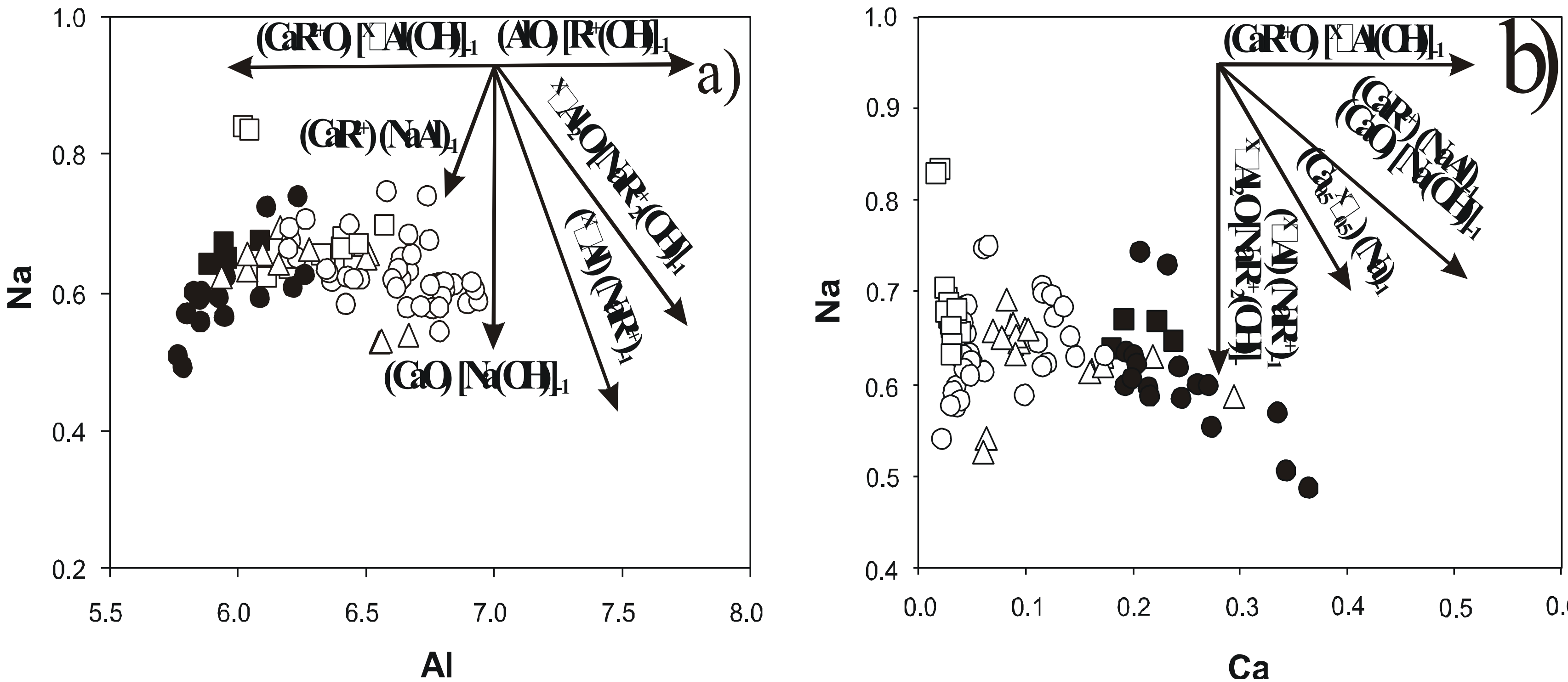
- **If tourmaline is Li-enriched then normalization Li = 3 – *Y* (where *Y* = YAl + Fe + Mg + Mn + Zn). This way expect no vacancy in this site, which is not necessary true. Moreover, valency of Fe is a compolication, hence commonyl amount of Li is overestimated.**
- **In both cases B = 3 from stoichiometry.**

Grafical diagrams of tourmaline composition

First, we have to define if our diagrams should show geochemical features or crystalographical features.



Grafical diagrams of tourmaline composition



Grafical diagrams of tourmaline composition

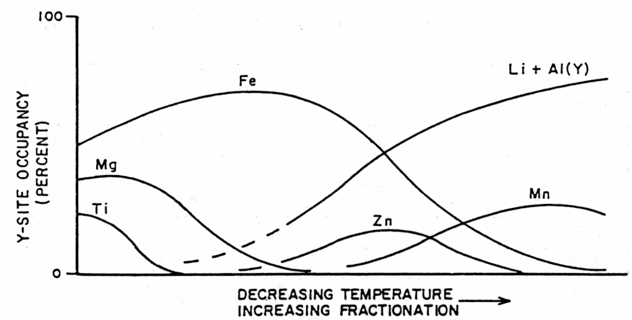
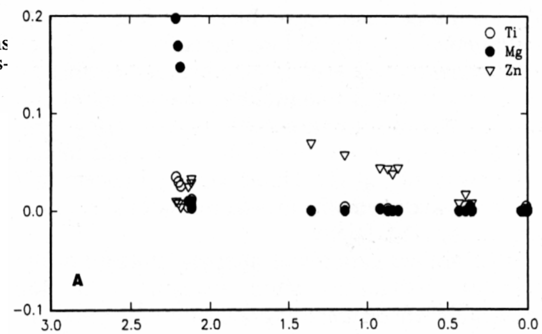
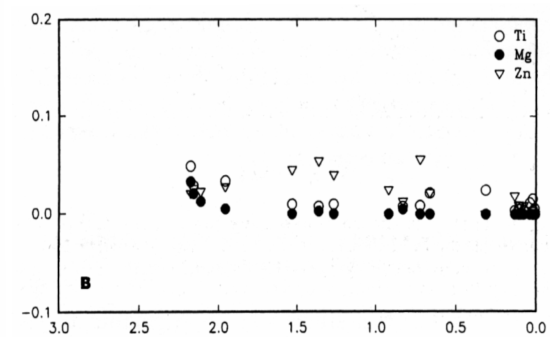


Fig. 6. Schematic illustration of ideal covariation of Y-site cations of tourmaline in response to decreasing temperature and increasing fractionation of melt (Jolliff *et al.* 1986).





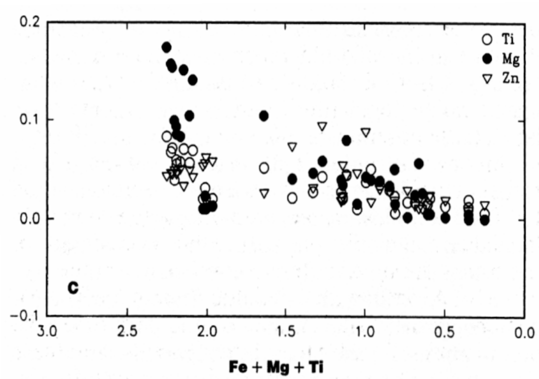


Fig. 2. Variation in concentrations of Ti, Mg and Zn per formula unit versus the FMT index. A - Lastovičky, B - Pikárec, C - Kracovice.

3. Tourmaline from different geological environments

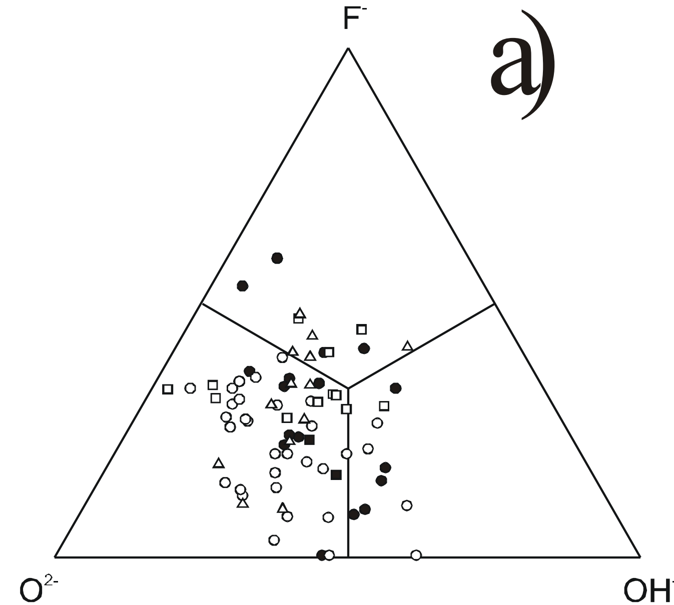
- **Tourmaline in granites**

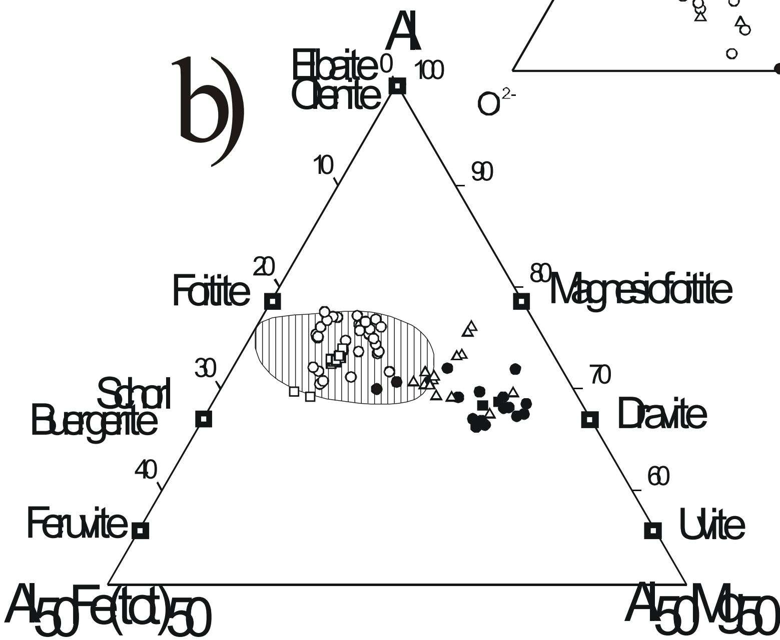
  Tourmaline is a typical mineral of peraluminous mostly leucocratic granites. Its presence in rock is limited by:
  content of B in melt
  content of Al in melt(ASI index)
  activity of Mg, Fe
  activity of H2O, *f*O2 (London 1999, Dingwell et al. 1996).

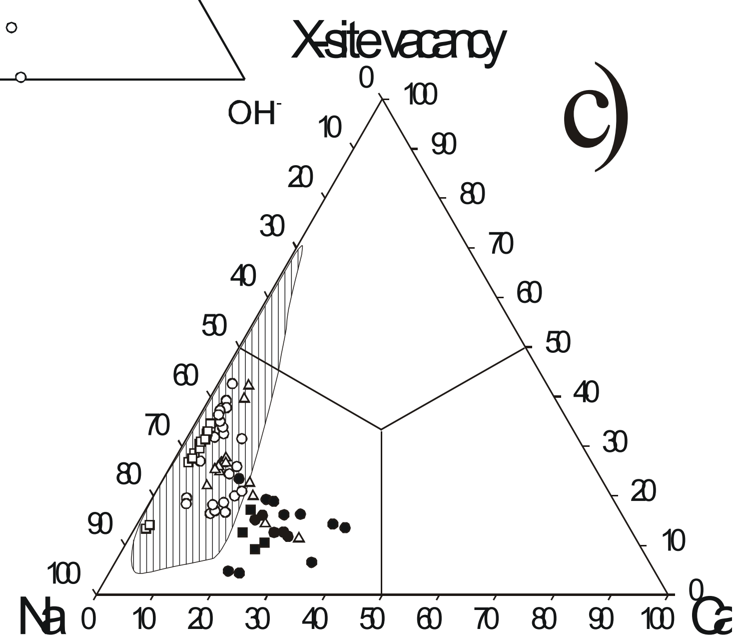
- **2 wt..% B2O3 and acidic conditions. Most of B commonly leave granite and react with host rocks.**

3. Tourmaline from different geological environments

Lavičky



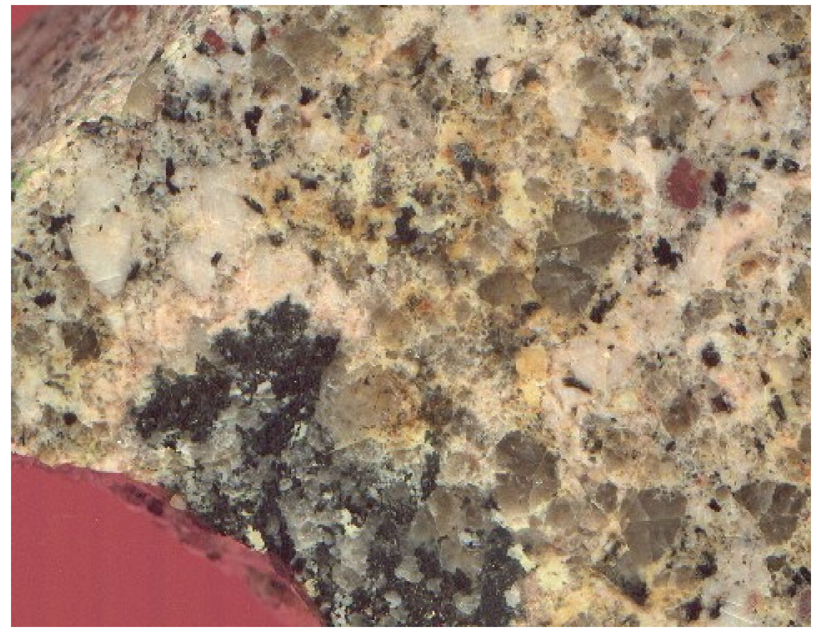




3. Tourmaline from different geological environments

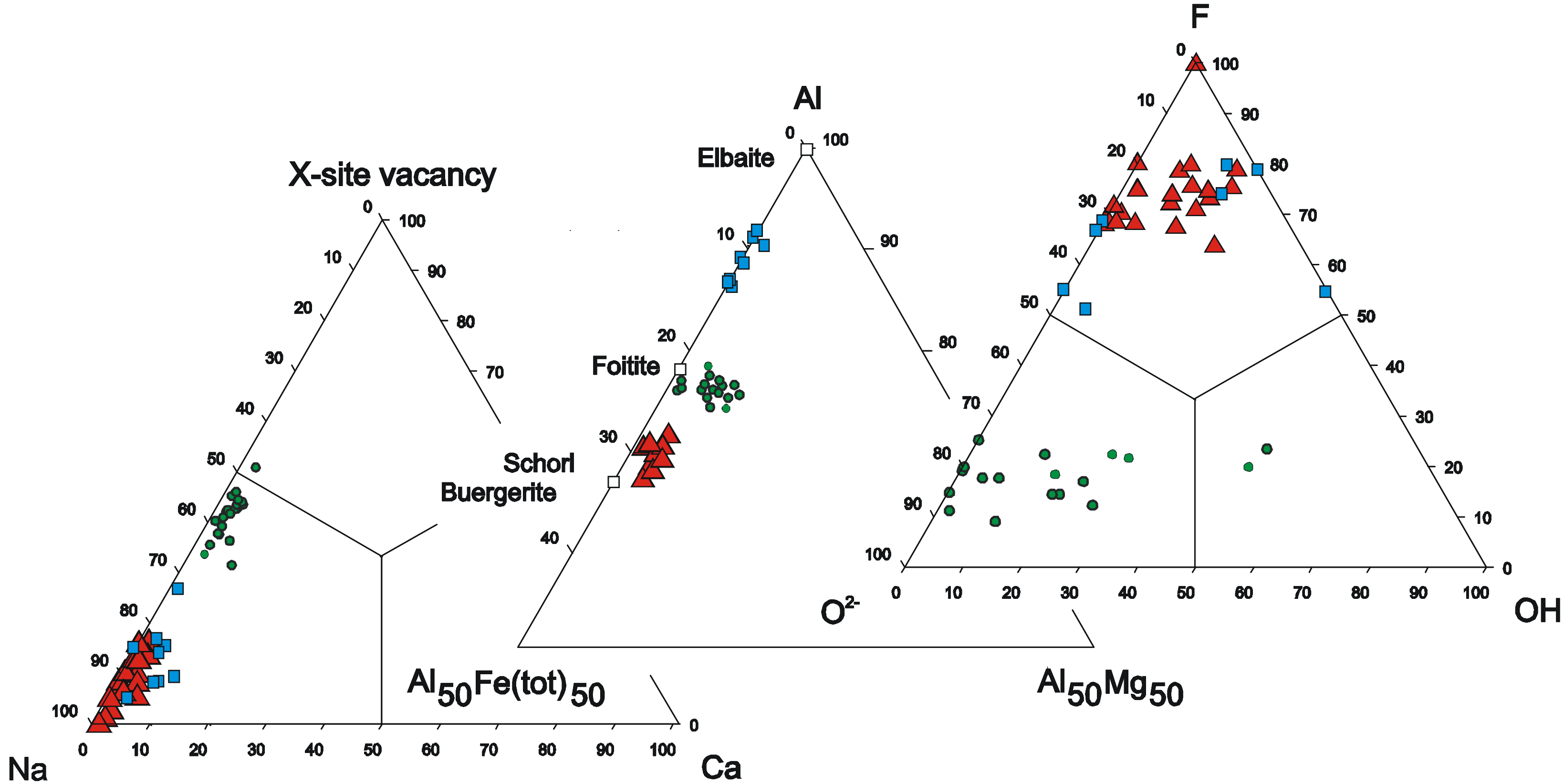
a)

b)



2 examples of tourmaline from granites, a) accessory, b) nodules

3. Tourmaline from different geological environments



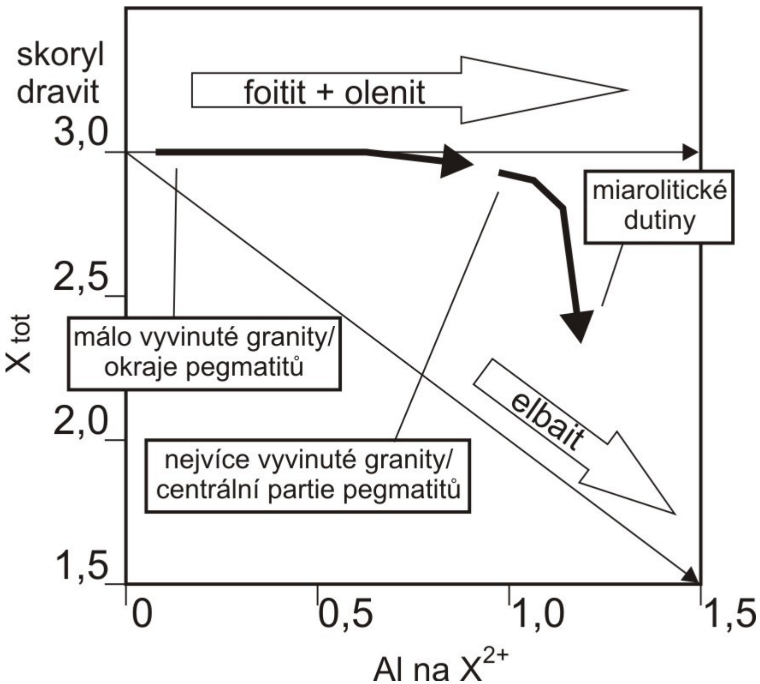
Chemical composition of tourmaline from distinct granites.

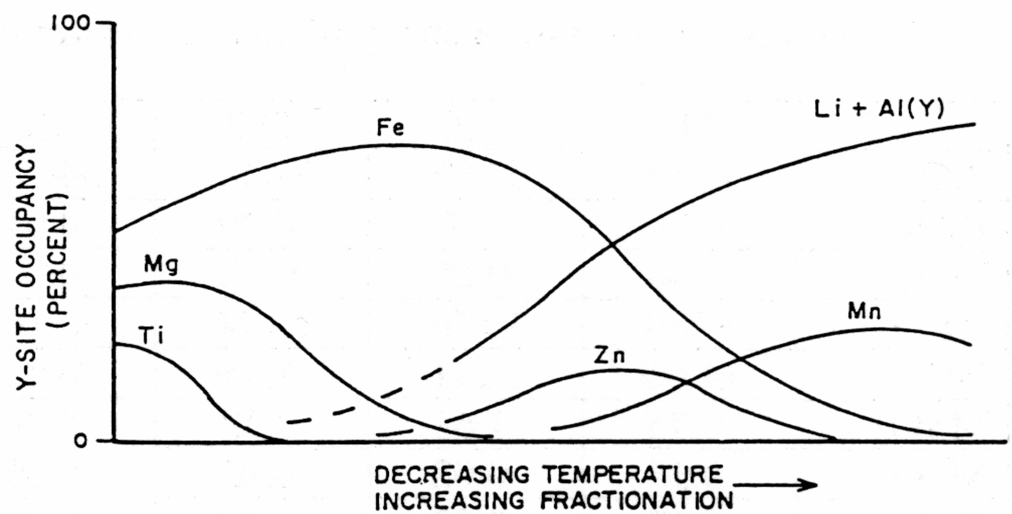
3. Tourmaline from different geological environments

- **Tourmaline in granitic pegmatites**

- **Formation of tourmaline is similar to granites in simple pegmatites.**
- **Transition for magmatic to hydrothermal crystallization is indicated by distinct change in chemical composition - foitite and Li-tourmalines (elbaite-schorl) with elevated Mg, Ca and Fe.**

3. Tourmaline from different geological environments





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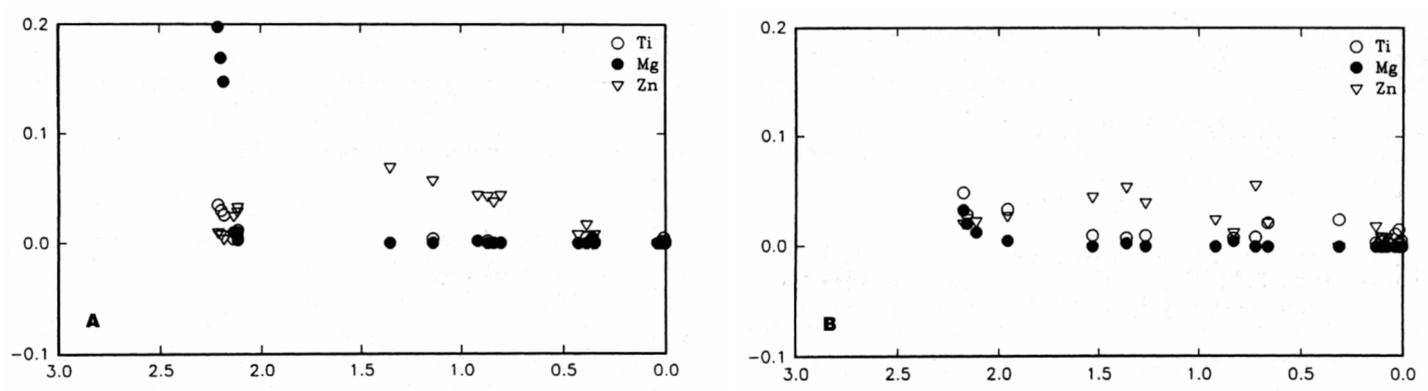
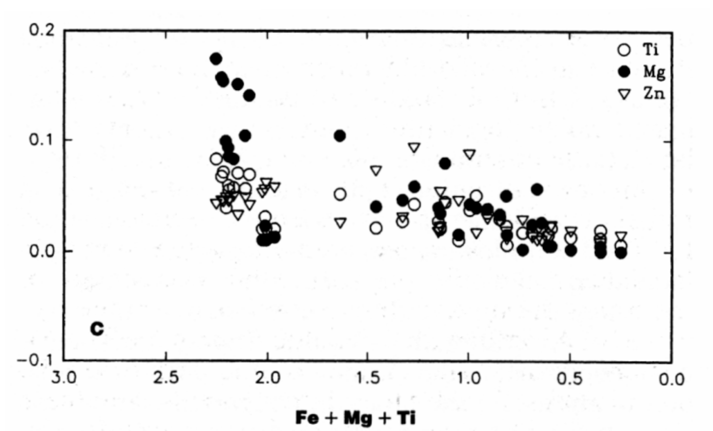
3. Tourmaline from different geological environments





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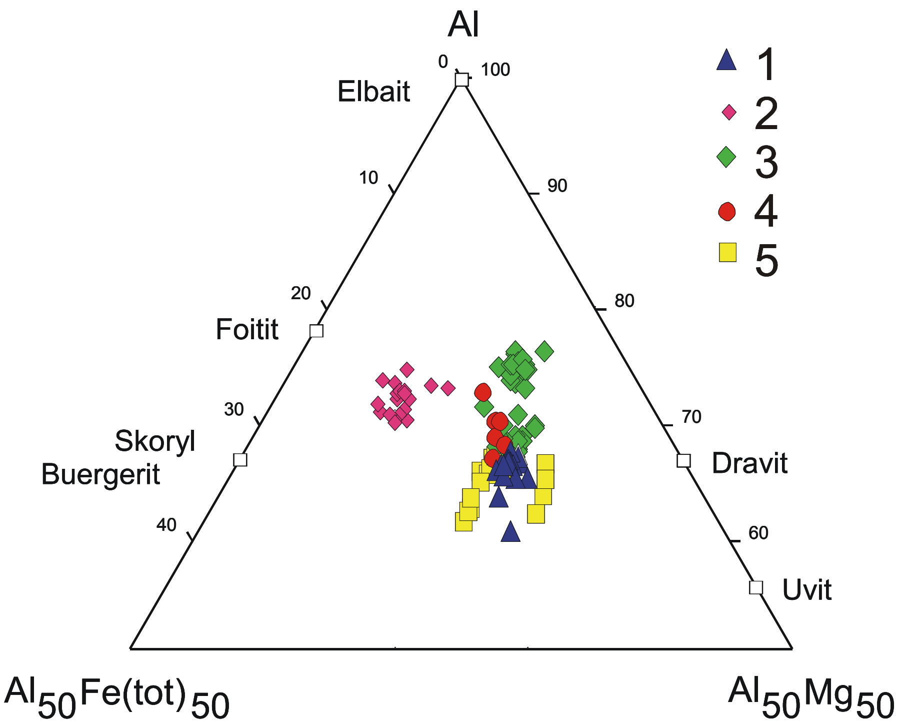
3. Tourmaline from different geological environments

- **Tourmalines from hydrothermal systems**

- **Tourmalines are common in distinct mineral assemblages occurring in hydrothermal veins and the source of B is commonly granite pluton. In stratiform deposits, source of B are volcanic exhalates or evaporites. Concentration of B in fluids is much lower relative to granitic melt to stabilize tourmaline.**

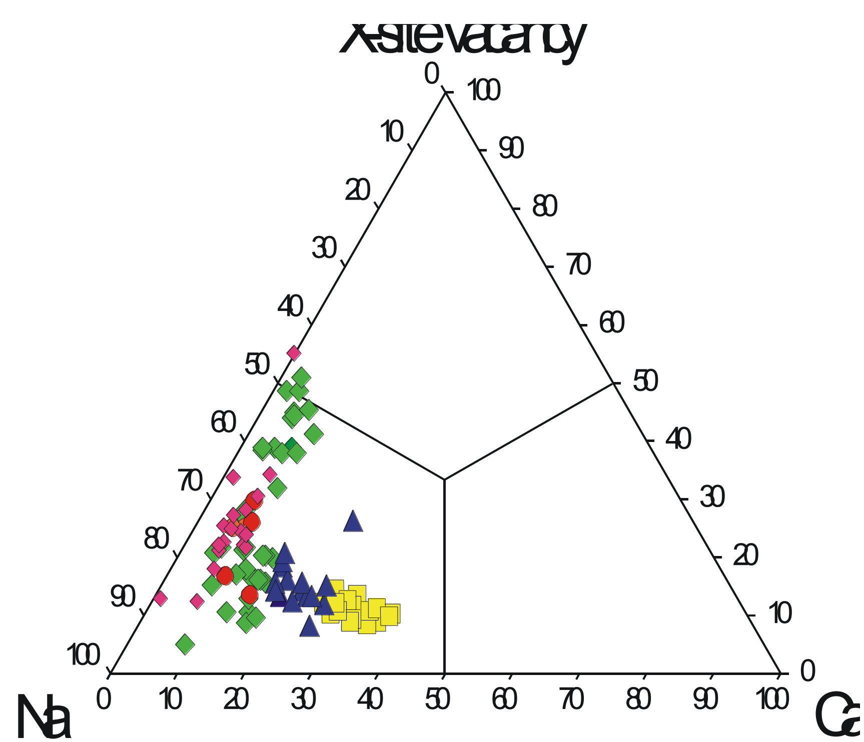
- **Typical feature of hydrothermal tourmaline – oscillatory zoning.**

3. Tourmaline from different geological environments



1 – turmalín v trondhjemitech, 2 – turmalín v ryolitech, 3 – turmalín v hydrotermálních žilách prorážejících diority, 4 - turmalín v hydrotermálních žilách prorážejících granity, 5 – turmalín na puklinách amfibolitů a dioritů.

Brněnský pluton



3. Tourmaline from different geological environments

- **Tourmaline from stratiform deposits and tourmalinites**

- **Tourmaline is a common mineral ín stratiform deposits with highly variable textures and grain size.**
- **Source of B - volcanic exhalates or evaporites, solutions from bazalts, clastic rocks. Tourmaline crystallized at low T of diagenesis at about 200 °C, when B is released from phylosilicates.**

- **Tourmalinites (10-20 vol.% of tourmaline) are similar to stratiform deposits.**

- **schorl-dravite-uvite-buergerite (Slack 1996).**

3. Tourmaline from different geological environments

- **Tourmaline from metamorphic rocks**

- **Tourmalines are similar to tourmalůineites and stratiform deposits but they show more variable composition. B is released from phylosilicates during prograde metamorphism. At high T, potential source of B is muscovite. Boromuscovite is stable at higher P relative to muscovite, hence during drop of P B is released from mica.**
- **Well-developed zoning is product of continuous reactions, when B is released from clay minerals, homogeneous tourmaline formed during discontinual reactions.**
- **schorl-dravite-uvite-buergerite chromdravite, vandiumdravite, magnesiofoitite.**

3. Tourmaline from different geological environments

Metamorphic rocks

Partitioning of the individual elements

- ***Y-site*:**
  Mg: decrease ^{X}Mg
- **Metapelites medium grade**

<u>tourmaline</u> > cordierite > chlorite > biotite > staurolite > garnet > ilmenit

- **metapelites high grade**

<u>tourmaline</u>, cordierite > biotite > safiríne

Li: decrease ^{X}Li

- **Metapelites medium grade**

staurolite > cordierite > biotite> muskovite > garnet, <u>tourmaline</u>, chloritoid

- **metapelites high grade**

kornerupine >> safiríne > biotite > cordierite > muskovite > <u>tourmaline</u>, plagioclase, garnet, ortopyroxene

3. Tourmaline from different geological environments

- ***X-site*:**
  Na: pokles XNa
- **Metapelites medium grade**

<u>tourmaline</u> > plagioclase

- **metapelites high grade**

<u>tourmaline</u>, pargasite, scapolite > serendibite > plagioclase, clinopyroxene

- ***W-site*:**
  F: decrease XF
- **metapelites high grade**

<u>tourmaline</u> > biotite > kornerupin

- **Calc-silicates high grade**

<u>tourmaline</u>, clinohumite > tremolite/pargasite > flogopite > talc

Tourmaline is generally enriched in Mg, Na and F and depleted in Ca and Li.

3. Tourmaline from different geological environments

Chýnov-mramor

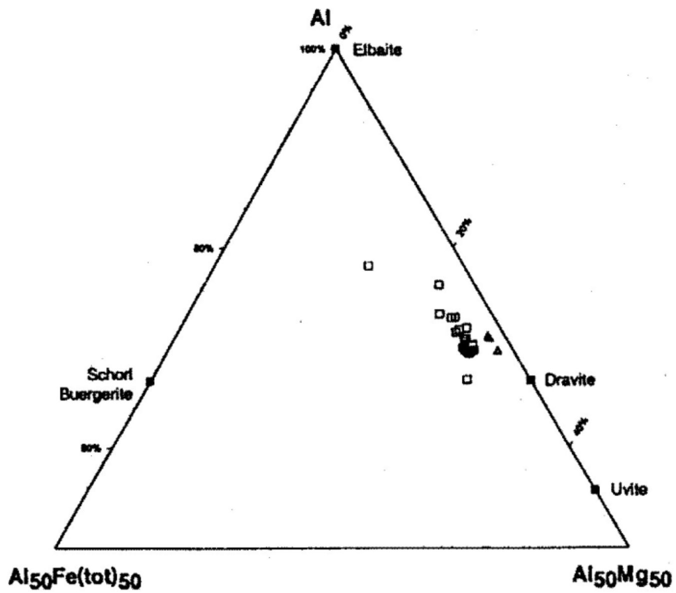


Fig. 2. Al - Fe(tot) - Mg diagram for tourmaline from Chýnov: ■ end members, □ mica-rich r
△ veinlets.

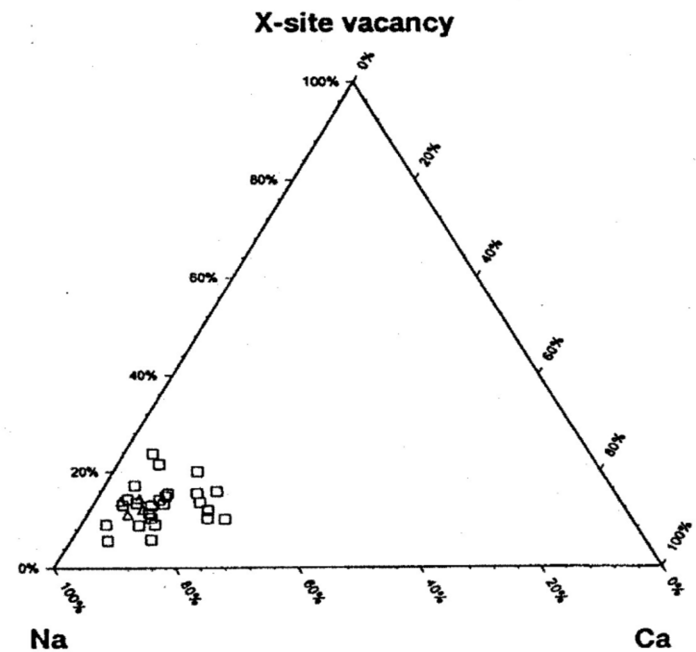


Fig. 3. Na - Ca - X-site vacancy diagram for tourmaline from Chýnov: □ mica-rich rock, △ veinlets.

3. Tourmaline from different geological environments

Detrital tourmaline as indicator of clasts provenience

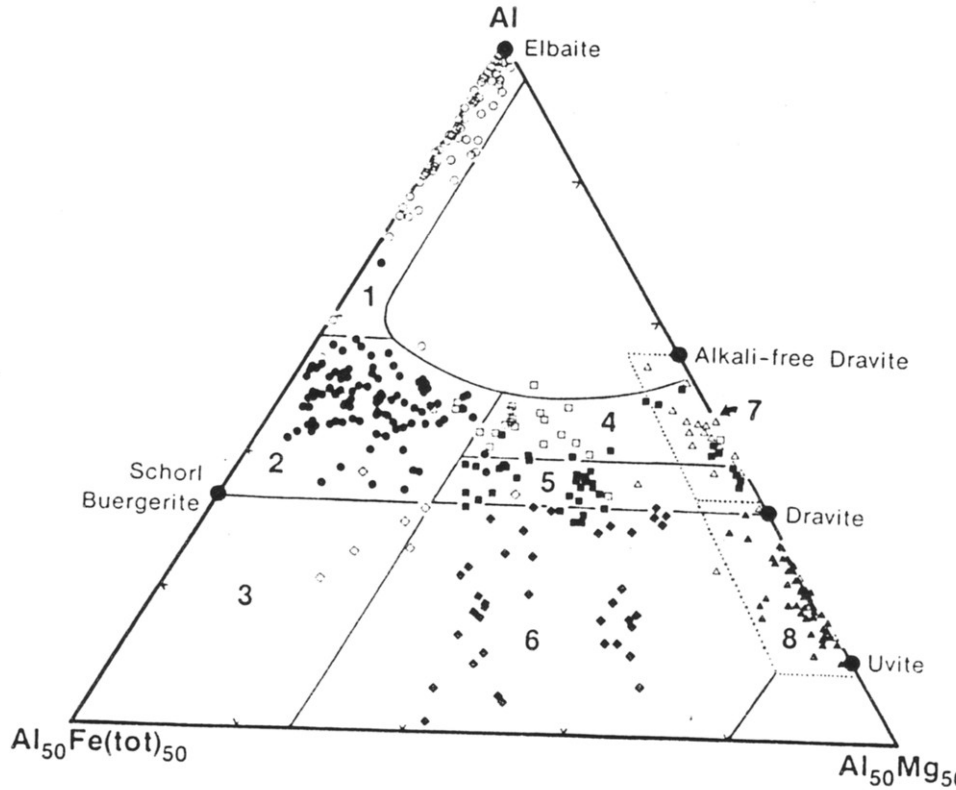


Fig. 1. Al–Fe(tot)–Mg diagram (in molecular proportions) for tourmalines from various rock types. Fe(tot) represents the total Fe in the tourmaline. Several end members are plotted for reference. This diagram is divided into regions that define the compositional range of tourmalines from different rock types. The rock types represented are (the values in brackets being the number of data points used to define the field): (1) Li-rich granitoid pegmatites and aplites [106] (○), (2) Li-poor granitoids and their associated pegmatites and aplites [98] (●), (3) Fe^{3+}-rich quartz-tourmaline rocks (hydrothermally altered granites) [7] (◇), (4) Metapelites and metapsammites coexisting with an Al-saturating phase [21] (□), (5) Metapelites and metapsammites not coexisting with an Al-saturating phase [45] (■), (6) Fe^{3+}-rich quartz-tourmaline rocks, calc-silicate rocks, and metapelites [38] (◆), (7) Low-Ca metaultramafics and Cr,V-rich metasediments [23] (△), and (8) Metacarbonates and meta-pyroxenites [55] (▲). Note the overlap of fields 4 and 5 with field 7.

3. Tourmaline from different geological environments

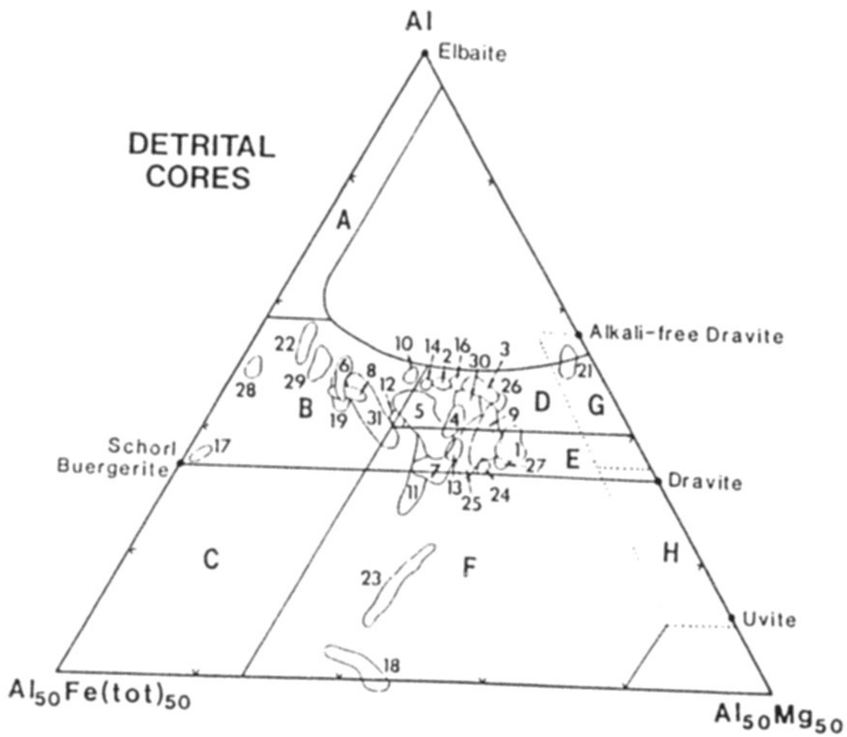


Figure 14. Al-Fe-Mg ternary diagram for 31 detrital tourmalines from a chlorite zone sample from western Maine (Henry and Dutrow, 1992). The numbers indicate individual tourmaline grains and the enclosed areas represent the compositional ranges of individual grains. Fields (defined by Henry and Guidotti, 1985) represent compositions of tourmaline for the following rock types: **A** Li-rich granitoids, pegmatites and aplites, **B** Li-poor granitoids, pegmatites and aplites, **C** Hydrothermally altered granitic rocks, **D** metapelites and metapsammites (aluminous), **E** metapelites and metapsammites (Al-poor), **F** Fe^{3+}-rich quartz-tourmaline rocks, calc-silicates and metapelites, **G** Low Ca ultramafics, and **H** metacarbonates and metapyroxenites.

4. Conclusions

Minerals of tourmaline group are very interesting and highly useful for study of different geological problems.