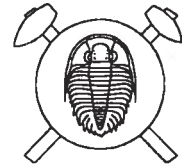


Is the partitioning of boron between tourmaline and muscovite dependent on the crystallization environment?



Závisí rozdělení bóru mezi turmalín a muskovit na prostředí krystalizace? (Czech summary)

(8 text-figs)

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According to classical mineralogical wisdom, tourmaline contains the constant amount of 3.0 boron atoms per formula unit (p. f. u.) located in trigonal (BO₃)-units of the structure, and muscovite is a boron-free mineral, so that a distribution coefficient D_B (= concentration of B in tourmaline / concentration of B in muscovite) is infinity. Recent analytical and experimental results show, however, that both assumptions do not always hold. Reviews are presented on natural and synthetic Al-rich tourmalines (olenites) containing up to 2.27 B p. f. u. of excess boron located in the tetrahedral ring site replacing silicon, and on natural and synthetic micas in the system muscovite – boromuscovite (KAl₂[BSi₃O₁₀](OH)₂). Like for excess-boron olenite, boromuscovite synthesis is favored by high pressures and low temperatures. The muscovite with the highest B-content found thus far coexists with excess-boron olenite (resulting in a D_B -value of 5.62) in a unique pegmatite that may have formed at, or been subjected to, relatively high pressures and low temperatures. However, Al-rich, very Mg, Fe-poor chemical environments alone may also favor tetrahedral boron in both minerals, because – if Mg, Fe²⁺ were present – these two elements would preferentially fractionate into tourmalines of the dravite-schorl series which thus far have always been found to contain only stoichiometric trigonal boron. At the same time, boron seems to fractionate preferably into these Mg, Fe-tourmalines rather than into muscovite, at least under normal crustal pressure conditions. More experimentation is warranted to determine variations of D_B as a function of PTX-conditions, with the possibility that this property be used to evaluate the conditions of formation of tourmaline – muscovite pairs.

Key words: tourmaline, olenite (with excess boron), muscovite, boromuscovite, high-pressure synthesis, element fractionation

Introduction

To many mineralogists and petrologists the question posed in the title of this paper may seem inadequate or superfluous. Tourmalines as studied over many decades, although known to exhibit extensive compositional variations, had been proven to contain stoichiometric amounts of boron (3.0 atoms per formula unit) located in the triangular (BO₃)-groups of their structure, thus following the general crystal chemical formula X Y₃ Z₆ [Si₆O₁₈] (BO₃)₃ (OH,F,O)₄. Muscovites, on the other hand, also often deviating rather strongly from their ideal formula K Al₂ [AlSi₃O₁₀] (OH)₂ by incorporation of other elements, are traditionally not known as boron-bearing minerals. Thus, a distribution coefficient D_B = (concentration of boron in tourmaline) / (concentration of boron in muscovite) should necessarily be infinity.

Results of research during the 1990ies imply that this attitude is hazardous, both from the angle of tourmaline and from that of muscovite. In 1991 a new mineral boromuscovite with the ideal formula K Al₂ [BSi₃O₁₀] (OH)₂ was discovered in nature (Foord et al. 1991) and has since been synthesized in the laboratory (Schreyer – Jung 1997). As a novelty to the tourmaline series, Wodara (1996) and Wodara – Schreyer (1997, 1998) reported the synthesis of an olenite, the Al end member of tourmaline (Sokolov et al. 1986), which carries excess boron replacing silicon. An excess-boron olenite of this type has since also been found in nature (Ertl et al. 1997).

The most important approach to the new problem of boron distribution between tourmaline and muscovite would, of course, be to obtain reliable boron analyses of

the two minerals, at best in coexisting pairs occurring in the same rock. Unfortunately, such data are extremely rare in the older literature, and are only gradually becoming available more recently due to the growing awareness of scientists of this open question. The other approach, experimental studies on the individual stability relations of both excess-boron tourmalines and of boron-bearing muscovites, as well as directly on the boron distribution between different tourmaline and muscovite phases as a function of PTX-conditions are either not very far advanced, or were not even started. Therefore, the discussion to follow here can only be an introduction to the problem, summarizing the results available and trying to stimulate further research. Obviously, there are severe analytical difficulties involved, because the light element boron is hard to analyze on a microscale, but this is necessary to ascertain element distribution between truly coexisting mineral phases.

Excess-boron in tourmaline

Despite recent questioning of the validity of evidence for boron excess in tourmaline (Bloodaxe et al. 1999) this is now a well established fact. Importantly, however, excess-boron is not a potential property of *all* chemical varieties of tourmaline, but seems to be confined to those carrying unusually high amounts of Al, or perhaps of other trivalent cations, linked with low Li in the Y position of the tourmaline structure.

On the experimental side, an excess-boron olenite synthesized at 25 kbar, 600 °C, analyzed by electron microprobe and studied by various spectroscopic methods was

given the hypothetical structural formula (Wodara 1996; Schreyer et al. 2000) $(\text{Na}_{0.65} \square_{0.35}) (\text{Al}_{2.72} \square_{0.28}) (\text{Al}_{5.42} \text{Si}_{0.58}) [\text{Si}_{3.73} \text{B}_{2.27} \text{O}_{18}] (\text{BO}_3)_3 (\text{OH})_{3.87} \text{O}_{0.13}$.

The hypothetical nature of this formula does not relate to the tetrahedral coordination of the excess boron replacing Si, which was clearly demonstrated by spectroscopy, but primarily to the octahedrally coordinated Si, that could not be substantiated structurally thus far.

The only natural counterpart to this synthetic phase known thus far is the olenite from the Stoffhütte pegmatite in the Koralpe, Styria, Austria, for which the combined results of wet chemical, electron microprobe and crystal structure analyses yielded the formula (Ertl et al. 1997) $(\text{Na}_{0.43} \text{Ca}_{0.24} \square_{0.33}) (\text{Al}_{2.43} \text{Li}_{0.33} \square_{0.28}) \text{Al}_6 [\text{Si}_{4.87} \text{B}_{1.23} \text{O}_{18}] (\text{BO}_3)_3 (\text{OH})_{3.36} \text{O}_{0.64}$.

Compared to the synthetic phase it contains a smaller amount of excess boron. The tetrahedral coordination of this excess boron was most recently substantiated by a new and independent crystal structure analysis (Hughes et al. 1999).

In contrast to these high-alumina tourmalines it was shown experimentally for the Mg end member phase dravite, ideally $\text{Na Mg}_3 \text{Al}_6 [\text{Si}_6 \text{O}_{18}] (\text{BO}_3)_3 (\text{OH})_4$, that – despite the presence of excess boron in the coexisting gas phase during the high-pressure syntheses – this synthetic tourmaline does not exhibit any excess boron beyond the theoretical value of 3.0 p. f. u. (Werdinger – Schreyer 1996).

In this same vein, it does not seem surprising that no tetrahedral boron could be found by the detailed investigations of Bloodaxe et al. (1999) on crystals of the schorl-dravite series. This obviously corroborates the earlier and much more extensive study by Povondra (1981) on 85 samples, primarily from Czechoslovakia, of that same series. Povondra (1981) had concluded that the boron atoms present in his tourmalines can only vary in the range 3.000 ± 0.025 .

Further impressive support from nature for the restriction of excess boron to aluminous tourmaline varieties was most recently contributed by Kalt et al. (1999) through complete chemical analyses (except for hydrogen) of tourmalines occurring within the contact zone of the unusual Stoffhütte pegmatite that carries the excess-boron olenite (see above). Within this contact zone against gneissose micaschists, tourmaline compositions cover the whole range of solid solutions from magnesian schorls to lithian olenites, which have excess-boron formulae similar to that given above. Most importantly, there is a positive linear relationship between the increasing amounts of excess boron per formula unit and the successive substitution of (Fe,Mg) in the octahedral Y site by Al.

The possibility of an introduction of excess boron into elbaitic tourmalines cannot be judged thus far. The careful analyses of 18 elbaite from Czechoslovakia by Povondra et al. (1985) only gave normal B values near 3.0 p. f. u. On the other hand, for the physical conditions of formation of the Stoffhütte pegmatite, a solid solution from the lithian olenite of Ertl et al. (1997) discussed before to ideal elbaite, $\text{Na} (\text{Li}_{1.5} \text{Al}_{1.5}) \text{Al}_6 [\text{Si}_6 \text{O}_{18}] (\text{BO}_3)_3$

$(\text{OH})_4$, would seem to be viable. Most recently, Tagg et al. (1999) reported small amounts of tetrahedral boron in elbaite and elbaitic tourmalines from several pegmatites in the United States.

While there is thus no longer any doubt about the possible presence of excess boron in tourmalines of specific compositions, the next question arising is whether or not this replacement of silicon by boron in the tetrahedral site of the structure is restricted to certain PT-conditions of the experiment or of petrogenesis in nature. Unfortunately, the data available thus far from both sides are not satisfactory.

The syntheses of excess-boron olenites reported by Schreyer et al. (2000) were confined to high pressures of 10 kbar and more. A preliminary stability field (Fig. 1) based on the work of Wodara (1996) applies only to these high pressures but leaves open, whether excess-boron olenite may, or may not, occur within the continental crust. Perhaps one might conclude by extrapolation that, if it occurs at all within the uppermost 35 km, it would be restricted to rather low temperatures. Another yet open problem discussed by Schreyer et al. (2000) refers to possible compositional variations of the synthetic olenites as a function of the PTX-conditions applied. Thus, the theoretical end-member composition of olenite as defined by Sokolov et al. (1986), $\text{Na}_{1-x} \text{Al}_3 \text{Al}_6 [\text{Si}_6 \text{O}_{18}] (\text{BO}_3)_3 (\text{O},\text{OH})_4$, or $\text{Na} \text{Al}_3 \text{Al}_6 [\text{Si}_6 \text{O}_{18}] (\text{BO}_3)_3 \text{O}_3 (\text{OH})$ (Hawthorne – Henry 1999), may also appear as a stable synthetic phase, although with unknown stability limits.

The natural olenite described by Sokolov et al. (1986) from the type locality in the Kola Peninsula, Russia, seems to exhibit a normal boron content near 3.0 B p. f. u., although no direct boron analyses are available. Judging from its type of occurrence in a pegmatite cross-cutting metadiabase, the pressure of its formation does not seem to have been very high. On the other hand, the excess-bo-

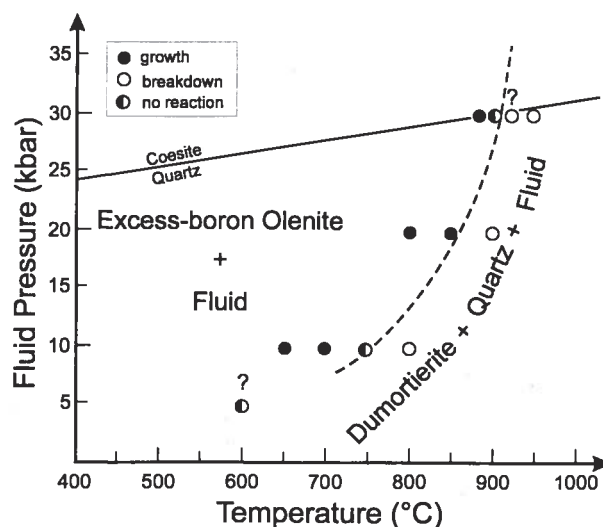


Fig. 1. Preliminary pressure-temperature stability field of excess-boron olenite for high pressures based on seeded runs by Wodara (1996). Note that there may be compositional variations of excess-boron olenite within the field of its growth (Schreyer et al. 2000).

ron olenite from the Stoffhütte pegmatite in Austria could have formed under rather high-pressure conditions. Its locality within the Koralpe is part of the Austroalpine Unit made up mainly of Hercynian crustal rocks that underwent subsequent Early Alpine subduction zone metamorphism. Following Hoinkes et al. (1999) pressures as high as 20 kbar may locally have been attained. Ertl-Brandstätter (1998) consider the occurrence to be a metapegmatite. However, the detailed field and time relations of the olenite-bearing pegmatite have not been worked out thus far, so that uncertainties remain. Nevertheless, at this stage of the investigations, the hypothesis that the excess-boron olenite of Stoffhütte formed at relatively high pressures and low temperatures is rather attractive.

Boron in muscovite and boromuscovite

Perhaps the earliest investigations on the presence of boron in muscovite are those of Harder (1959), who analyzed spectrographically 12 muscovite samples from various localities and obtained concentrations ranging from 11 to 1480 ppm B equalling 0.003 to 0.46 wt. % B_2O_3 . One sample that coexisted with tourmaline gave 0.016 wt. % B_2O_3 . Relatively high values were from granite and pegmatite muscovites, the highest one from a muscovite of a tin deposit. Černý et al. (1995) analyzed muscovites and other micas from two tourmaline-bearing pegmatites of the Czech Republic, determining boron with an ion microprobe. They reported values between 0.048 and 0.239 wt. % B_2O_3 and one exceptionally high concentration of 1.10 wt. % from Rožná. This amounts to 0.127 B atoms p. f. u. in muscovite using the formula $KAl_2[AlSi_3O_{10}](OH)_2$, or to about 13 mol % of end member boromuscovite, $KAl_2[B_2Si_3O_{10}](OH)_2$ (see Fig. 2). No record is available as to whether or not any of these muscovites occurred in direct grain contact with tourmaline or other boron-bearing minerals. At any rate, these muscovites represent primary and early products of pegmatite crystallization, probably more or less contemporaneous with tourmaline formation.

In contrast, the occurrences of boromuscovite known thus far (Foord et al. 1991; Novák et al. 1999) were clearly deposited from late hydrothermal fluids within pegmatites. They form fine-grained, snowlike coatings with thicknesses in the cm-range on primary minerals such as orthoclase and elbaite (!), either along ruptures or within miarolitic cavities. In the type locality, Little Three Mine of southern California (Foord et al. 1991), the composition of boromuscovite constitutes about 77 mol % of the ideal end member (Fig. 2), whereas at Řečice, Moravia, Czech Republic (Novák et al. 1999), boromuscovite occurs in two generations and varies compositionally between 61 and 97 mol % end member (Fig. 2; note however, that boron in the near-end-member mica was not analyzed but calculated by difference). All natural boromuscovites represent mixtures of the two polytypes $2M_1$ and $1M$ in variable proportions. According to a Rietveld refinement of the Řečice material by Liang et al. (1995), boron in the tetrahedral sites is evenly distributed between the two polytypes.

Pure end-member boromuscovite was first synthesized as a single-phase product at high pressures (15–30 kbar) by Jung (1996). Only some selected results of this work were published thus far in abstracts by Schreyer – Jung (1997) and Schreyer (1999). Using the seeding technique, Jung (1996) had determined the approximate stability field of boromuscovite (Fig. 3), with the surprising result that it is actually a high-pressure mineral, requiring minimum pressures of about 5 kbar at 500 °C and 10 kbar at 750 °C. At lower pressures, that is under conditions where the normal muscovite end member is stable (compare Fig. 3), boromuscovite breaks down to K feldspar + an Al-borate (probably $Al_4B_2O_9$) + a boron-bearing fluid. At pressures >10 kbar and high temperatures, boromuscovite – in the presence of water – melts, or dissolves, congruently, at temperature values consistently about 100 °C lower than the upper stability limit of muscovite (Fig. 3). This type of stability field would explain readily why boromuscovite does not form under the low-pressure, medium-temperature conditions of pegmatite

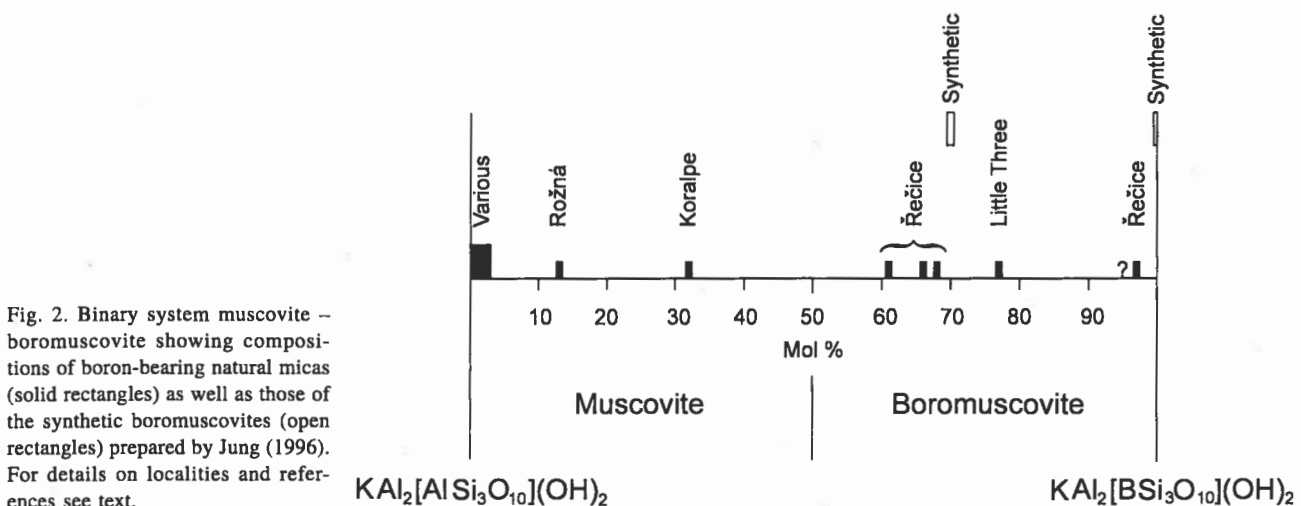


Fig. 2. Binary system muscovite – boromuscovite showing compositions of boron-bearing natural micas (solid rectangles) as well as those of the synthetic boromuscovites (open rectangles) prepared by Jung (1996). For details on localities and references see text.

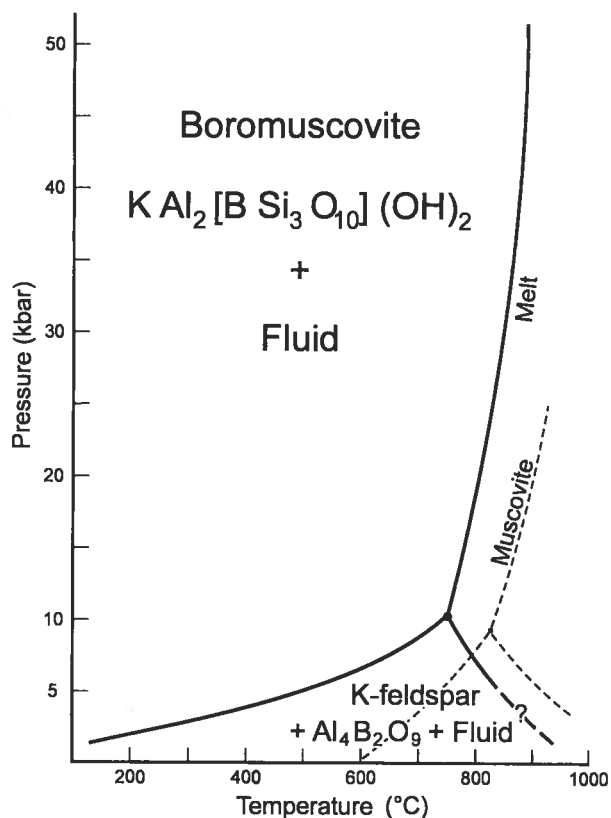


Fig. 3. Pressure-temperature stability field of end-member boromuscovite based on seeded runs by Jung (1996). The upper thermal stability of muscovite (dashed lines) shown for comparison is taken from Chatterjee – Johannes (1974).

crystallization, but only when – upon cooling at \pm constant pressure – lower temperatures in the hydrothermal range (near 300 °C?) had been attained. However, the relations seem to be more complex, because Jung (1996) could readily synthesize – at low as well as at high pressures (Fig. 4) – an aluminous boromuscovite with the composition $\text{K Al}_2 [\text{B}_{0.7}\text{Al}_{0.3}\text{Si}_3\text{O}_{10}] (\text{OH})_2$. Although no reversed experiments were performed with this composition, it seems that incorporation of tetrahedral Al into boromuscovite stabilizes this phase towards lower pressures. Thus, if this were true, the Al-bearing boromuscovites from Little Three Mine and Řečice (Fig. 2) would actually have been physically stable also under the conditions of primary pegmatite crystallization.

Powder X-ray diffraction studies of natural and synthetic boromuscovites yield interesting results on their cell parameters as a function of Al-contents. Like the natural minerals, the end-member boromuscovite of Jung (1996) was made up of a mixture of the two polytypes $2M_1$ and $1M$. All lattice parameters determined for these two polytypes are decidedly lower than those of the same polytypes of normal muscovite, the cell volumes decreasing by 6–7 % (Schreyer – Jung 1997). In Fig. 5 the cell volumes of boron-free and boron-bearing muscovites as well as of all boromuscovites known to date are plotted as a function of their B-contents. Although the values of the natural boromuscovites are certainly influenced by

other chemical variables as well, it is clear that their cell volumes plot consistently below the linear extrapolation curves between the pure muscovite and pure boromuscovite data. The same holds for the synthetic boromuscovite solid solution of Jung (1996) containing 70 mol % of the end member. It seems, therefore, that aluminous boromuscovites exhibit an extremely non-ideal behaviour with strongly negative excess mixing volumes, which would explain the apparently preferable formation of these members of the solid solution series, both in nature and experiment, over a wide PT-range (see Fig. 4).

Importantly, the boron-richest natural muscovite known thus far was recently discovered in the Stoffhütte pegmatite of the Koralmpe, which is the host rock of the excess-boron olenite discussed in the previous section. The analyses reported by Bernhardt et al. (1999) were obtained on books of up to 20 by 1.5 cm size and yielded 2.86 wt. % of B_2O_3 equalling 32 mol % of boromuscovite end member. $2M_1$ is the only polytype present. Its cell volume is also given in Fig. 5 and seems to indicate that there is no excess mixing volume in this range of the muscovite–boromuscovite solid solution series.

Discussion

In order to approach the problem of boron distribution between tourmaline and muscovite it may be convenient

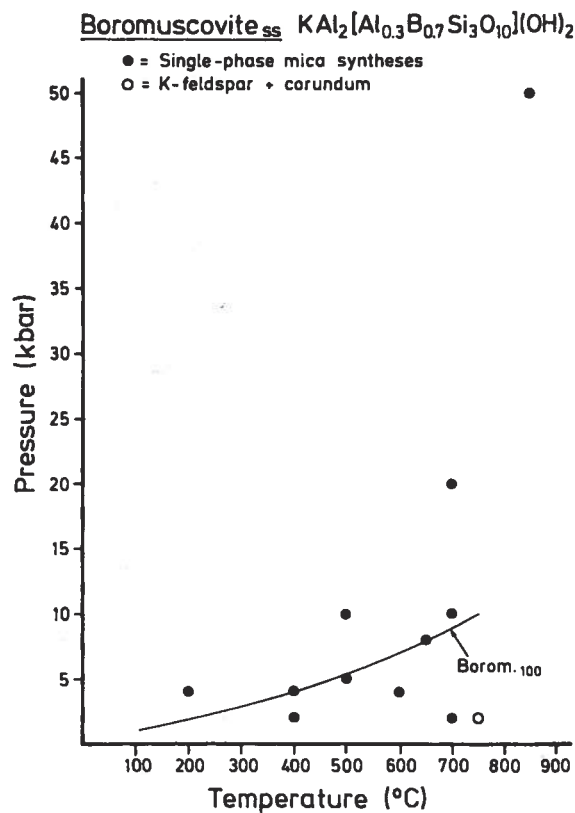


Fig. 4. Pressure-temperature growth field of a 70 mol % end-member boromuscovite (solid dots) as determined by Jung (1996). The solid line marks the lower-pressure stability limit of end-member boromuscovite as in Fig. 3.

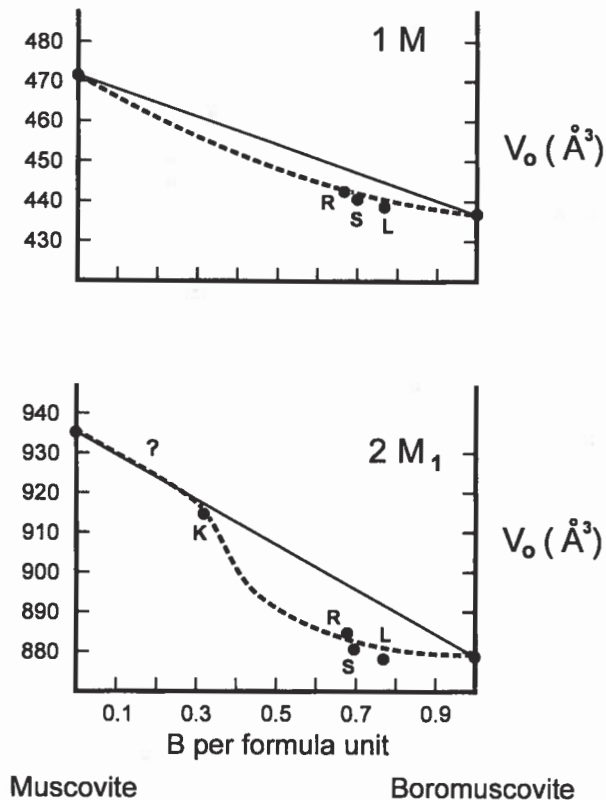


Fig. 5. Cell volumes of micas in the system muscovite-boromuscovite (Fig. 2): K=Koralpe; R=Řečice; S=Synthetic; L=Little Three. Sources of data: K: Bernhardt et al. (1999); R: Novák et al. (1999, sample R 15); S: Jung (1996); L: Foord et al. (1991); end-member boromuscovite: Jung (1996); end-member muscovite: PDF 6–263 for $2M_1$ and PDF 7–25 for 1M as in Foord et al. (1991).

to define a distribution coefficient as $D_B = (B_2O_3 \text{ in tourmaline in wt. \%}) / (B_2O_3 \text{ in muscovite in wt. \%})$.

Applying this to the few cases in the more recent literature where boron analyses of muscovite were reported (Fig. 2), and where these muscovites are known to coexist with tourmaline, or – if not directly – occur in pegmatites that carry abundant tourmaline, the following picture arises.

For the two Moravian pegmatites Rožná and Dobrá Voda studied by Černý et al. (1995) tourmaline (schorl to elbaite) occurs among the primary minerals and appears to be often associated (although perhaps not in grain contact) with the muscovites that were analyzed. If we assume the tourmalines to exhibit stoichiometric boron contents and take for them an average B_2O_3 -content of 10.0 wt. %, the D_B -values range from 208 to 9.1, the latter applying to the exceptionally high-boron muscovite of Rožná with 13 mol % boromuscovite end member (Fig. 2).

For the unusual olenite-muscovite pegmatite of Stoffhütte in the Alps, the D_B -value of 5.6 is still lower, although now the B_2O_3 -content of the tourmaline phase has risen to 16.06 wt. % (Ertl et al. 1997).

For the two localities of boromuscovite known thus far, it is rather questionable that an equilibrium distribution of boron has been attained between the late hydrothermal mica phases and any tourmalines of earlier gen-

erations on which these micas had precipitated. On the other hand, according to Novák (1999, Fig. 2) the stages of elbaite and boromuscovite precipitation may be relatively closely spaced in time. At any rate, if equilibrium existed, the lowest D_B -values (1.80–1.12) would result, again assuming 10 wt. % B_2O_3 for tourmaline. Judging from the facts that tourmaline stability fields extend to very low temperatures (see Fig. 1 here and Werding – Schreyer (1996) for other tourmalines) and that tourmaline may occur as an authigenic mineral, there should theoretically be no difficulty for the coexistence of boromuscovite and tourmaline (see also Novák 1999).

Thus, there may be a remarkable decrease of the boron distribution coefficient D_B between tourmaline and muscovite phases from the classically assumed value of infinity, which may indeed be true for many geologic environments, to nearly unity. Once understood and calibrated, this property carries the potential to be used for evaluating the conditions of formation or equilibration of tourmaline-muscovite mineral pairs and their enclosing rocks.

The most important question to be solved is, of course, which parameters can influence the distribution coefficient D_B . Temperature and especially pressure are obvious candidates, if the conditions of formation of the Stoffhütte, Koralpe, pegmatite really involved relatively high pressures. In addition, there may be bulk compositional effects, above all the amount of boron in the rock-forming system, for pegmatites the boron activity of the fluid phases during their cooling history. In a very qualitative empirical and partly hypothetical way, the sketch of Fig. 6 may help to initiate discussion.

The abscissa of Fig. 6 separates Mg, Fe-rich mafic silicate minerals on the left side from Al-rich salic silicate minerals on the right side. For boron-free systems or rocks along the top line it is well known that the two mineral groups can coexist. If boron is added along the ordinate axis downwards, most of the mafic minerals are being converted, as a function of growing boron activity, into Mg, Fe-tourmalines. The experiments of Frondel and Colette (1957), who reacted various kinds of silicate mineral grains and magnetite with borate solutions, may serve as an example for this kind of boron metasomatism. At moderate boron activities these tourmalines coexist with the boron-free mafic minerals. It should be remembered here, that biotites may also incorporate boron: Stubican – Roy (1962) as well as Hazen – Wones (1972) were able to synthesize phlogopite phases, in which all tetrahedral Al is replaced by boron. However, no biotites with high B-values were ever described from nature, and the boron concentrations found in biotite by Harder (1959) are in the low ppm range. Therefore, possible solid solubility is ignored in Fig. 6. Among the salic minerals, it is clear that all the Al in albite may be substituted by boron to form the feldspar reedmergnerite (for further information see Werding – Schreyer 1996; Schreyer – Werding 1997). On the other hand, petrographic work on the pegmatite from Stoffhütte, Austria,

by Kalt et al. (1999) indicates that the sodic plagioclase of this rock is being partly replaced by myrmekitic intergrowths of quartz with the excess-boron olenite cited earlier in this paper. Thus, plagioclase is apparently not stable in the presence of excess boron, and the two minerals, olenite and plagioclase, may coexist at intermediate boron activities. Between muscovite and boromuscovite a series of solid solution exists as discussed in the last section. Pure Al-silicates like kyanite or andalusite carry no, or only trace amounts of, boron (Harder 1959), but with increasing boron activity growing amounts of the boron-bearing mineral dumortierite (Werding – Schreyer 1996) will coexist. From the analytical work of Kalt et al. (1999) on samples from the Stoffhütte pegmatite it is now clear that a complete solid solution exists between magnesian schorl and excess-boron olenite (see Fig. 6). The other salic boron minerals shown at the lower right corner of Fig. 6 (reedmergnerite, dumortierite) are probably compatible with the Mg, Fe-tourmalines. Finally, it is evident from many rock types that these Mg, Fe-tourmalines may also coexist with the boron-free salic minerals, so that the diagonal “tie line” is justified. On the other hand, no coexistence seems to be possible between the boron-free mafic minerals in the upper left corner with the salic boron minerals in the lower right.

While the sketch of Fig. 6 yields a first survey of compatibility and solubility relations between the minerals involved, it is unable – because of its multicomponent, multiphase nature – to depict element fractionations between the coexisting minerals and solid solutions. Thus, for the topic of this paper, a closer approach is necessary. The chemical system comprising all the tourmalines of the base line of Fig. 6 together with the muscovite-boromuscovite solid solutions (Fig. 2) includes at least

eight components (Na_2O , K_2O , MgO , FeO , Al_2O_3 , B_2O_3 , SiO_2 , H_2O), so that the construction of simplified concentration triangles for depicting phase relations becomes very difficult. Therefore, in Fig. 7 two relevant partial systems of solid solution are selected and compared to each other. In the lower portion, the system muscovite-boromuscovite (Fig. 2) with some of the known micas is shown again, whereas the upper portion represents a simplified series of solid solution between ideal olenite and the theoretical end member resulting solely from substitution of tetrahedral Si by B+H as discussed by Schreyer et al. (2000), including (in projection) the excess-boron olenite synthesized by these authors as well as the natural excess-boron olenite described from the Stoffhütte pegmatite (Ertl et al. 1997). The only “tie line” drawn is that of the olenite – muscovite pair of the Stoffhütte pegmatite with its D_B -value shown in between. The remaining D_B -values given ranging from infinity for ideal olenite – muscovite to 2.51 for the theoretical end member excess-boron olenite with boromuscovite are calculated, but may not apply under any condition. Here is where experiments are needed.

In Fig. 8 a similar plot is presented for the two partial systems muscovite – boromuscovite and the Mg, Fe-tourmalines with the end member dravite as an example. According to present knowledge (see above) there is no excess boron in these tourmalines. Depending on the boron contents of the micas, the D_B -values would vary from infinity to 1.15, but – except for the Rozna muscovite – such mica-tourmaline coexistences were not discovered as yet. The Koralpe muscovite is not plotted here, because no grain contacts exist for this mica with a Mg, Fe-tourmaline. However, such observations may become available in the future from boron analyses of coexisting muscovites and tourmalines in the contact zone of this pegmatite.

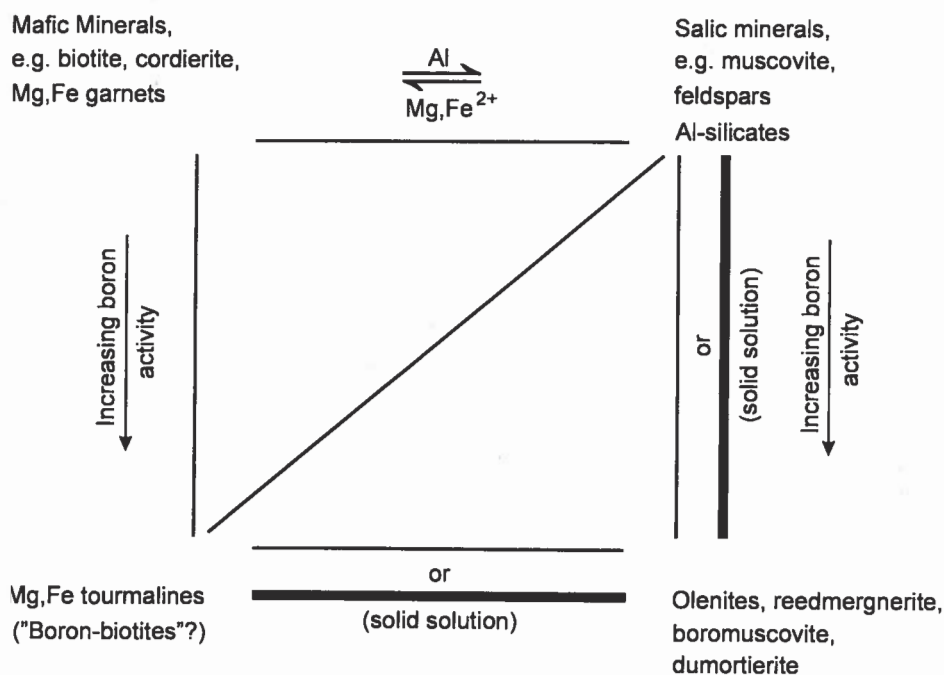


Fig. 6. Simplified sketch showing compatibility (thin lines) and solid solubility relations (heavy lines) between various groups of boron-free and boron-bearing silicate minerals. For detailed discussion see text. Note incompatibility of mafic minerals in the upper left with the boron-rich phases in the lower right. This is not a phase diagram!

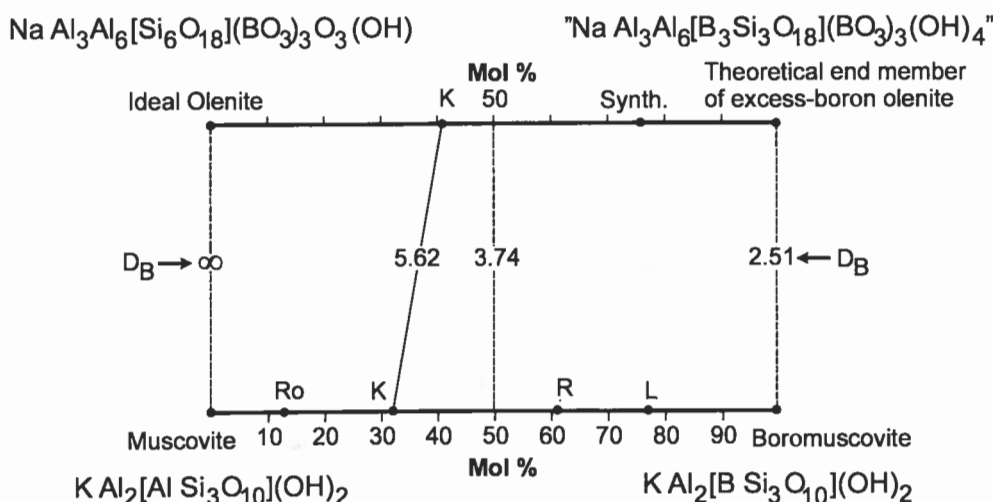


Fig. 7. Comparison between the binary system muscovite-boromuscovite (Fig. 2) in the lower part and the hypothetical join from idealized olenite (Hawthorne – Henry 1999) to a theoretical excess-boron olenite end member (Schreyer et al. 2000) above. Abbreviations K, R, L are for the localities as explained in Fig. 5, where also the references for these mica data are listed. Ro stands for Rožná (Černý et al. 1995, sample H-8M). Reference for the natural excess-boron olenite K in the upper part is Ertl et al. (1997), for the synthetic olenite phase Schreyer et al. (2000). Note that these two tourmaline phases are projected onto the hypothetical join. Numbers in the middle represent values for the distribution coefficient $D_B = (B_2O_3 \text{ in tourmaline in wt. \%}) / (B_2O_3 \text{ in mica in wt. \%})$, that could be calculated from analytical data only for the coexisting pair (solid line) at locality K (Koralpe). The remaining values are theoretical numbers applying to the pairs indicated by dashed lines.

In summary, it is quite clear that boron partitioning between tourmaline and muscovite may vary widely, but the reasons are only poorly understood at present. The following influences should be considered:

1. High pressures may favor boron introduction into the muscovite phase and into the silicon position of tourmaline, which would be in accordance with the crystal chemical prediction of preferential boron fractionation into tetrahedral sites with increasing pressures. The unique Stoffhütte pegmatite from Koralpe, Austria, may be an example.

2. A potential temperature influence is expected to be in the direction that lower temperatures would favor bo-

ron introduction into both minerals, as shown by the boromuscovite stability field (Fig. 3).

3. The bulk chemistry of the rock excluding boron may also be important (compare Fig. 6), so that highly aluminous, Mg, Fe-poor systems favor the introduction of boron into muscovite as well as of excess boron into tourmaline (olenite) as also suggested by the Stoffhütte pegmatite. On the other hand, in Mg, Fe-bearing systems, boron may preferentially fractionate into the dominantly Mg, Fe-rich tourmalines. Or – looking at the picture from the side of element distribution of the basic components – Mg and Fe in such systems may be preferentially partitioned into the tourmaline phase to form essentially members of the

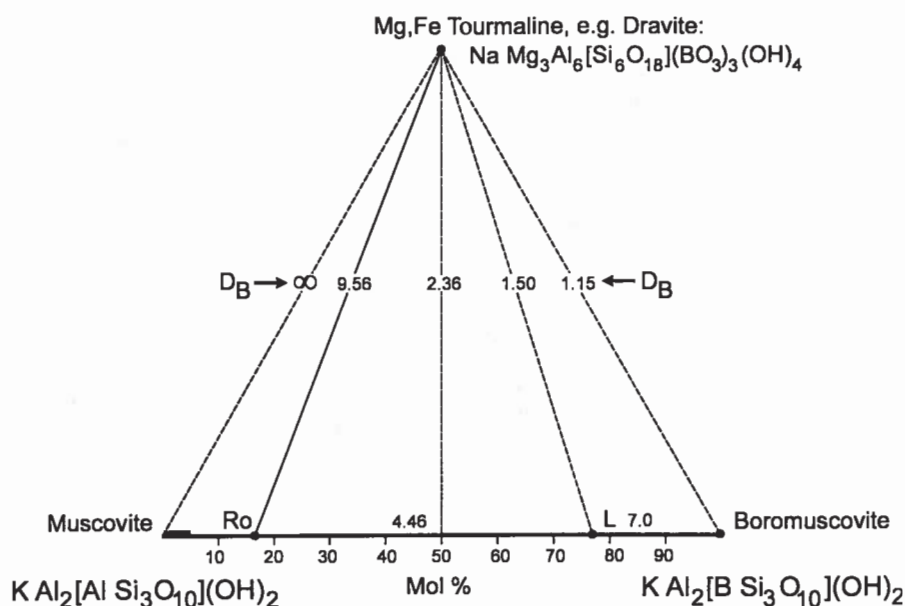


Fig. 8. Comparison between the system muscovite-boromuscovite as in Fig. 7 (lower part) and the theoretical end member dravite at the top. Dashed connecting lines with theoretical D_B -values calculated are speculative. The solid line may mark a true coexistence between the muscovite H-8M from Rožná (Černý et al. 1995) and a tourmaline of the schorl-elbaite series with normal B content of 3.0 p. f. u., occurring in this same pegmatite (loc. cit.).

dravite-schorl series without any aluminous (olenite) component. Such fractionation mechanism might also explain why olenite is apparently such a rare natural tourmaline.

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References

- Bernhardt, H.-J. – Brandstätter, F. – Ertl, A. – Körner, W. – Mikenda, W. – Pertlik, F. (1999): Untersuchungen an einem borhaltigen Muskovit $2M_1$ von der Koralpe, Steiermark. – Ann. Naturhist. Mus. Wien 100 A, 1–11.
- Bloodaxe, E. S. – Hughes, J. M. – Dyar, M. D. – Grew, E. S. – Guidotti, C. V. (1999): Linking structure and chemistry in the schorl-dravite series. – Amer. Mineral., 84, 922–928.
- Černý, P. – Staněk, J. – Novák, M. – Baadsgaard, H. – Rieder, M. – Ottolini, L. – Kavalová, M. – Chapman, R. (1995): Geochemical and structural evolution of micas in the Rožná and Dobrá Voda pegmatites, Czech Republic. – Mineral. Petrol., 55, 177–201.
- Chatterjee, N. D. – Johannes, W. (1974): Thermal stability and standard thermodynamic properties of synthetic $2M_1$ muscovite, $KAl_2[AlSi_3O_{10}(OH)_2]$. – Contrib. Mineral. Petrol., 48, 89–114.
- Ertl, A. – Brandstätter, F. (1998): Olenit mit Borüberschuß aus einem Metapegmatit östlich der Stoffhütte, Koralpe, Steiermark, Österreich. – Mitt. Abt. Miner. Landesmuseum Joanneum 62/63, 3–21.
- Ertl, A. – Pertlik, F. – Bernhardt, H.-J. (1997): Investigations on olenite with excess boron from the Koralpe, Styria, Austria. – Öster. Akad. Wiss., Math. – Naturw. Kl. Anzeiger Abt. I, 134, 3–10.
- Foord, E. E. – Martin, R. F. – Fitzpatrick, J. J. – Taggart, Jr., J. E. – Crock, J. G. (1991): Boromuscovite, a new member of the mica group, from the Little Three mine pegmatite, Ramona district, San Diego County, California. – Amer. Mineral., 76, 1998–2002.
- Frondele, C. – Collette, R. L. (1957): Synthesis of tourmaline by reaction of mineral grains with $NaCl-H_3BO_3$ solution and its implication in rock metamorphism. – Amer. Mineral., 42, 754–758.
- Harder, H. (1959): Beitrag zur Geochemie des Bors. Teil I: Bor in Mineralen und magmatischen Gesteinen. – Nachrichten der Akademie der Wissenschaften Göttingen II. Math.-physik. Klasse. 5, 67–122.
- Hawthorne, F. C. – Henry, D. J. (1999): Classification of the minerals of the tourmaline group. – Eur. J. Mineral., 11, 201–215.
- Hazen, R. M. – Wones, D. R. (1972): The effect of cation substitutions on the physical properties of trioctahedral micas. – Amer. Mineral., 57, 103–129.
- Hoinkes, G. – Koller, F. – Rantitsch, G. – Dachs, E. – Höck, V. – Neubauer, F. – Schuster, R. (1999): Alpine metamorphism in the Eastern Alps. – Schweiz. Mineral. Petrogr. Mitt., 79, 155–181.
- Hughes, J. M. – Ertl, A. – Dyar, M. D., – Grew, E. S. – Shearer, C. K. – Yates, M. G. (1999): Boron in the tourmaline tetrahedral site: chemistry and structure of a boron-rich olenite. – Abstract 2nd European Workshop on Tourmaline and Borosilicates, Paris 21–24 September 1999, Bull. Liaison S. F. M. C. 11, 117 pp.
- Jung, I. (1996): Experimentelle Studien über borhaltige Glimmer im System $K_2O-MgO-Al_2O_3-B_2O_3-SiO_2-H_2O$. – Unpublished Diploma Thesis, Ruhr-Universität Bochum, 101 pp.
- Kalt, A. – Schreyer, W. – Bernhardt, H.-J. – Ertl, A. (1999): Complete solid solution between magnesian schorl and lithian excess-boron olenite in the Koralpe pegmatite. Abstract 2nd European Workshop on Tourmaline and Borosilicates, Paris 21–24 September 1999, Bull. Liaison S. F. M. C. 11, 117–118.
- Liang, J.-J. – Hawthorne, F. C. – Novák, M. – Černý, P. (1995): Crystal-structure refinement of boromuscovite polytypes using a coupled Rietveld-static-structure energy-minimization method. – Canad. Mineral., 33, 859–865.
- Novák, M. (1999): Cassiterite and tusionite as monitors of B and Sn behaviour in the elbaite pegmatite at Řečice near Nové Město na Moravě, western Moravia, Czech Republic. – N. Jb. Mineral. Mh., Jg 1999, 481–493.
- Novák, M. – Černý, P. – Cooper, M. – Hawthorne, F. C. – Ottolini, L. – Xu, Z. – Liang, J.-J. (1999): Boron-bearing $2M_1$ polyolithionite and $2M_1+1M$ boromuscovite from an elbaite pegmatite at Řečice, western Moravia, Czech Republic. – Eur. J. Mineral., 11, 669–678.
- Povondra, P. (1981): The crystal chemistry of tourmalines of the schorl-dravite series. – Acta univ. Carol., Geol., 3, 223–264.
- Povondra, P. – Čech, F. – Staněk, J. (1985): Crystal chemistry of elbaites from some lithium pegmatites of the Czech Massif. – Acta univ. Carol., Geol., 1, 1–24.
- Schreyer, W. (1999): Boron in muscovite. – Berichte der Deutschen Mineralogischen Gesellschaft, Beih. z. Eur. J. Mineral. Vol. 11, 1999, 1, 206 pp.
- Schreyer, W. – Jung, I. (1997): Boromuscovite, $KAl_2[BSi_3O_{10}]_2(OH)_2$: A high-pressure mineral. – Abstract Supplement No. 1 to TERRA nova, Vol. 9, 32–33.
- Schreyer, W. – Werding, G. (1997): High-pressure behaviour of selected boron minerals and the question of boron distribution between fluids and rocks. – Lithos, 41, 251–266.
- Schreyer, W. – Wodara, U. – Marler, B. – van Aken, P. A. – Seifert, F. – Robert, J.-L. (2000): Synthetic tourmaline (olenite) with excess boron replacing silicon in tetrahedral sites: I. Synthesis conditions, chemical and spectroscopic evidence. – Eur. J. Mineral. (in press)
- Sokolov, P. B. – Gorskaya, M. G. – Gordienko, V. V. – Petrova, M. G. – Kretzer, Yu. L. – Frank-Kamenitskii, V. A. (1986): Olenite $Na_{1-x}Al_3Al_6B_3Si_6O_{27}(O, OH)_4$ – A new high-alumina mineral of the tourmaline group. – Zapiski Vses. Mineralog. Obshch., 115, 119–123 (in Russian).
- Stubican, V. – Roy, R. (1962): Boron substitution in synthetic micas and clays. – Amer. Mineral., 47, 1166–1173.
- Tagg, S. L. – Cho, H. – Dyar, M. D. – Grew, E. S. (1999): Tetrahedral boron in naturally occurring tourmaline. Amer. Mineral., 84, 1451–1455.
- Werdning, G. – Schreyer, W. (1996): Experimental studies on borosilicates and selected borates. – Rev. Mineral., 33, 117–163.
- Wodara, U. (1996): Synthese und Eigenschaften von Turmalinen im System $Na_2O-Al_2O_3-SiO_2-B_2O_3-H_2O$. – Unpublished Diploma Thesis, Ruhr-Universität Bochum, 99 pp.
- Wodara, U. – Schreyer, W. (1997): Turmaline mit Borüberschuß im System $Na_2O-Al_2O_3-B_2O_3-SiO_2-H_2O$ (NABSH). Berichte der Deutschen Mineralogischen Gesellschaft, Beih. z. Eur. J. Mineral., v. 9, No. 1, 394 pp.
- Wodara, U. – Schreyer, W. (1998): Tetrahedral boron in tourmalines of the system $Na_2O-Al_2O_3-B_2O_3-SiO_2-H_2O$. – Abstract supplement No. 1 to TERRA nova, v. 10, 68 pp.

Závisí rozdělení bóru mezi turmalín a muskovit na prostředí krystalizace?

Je zřejmé, že rozdělení bóru mezi turmalín a muskovit může kolísat v širokém rozpětí, ale důvody pro tuto skutečnost nejsou zatím příliš jasné. Můžeme uvažovat následující vlivy:

(i) Vysoký tlak upřednostňuje vstup bóru do muskovitu a do tetraedrické pozice křemíku v turmalínu, což by mohlo být v soulase s krystalochemickými předpoklady přednostní frakcionace bóru do tetraedrické pozice se vzrůstajícím tlakem. Unikátní Stoffhütte pegmatit v Alpách (Koralpe) v Rakousku může být typickým příkladem.

(ii) Lze očekávat, že pokles teploty upřednostní vstup bóru do obou minerálů, jak je ukázáno na poli stability boromuskovitu (Obr. 3).

(iii) Celkové složení horniny, nehledě na bór, může být také důležité (srovnej Obr. 6). Vysoce hlinité systémy chudé Mg a Fe upřednostňují vstup bóru do muskovitu a také mohou ovlivnit vznik přebytku bóru v turmalínu (olenit), tak jak to bylo zjištěno ve Stoffhütte pegmatitu. Podíváme-li se na problém z jiné strany, v systémech obsahujících Fe a Mg je bór frakcionován do převládajících Fe, Mg-turmalínů. Nebo z pohledu distribuce základních komponent, Fe a Mg mohou být v takových systémech přednostně frakcionovány do turmalínu a produkovat turmalínové řady skoryl-dravit bez hlinité (olenitové) komponenty. Takový mechanismus frakcionace by mohl vysvětlit skutečnost, proč je olenit v přírodě tak vzácný.