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KEYWORDS

Alpine shear zone, East Carpathians, metamorphic petrology, geothermobarometry, microprobe, schorl-dravite

Abstract

This study describes mineralogical and crystallochemical characteristics of metamorphic tourmalines from an Alpine shear zone in a Variscan metamorphic rock sequence from the Maramures region in the northern part of the East Carpathians. We use this mineral to unravel aspects of the evolution of the tourmaline bearing host rocks and compare the crystallo-chemical characteristics to other tourmalines from Alps. Petrographic and microstructural observations, as well as electron microprobe analyses on several zoned tourmalines and associated minerals (mica, feldspar) from mylonitic schist of the Rebra terrane (Maramures Mountains), indicate that the pre-kinematic tourmalines belong to the alkali group (Na dominant), hydroxyl dominated on the crystallographic W-site and can be assigned to the species dravite and schorl. The tourmaline-bearing rocks have a metasedimentary protolith. The analysed porphyroblasts, rotated by simple shear, show corroded rim that are interpreted to have formed due to pressure release. Three main compositional zones were evidenced on a tourmaline porphyroblast: a core zone and two asymmetrically arranged inclusion-poor/ free rims, all formed in pre-alpine prograde metamorphic conditions. Based on mineral microstructural relations and geothermobarometry (tourmaline–muscovite, tourmaline–plagioclase geothermometry and phengite geobarometry), the metamorphic peak conditions of the investigated Rebra terrane were evaluated to have been at a temperature of ca. 590 to 620 \pm 22 °C and P_{min} = 5.5 - 6.0 \pm 0.5 kbar. By observing dynamically recrystallized microstructures in quartz and feldspar in the shear zone a temperature of 350 - 400 °C was estimated and the quartz paleopiezometry outlined a differential stress of about 1.5 kbar that implied only minor chemical change in tourmaline outer zone.

1. Introduction

The East Carpathians are an eastward prolongation of the Alps and Western Carpathians. Its Alpine (Cretaceous and Cenozoic) structure is developed in relation with a European megasuture formed by subduction and collision between the European and Adria plates, resulting an orogen structure composed by: External foredeep, Miocene thrust belts (Outer Dacides, Moldavides), Ophiolites (Transylvanian-Vardar and Piennini Klippen Belt), European derived allochtons (Dacia Mega-Units), the later intruded by Neogene island arc magmatic products and finally post-tectonic (post-late Cretaceous) Neogene sedimentary cover (Linzer et al., 1998; Schmid et al., 2004; Schmid et al., 2008) (Fig. 1).

Figure 1 shows a few locations of tourmalinebearing rocks formed in Pre-alpine or Alpine UHP-HP metamorphic events in the Alpine-Carpathian orogenic

belt. The tourmalines are frequently involved in shear zones of nappe stacking. In the East Carpathians there were also Alpine nappe stacking events, summarised by Săndulescu (1984), in which shear zones were identified a HP/LT dynamic metamorphic processes overprinted on the Variscan metamorphic basement (Balintoni et al., 1983; Kräutner, 1988; Kräutner, 1996; Munteanu and Tatu, 2003; Balintoni and Balica, 2013; Balintoni et al., 2014). Such an Alpine shear zone in Maramureş Mountains contains the tourmalines studied here (Zincenco et al., 1982; Zincenco, 1995; Kräutner and Bindea, 2002; Gröger, 2006). The question arises as to how this tourmaline can retain information regarding metamorphic evolution of its host rocks implied in an Alpine shear zone at pressures and temperatures much lower than in Alps. In particular, this study aims to use the mineral chemistry and crystal

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Figure 1: The structure of the Alpino-Carpathian-Dinaric orogen (after Linzer et al., 1998; Schmid et al., 2008; modified). (DVF = Dragoş Vodă Fault, PC = Peceneaga Camena Fault, SCF = South Carpathian Fault, CJF = Cerna Jiu Fault, MHL = Mid Hungarian Line, SEMP = line Salzach-Ennstal-Mariazell-Puchberg fault, TTZ = Teisseyre–Tornquist Zone) Red points are few tourmaline locations; black square = studied Maramureş Mountain area.

structure of several tourmalines from the dynamically retrogressed schists, to estimate their growth temperature and thus the evolution of their host rock and compare tourmaline crystallo-chemistry to other metamorphic tourmalines from Alps or Carpathians.

Tourmaline is an important accessory borosilicate of granitic, pegmatitic, and metamorphic rocks metamorphic origin, recording the host rock history and/or preserving some of its characteristics. This mineral super-group can respond to chemical changes in coexisting minerals (e.g., white micas, dark micas, chlorites) and fluids, due to variation of the pressure and temperature conditions. Consequently, it records the metamorphic history of the rock and sometimes may preserve the state before metamorphism (Henry and Guidotti, 1985; Henry and Dutrow, 1992). Tourmaline is also a good kinematic indicator in brittle-ductile deformed rocks (Simpson, 1986). It crystallizes in the rhombohedral system (space group R3m, Z = 3) and its structure can accommodate a large number of major, minor, and trace elements.

Tourmaline has the generalized structural formula $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$ (Novák et al., 2009; Henry et al., 2011), where the major and minor substitutions take place in the crystallographic sites X (Ca, Na, K, vacancy), Y (Li, Mg, Fe²⁺, Mn²⁺, Al, Cr³⁺, V³⁺, Fe³⁺, Ti⁴⁺), *Z* (Mg, Al, Fe³⁺, V³⁺, Cr³⁺), *T* (Si, Al, B), V (OH, O), and W (OH, O, F). The structural formula contains 31 anions (O, OH, F) that occupy the corners of coordination polyhedra. These anions are in eight sites, the O²⁻occupies O(2) and O(4)-O(8) sites. Three O(3) sites collectively termed the crystallographic V-site, which is filled by (OH)⁻ whereas one O(1) site, termed

the crystallographic W-site can accommodate OH⁻, F⁻ and O²⁻. Tourmaline shows a compositional polarity up to staurolite isograde ("+c" pole is richer in Al and Mg than "-c" pole), which disappears at higher grades (Bridge et al., 1977; Henry, 1992; Henry and Dutrow, 1992; Henry and Guidotti, 1985). Its zoning is frequently associated with specific fluid and mineral inclusions (Dutrow and Henry, 1994).

In metapelites, tourmaline chemistry depends on the type of protolith, metamorphic reactions, and the presence or absence of boron. Tourmaline may form diagenetic and epigenetic overgrowths on detrital tourmaline (O'Connor, 1990; Dutrow and Henry, 1994), may occur in salt domes (Erd, 1980), or be associated with Precambrian stromatolites (Byerly et al., 1986), in pegmatites, in high-grade pelitic gneisses and migmatites, and sometimes in eclogites (Schertl et al., 1991). Its *P-T* stability field is between ~ 150 °C under pressure conditions near the surface and 895 °C under pressure of 5 kb (dravite stability) (Manning and Pichavant, 1983).

1.1 Geological background

In the structure of the East Carpathians, Median Dacides represent a pile of Variscan metamorphic basement rocks of north-western Gondwana margin origin and Mesozoic sedimentary cover, stacked in three main Alpine tectonic units during the early–late Cretaceous Austrian tectonic phase (from bottom to top): Infrabucovinian, Subbucovinian, and Bucovinian nappes. In the basement of the Alpine nappes, Variscan nappes have also been recognized (Săndulescu, 1984; Săndulescu et al., 1991; Kräutner and Bindea, 2002; Munteanu and Tatu, 2003; Balintoni et al., 2009; Balintoni and Balica, 2013; Balintoni et al., 2014).

In Maramures Mountains all three Alpine tectonic units crop out (Figs 2a, 2b): Infrabucovinian (with Bretila terrane rocks), Subbucovinian (Rebra terrane, ± Negrișoara terrane and Pietrosu porphyroid, Tulgheș terrane) with its Mesozoic sedimentary cover and Bucovinian (Rebra terrane, \pm Negrisoara terrane, Tulghes terrane) with its Mesozoic sedimentary cover. Both Alpine and Variscan nappes are separated by thick (up to many hundreds of meters thick) brittle-ductile shear zones. Alpine tectonic nappe stacking also remobilised the older nappe detachment zones. On the north side of Vaser Valley, in Subbucovinian Rebra terrane, zircon fission track data of Gröger et al. (2013) evidenced a 96.6 Ma (Alpine) metamorphic event of sub-greenschist facies conditions, a late Cretaceous cooling and exhumation by 7 - 11 km. The Miocene lateral extrusion tectonics in Europe (Ratschbacher et al., 1991) have complicated the previous structure by faulting, wrenching, and imbrications. This is the reason why in this region many tectonic interpretations of geologic map have been made (Săndulescu et al., 1991; Zincenco et al., 1982; Zincenco, 1995; Kräutner and Bindea, 2002; Munteanu and Tatu, 2003).

The study of Alpine nappe detachment zones associated with brittle-ductile shear zone rock sequences could be a key to deciphering the complex evolution of this area. In the southern part of the Maramureş Mountains, along the Vaser Valley (a tributary of Vişeu Valley, in Fig. 2a) there are the lowermost Alpine Infrabucovinian unit rocks, represented by Bretila terrane mylonite micaschists, amphibolites and augen gneisses, overridden by Alpine Subbucovinian unit, consisting of Rebra terrane (sheared dolomitic marbles, amphibolites, micaschists, quartzites), ± Negrişoara biotite schists with Pietrosu porphyroid and Tulgheş terrane mylonitised metariolites (Fig. 2a).

The sheared Subbucovinian unit crops out under the Bucovinian unit in a tectonic half-window on west part of Vaser Valley, making up an imbrication structure (Fig. 2b). On east part of map in Figure 2a, along the Vaser Valley, Subbucovinian Tulgheş terrane rocks occur in a tectonic window under Bucovinian Rebra- and Tulgheş terrane rocks. The structure was intruded by Neogene magmatites hosting hydrothermal polymetallic ore deposits (Cook, 1997).

Retrogressed micaschist \pm garnet, \pm kyanite, amphibolite \pm garnet, leptite, layered and augen gneiss build up the Bretila terrane rocks from Infrabucovinian (Kräutner and Bindea, 2002). The marbles are missing in these rock sequences. According to Pană et al. (2002), the rocks have sedimentary protoliths of 1.65 Ga (by the Sm-Nd dating method), intruded by granitoids (zircon U-Pb age 433 -468 Ma, crystallization ages) and suffered a Variscan MP/ MT metamorphic peak event (464 Ma after Balintoni et al., 2009; Balintoni and Balica, 2013) followed by local migmatic processes (with supposed ages between 300 Ma and the crystallization age of granitoids). The rocks were later overprinted by an Alpine (~ 100 Ma- Ar-Ar method on phengitic micas, (Culshaw et al., 2012) dynamic metamorphism.

The Rebra terrane (the lowermost unit both from Subbucovinian and Bucovinian unit) consists of retrogressed micaschist ± garnet ± sillimanite, more or less mylonitised quartz-feldspar schist, grading into micaschist, orthogneiss, and lenses of dolomitic marble and amphibolite. It was divided into three lithostratigraphic formations, according to Kräutner et al. (1978); Kräutner et al. (1982); Kräutner et al. (1983); Kräutner et al. (1989): Rb1 and Rb3 formations comprises mainly metaterrigenous rock assemblages and Rb2 formation contains an assemblage dominated by amphibolite and marble lenses. The Rb2 formation hosts polymetallic Mississippi Valley type ore deposits. The Rebra terrane rocks, with a protolith age of 1.7 - 2.07 Ga (Sm- Nd method in Pană et al., 2002), have been initially metamorphosed under MP/MT peak conditions, corresponding to the crystallization of Nichitaş metagranite, locally overprinted by a LP/MT metamorphism (Balintoni, 1997). This metamorphic event was followed by retrogression during the post-Variscan and Alpine thermotectonic or deformational stages. Pană et al., (2002) and Balintoni et al., (2009); Balintoni et al., (2014) derived U-Pb data on zircons and suggested a Variscan age of peak metamorphism (376 - 407 Ma (LI), which has been followed by Alpine age dynamic metamorphic event (Ar/Ar data ~ 100 Ma on phengitic micas, Culshaw et al., 2012). Based on monazite ages from the Rebra unit of the Rodna Mountains, Reiser et al. (2019) suggested an Alpine (mid-Cretaceous) prograde metamorphism in these rock sequences.

The Negrisoara terrane of MP/MT peak metamorphism (461 Ma, Balintoni et al., 2014) is composed by a lower biotitic quartzitic schist sequence and the upper metadacitic Pietrosu Bistriței porphyroid (Kräutner and Bindea, 2002; Balintoni et al., 2009). In the studied area, this terrane is extremely deformed due to progressive shearing or missing specific rocks (ex. Pietrosu porphyroid) for recognise its rocks sequence. The Tulghes terrane rocks crop out both in the Subbucovinian and Bucovinian units. Its protolith are considered to be of Cambrian - Ordovician age (Vaida, 1999; Balintoni et al., 2014), metamorphosed during the regional prograde Variscan (462 Ma, Balintoni et al., 2014) and Alpine retrograde conditions (Kräutner, 1987). The Rb-Sr data of Zincenco (1995) evidenced the Variscan (Ordovician) peak metamorphic event suffered by Tulghes terrane rocks, under HP/LT conditions (metamorphic conditions based on the mineralogy of Mn ore from Tg2 formation (Hârtopanu, 2004)). The Tulghes terrane rocks are quartzitic schists, black quartzites with Mn ore deposits, metarhyolites (quartzo-feldspathic schists), greenschists with chalcopyrite mineralizations of Kuroko type.



Figure 2: The Maramureş Mountains tectonic and geologic background. **(a)** Tectonic sketch of Maramureş Mountains (Săndulescu et al., 1991, modified); **(b)** W-E Geological profile, marked on Figure 2 (a). (B = Bucovinian unit, SB = Subbucovinian unit, IB = Infrabucovinian unit).

2. Material and methods

From the polymetamorphic Rebra terrane rock sequence in the southern Maramureş Mountains, a rock type was chosen, which appeared to contain the most numerous relic minerals (such as white and dark micas, plagioclase, Ti-minerals), favouring to unravel the metamorphic evolution of host rock sequences. Rock samples collected from an Alpine shear zone contain tourmaline porphyroblasts/porphyroclasts as accessory mineral of different grain sizes. Sometimes they occur as needle-like prisms that are observable with the naked eye.

The samples were collected from a tectonic half-window along the Vaser Valley tributary (Pestilor Creek), from an outcrop of mylonitized rocks (Fig. 2a). The collected rock samples were cut normally to foliation and parallel to the extension lineation, and then prepared as normal thin sections for petrographic microstructural observations and uncovered thin sections for microprobe analysis. Tourmaline and associated minerals were analysed with CAMECA SX-100 electron microprobe at the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances in Warsaw, calibrated with natural and synthetic standards: albite (Na), orthoclase (K), wollastonite (Ca), corundum (Al), diopside (Mg, Si), rutile (Ti), hematite (Fe), rhodonite (Mn), synthetic phlogopite (F). Microprobe analyses were carried out at 15 kV and 20 nA, with 20 s count times for all elements. Data were reduced using the correction procedure of Pouchou and Pichoir (1985), the so-called "PAP correction". The thin section studied in Warsaw were also investigated for element distribution maps (EMPA-WDS) at the Babes-Bolyai University from Cluj-Napoca on CAMECA SX-Five (at 15kV, 40nA and counting times of 20s).

The crystallo-chemical formulae of tourmalines were calculated for 31 (O, OH, F)/ apfu according to the general formula: $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$. B_2O_3 was calculated as B = 3.00 apfu. H_2O was calculated for (OH+ F) = 4.00 apfu. The total Fe calculated as Fe²⁺ and the total number of anions 18. The WinClastour v.1.5 software of Yavouz et al. (2006) was used for calculations. Mg was computed in crystallographic Y- and Z-sites, after Grice and Ercit (1993). The Li₂O(c) content of tourmaline was calculated stoichiometrically by initially normalizing to 29 oxygens basis (with B calculation), and then estimating Li by the expression: Li = 3-(Σ Y site) (Henry and Dutrow, 1996).

3. Results

3.1 Petrography

In mylonitised gneisses and retrogressed garnet micaschists of Bretila terrane, the tourmaline grains are visible either in the rock matrix or as inclusions in garnet and feldspar porphyroblasts/porphyroclasts (Figs 3a, b). Some tourmaline grains from the rock matrix show S-shaped inclusion trails of quartz, mica, opaque minerals due to blasthesis over a previously microcrenulated foliation (Fig. 3a). The mylonitised gneisses locally grade into phyllonites and low-temperature mylonitic schists.

In the studied area, the Tulghes terrane is represented by: metaacidic tuffs, graphitic phyllonites, and sericitechlorite-carbonate mylonitic schists with albite porphyroblasts (Fig. 3c). The Rebra terrane rocks were sampled along the Vaser- and Peştilor Creek outcrops (Fig. 2a, samples 2449, 2450). The analysed rock sample (Figs 3d, e, Sample 2450) is a fine-grained carbonate-bearing quartz-feldspar schist. It consists of 35 % phyllosilicates, 30 % guartz, 25 % feldspar, the remaining 10 % being represented by carbonate and other accessory minerals such as tourmaline. The rock is composed of at least two mineral assemblages: The first assemblage comprises "fish-shaped" mica flakes (phengitic mica 1, intergrown with reddish brown dark mica), feldspar porphyroclasts (oligoclase 12 % An and microcline), quartz and accessory minerals (tourmaline, zircon, apatite, hercynite-Fe-Mg-Mn-spinel); the retrogressive second assemblage is composed of albite ("chessboard- albite" replacing the first generation of alkali-feldspar or fissure-infilling veins on previous feldspar), chlorite, white phengitic mica 2, carbonate and magnetite- or Ti-bearing opague minerals. The rock with an S-C mylonitic fabric possesses a relic microcrenulated foliation marked by fish-mica 001 cleavage planes with Ti-bearing opaque mineral needles and a penetrative C-foliation plane. Mylonitic foliation is evidenced by quartz-feldspar, quartz-phyllosilicate microlithons and carbonate microbudines. The quartzitic layers show a mylonitic oblique foliation (S-type) occasionally transposed after the relic foliation, and a parallel position resulted due to progressive deformation. Mica 1 (micafish) is intergrown with dark mica and/or chlorite flakes along the cleavage plane and possesses compositional zonality. The phyllosilicates also appear as small oriented flakes of white mica 2 and chlorite. The chlorite is oriented along mylonitic C foliation or occupies the pressure shadows of porphyroblasts/ porphyroclasts along the mylonitic foliation plane. Feldspars are rotated, dynamically recrystallized porphyroclasts of microcline and oligoclase (as mantled porphyroclast, Passchier and Trouw, 2005), containing mica, epidote, and tourmaline inclusions (Fig. 3d). During retrogression, feldspar was partially replaced by albite ("chessboardalbite"), carbonate, chlorite and sericite. Several feldspar porphyroclasts have asymmetric pressure shadows (infilled with quartz and micas) oriented along the penetrative foliation plane. The garnet bearing plagioclase gneisses are rare in the investigated area. The garnets (more or less broken and synkinematically rotated porphyroclasts) show zonal structure (inclusionrich core and inclusion-poor rim), with prekinematic and synkinematic evolution. Tourmaline, an accessory mineral in Rebra terrane rocks (< 2 % of rock volume), may be present as porphyroblasts/porphyroclasts (more or less broken grains in Fig. 3e) or as small idiomorphic needle-shaped crystals (Fig. 3f), sometimes trapped in other porphyroclasts/porphyroblasts (ex. in plagioclase from Fig. 3d). The size varies from several tens of micrometers (idiomorphic crystals) to hundreds of micrometers (± broken grains translationally moved and externally rotated). The tourmalines present gradational optical zoning with a yellowish-brown colour in the rim zone but an olive-greenish colour in the core zone. In thin sections of Rebra terrane rocks cut parallel to the extension lineation (marked by chlorite and mica flakes long axes), several tourmaline grains present asymmetrically developed pressure shadows, mainly infilled by pressure solution mobilised quartz (hinting pre-kinematic tourmaline growth). The coarse-grained tourmalines from Rebra sequences sometimes present irregular boundaries in contact with quartz, whereas the inner zone boundaries remain idiomorphical. (Fig. 4, Cadistribution map).

Other tourmaline porphyroblasts show spiral-shaped inclusion trails of quartz (blastesis during rotation of the "snowball" porphyroblast). (Fig. 3e). The "tur 2" grain core (from sample S 2450) in centre of Figure 4e has mainly idiomorphic prismatic shape, with linear trails of opaque mineral films and guartz inclusions discordantly arranged in relation to penetrative foliation $(S_i \neq S_i)$ due to prekinematic growth. Its core zone boundary is surrounded by mineral inclusions (quartz, plagioclase, opague mineral films, and zircon), but such inclusions are missing in the outer boundary. The "c" axis position of the "tur2" grain was estimated to be mainly perpendicular to the thin section plane. The smaller needle-shaped synkinematic idiomorphic grains aligned along the mylonitic foliation and rarely broke. They show the same colours as the larger ones, also illustrating a core and a rim zone (Fig. 3f).

3.2 Tourmaline compositions and classification

The analytical data on Rebra sequence tourmalines consist of two sets: one belongs to a zoned tourmaline grain profile (tur2), with 9 measurement points (RTR1-RTR9 in Tab. 1), the other set represents several different grain data at the core, middle, and rim points (Tab. 2). Site occupancies were calculated assuming that Si deficiency in the tetrahedral site (T) is compensated by Al up to 6 apfu, the remaining Al, Ti, Fe and Mg entering the Z - site (Ertl et al., 2011).

Consequently, if Al < 6, Ti, Fe and Mg compensate Z-site occupancy (Hawthorne et al., 1993; Yavuz et al., 2006), while octahedral site (Y) is filled by the remaining Al, Mg, Mn, Fe²⁺cations. To assign the Mg²⁺ content to the crystallographic Z-site, we used the procedure based on the correlation established by Grice and Ercit, (1993) between Fe/(Fe+Mg) ratio and Mg²⁺ in the crystallographic Z-site so that ^YMg²⁺ \approx 3[1 – Fe/(Fe+Mg)] and ^ZMg²⁺ \approx Mgtotal – ^YMg²⁺. The Al-Mg disorder between the crystallographic Y- and Z-site could be larger, but because no <Y-O> and <Z-O> distances were available, a more precise assignment of Mg to the [6]-coordinated atomic positions was not possible. The X-site position is occupied by Na, Ca (Ba) or may be vacant (MacDonald et al., 1993; von Goerne et al., 1999). The OH content was assessed by charge balance. Although the mean calculated Li_2O content of all investigated tourmalines is around 0.1 wt%, the actual Li_2O content in these Mgrich and Mg-bearing tourmalines could also be <0.05 wt%. The tourmaline classification scheme of Henry et al. (2011) was applied.

The bulk composition of tourmalines incorporates different solid solutions. These may involve homovalent substitutions in a given site or heterovalent substitutions in single or multiple sites. These can be inferred on the basis of binary diagrams and/or correlation matrix of main cations from analysed tourmalines. The correlation matrix between the main chemical elements of tourmalines (Tab. 3, complete with correlations Mgtot: Li = + 0.7 and Fe: Li = - 0.77) allowed us to establish several site substitutions and corresponding exchange vectors in the studied tourmalines (Tab. 4).

For identification of the wider range of natural or synthetic tourmaline species, there are general procedures (Novák et al., 2009; Henry et al., 2011). For example, after the primary crystallographic X-site group is established, the appropriate subgroup should be determined within each of the primary groups. Identification of the subgroup within each of the primary tourmalines of the crystallographic X-site group can be established with a series of diagrams using the occupancy of the X-site and $^{\rm YZ}R^{2+}\!/(^{\rm YZ}R^{2+}\!+\,2Li^{+}\!)$ ratio as the primary discriminating criteria, followed by the occupancy of the crystallographic W-site, which will refine the species within the subgroup. Our tourmaline microprobe data, without direct measurement of B, H, Li, and oxidation state of transitional elements, permit classification procedure 3, recommended by Henry et al. (2011), for partial tourmaline compositional data.

Tourmaline (core, middle, and rim zone) classifications were established (after LiO₂, OH⁻ and O²⁻ countings, cation and anion allocations in crystallochemical formula), based on dominant cations, anions, and valency rule in relevant crystallographic sites X, Y₃, Z₆, V₃-, W- as follows. The dominance of the cation in site X allowed the establishment of the main tourmaline group (Fig. 5a): alkali, with Na⁺+ K⁺ \ge Ca²⁺ and Na⁺ + K⁺ \ge X_{vac}. The dominant valency in the crystallographic X-site is due to Na (+K). Taking into account the dominant anion (OH⁻, F⁻, O²⁻) in the crystallographic W-site (in the absence of measurements / estimations of the H data, it is recommended to use the measured F data, which are less than 0.5 apfu), it means an alkali general hydroxyl species with (OH + F) \ge O²⁻ and OH > F (see Fig. 5b).

According to the current state of knowledge, tourmalines are mainly dominated by OH⁻ at the crystallographic V-site and the assumption that V(OH)⁻ = 3 is generally considered correct. By checking the occupancy of crystallographic T-site, the Si⁴⁺ > 4.5 apfu was determined (Tabs 1 and 2), as in natural tourmalines. The dominant cation at the crystallographic Z-site appears to be Al³⁺ (Tabs 1 and 2), Fe³⁺ being undetermined. It was assumed that Fe³⁺ is only as a minor component. According to



Figure 3: Thin section images of the studied rocks. **(a)** "Flame perthitic" (Vernon, 2018) microcline porphyroclast with albitisations on its fissures and tournaline (in extinction) with quartz, plagioclase inclusion trails (Sample 2428b, under cross polarised light, Infrabucovinian Bretila terrane); **(b)** Broken relic garnet porphyroclast with quartz, opaque mineral, biotite, tournaline inclusions trails and pressure shadows filled by epidote – zoisite group minerals, quartz, chlorite, sericite. An inclusion-poor rim and an inclusion- rich core zone can be observed. (Sample 2423, under cross polarised light, Infrabucovinian Bretila terrane); **(c)** White micas, albite porphyroblast and Ti-rich opaque minerals (ilmenite- rutile transformation) marking the relic microcrenulated foliation plane. Albite pressure shadows contain carbonate (Cb), quartz, micas. (Sample 2453, under cross polarised light, Subbucovinian Tulgheş terrane); **(d)** Broken and roughly recrystallized feldspar porphyroclast with inclusions of zircon, muscovite, opaque minerals, tourmaline. Nearby are some carbonate seggregations (bottom zone). At the bottom-central part a tourmaline porphyroclast beside fish-mica can be observed. (Dextral shear sense). (Sample 2450, under cross polarised light, Subbucovinian Rebra terrane); **(e)** Mica fish and rotated synkinematic tourmaline porphyroblast inclusions of quartz, opaque minerals and zircon in spiral-shaped trail. In the top-left corner of the image, the porphyroblast inclusion trail continues into the matrix. There are dynamically recrystallized grains (bottom right) of 5 - 10 µm size around relic quartz grain containing subgrain boundaries. (Sample 2450, under cross polarised light, Rebra terrane); **(f)** Mica fish and small tourmaline needles along the S plane in the S-C mylonitic schist (Sample 2449, with position very close to sample 2450, under plane polarised light, Subbucovinian Rebra terrane).



Figure 4: Electron microprobe (EMPA-WDS) image of sample S 2450. Beside "tur2" grain, which evidences the compositional zonality in Ca, Fe and Mg, there are also white mica-fishes. Investigation images were taken on CAMECA SX 100 at the University Babeş-Bolyai from Cluj-Napoca. (a) Mg distribution map; (b) Ca distribution map; (c) Fe distribution map; (d) Al distribution map; (e) Microphotograph of studied thin section (under plane polarised light) with S-C mylonitic fabric (dextral shear sense, based on oblique foliation S of quartz, fish micas). In the centre of image there is the investigated "tur2" grain, with color zoning, having pressure shadows filled with quartz, chlorite. In the upper left corner of images from (a, b, c, d) is also tourmaline with same element distribution map as in "tur2" grain.

Points anal/ Wt%	RTR1	RTR2	RTR3	RTR4	RTR5	RTR6	RTR7	RTR8	RTR9
SiO ₂	35.48	35.78	35.58	35.58	35.97	35.92	35.82	35.6	35.52
TiO ₂	0.7	0.91	0.75	1.03	0.61	0.84	0.81	0.89	0.74
Al_2O_3	29.8	30.41	32.12	29.83	31.69	31.94	31.2	29.91	29.78
FeO	9.27	7.82	6.11	8.23	6.2	5.74	6.17	7.9	9.12
MnO	b.d	0.04	b.d	0.001	b.d	0.003	b.d	b.d	b.d
MgO	6.53	7.28	7.43	7.06	7.68	7.5	7.4	7.35	6.72
Na ₂ O	2.72	2.7	2.03	2.8	2.28	2.11	2.32	2.83	2.68
K ₂ O	0.02	0.03	0.01	b.d	0.004	0.004	0.01	b.d	b.d
CaO	0.29	0.36	0.89	0.29	0.84	0.78	0.74	0.27	0.31
F	0.06	0.1	0.12	0.05	0.03	0.04	0.07	0.12	0.05
O=F	0.02	0.04	0.05	0.02	0.01	0.02	0.03	0.05	0.02
$H_2O(c)$	3.52	3.54	3.55	3.53	3.6	3.59	3.54	3.51	3.53
$B_2O_3(c)$	10.27	10.4	10.45	10.3	10.48	10.45	10.36	10.32	10.29
Li ₂ O(c)	0.07	0.11	0.15	0.14	0.16	0.18	0.24	0.14	0.08
Total wt%	98.46	99.16	98.35	98.57	98.71	98.34	97.97	98.62	98.53
		Crystalloci	nemical formu	lae apfu /31 a	nions, 3B, 4(C	, OH, F), T+Z-	+Y=15		
Si(T)	5.989	5.95	5.88	5.97	5.93	5.93	5.95	5.96	5.98
Al(T)	0.018	0.05	0.12	0.03	0.07	0.07	0.05	0.04	0.02
Total T	6	6	6	6	6	6	6	6	6
Al(Z)	5.91	5.92	6	5.86	6	6	6	5.86	5.88
Mg(Z)	0.09	0.08	0	0.14	0	0	0	0.14	0.12
Total Z	6	6	6	6	6	6	6	6	6
Al(Y)	0	0	0.13	0	0.08	0.14	0.05	0	0
Ti(Y)	0.09	0.11	0.1	0.13	0.08	0.11	0.1	0.11	0.09
Mg(Y)	1.56	1.72	1.83	1.62	1.89	1.85	1.83	1.69	1.57
Mn(Y)	0	0.01	0	0.00	0	0	0	0	0
Fe(Y)	1.31	1.09	0.84	1.15	0.85	0.79	0.86	1.11	1.28
Li(Y)	0.048	0.071	0.103	0.096	0.104	0.122	0.161	0.095	0.055
Total Y	3	3	3	3	3	3	3	3	3
Ca(X)	0.05	0.07	0.16	0.05	0.15	0.14	0.13	0.05	0.06
Na(X)	0.89	0.87	0.65	0.91	0.73	0.68	0.75	0.92	0.88
K(X)	0.004	0.01	0.003	0	0.001	0.001	0.001	0	0
Total X	0.944	0.95	0.813	0.96	0.881	0.821	0.881	0.97	0.94
Xvac	0.056	0.05	0.187	0.04	0.119	0.179	0.119	0.03	0.06
OH*	3.49	3.48	3.47	3.5	3.49	3.49	3.48	3.47	3.49
O*	30.97	30.95	30.94	30.97	30.98	30.98	30.96	30.94	30.97
F	0.029	0.05	0.06	0.029	0.018	0.022	0.036	0.061	0.026
В	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
y mf =Mg/(Fe+Mg)	0.54	0.61	0.68	0.58	0.69	0.70	0.68	0.60	0.55
Y(Fe/Mg)	0.84	0.63	0.46	0.71	0.45	0.43	0.47	0.66	0.82
Vsite (OH)	3	3	3	3	3	3	3	3	3
W site(OH+F+	0.49+0.03	$0.\overline{48+0.05+}$	$0.\overline{47+0.06+}$	0.5 + 0.03 +	$0.\overline{49+0.02+}$	0.49+0.22+	$0.\overline{48+0.04+}$	0.47+0.06+	0.49+0.03+
		0.00	0.01		0.22	0.22	0.01	0.21	0.00

Table 1: Chemical composition and corresponding crystallochemical formula of the tourmaline studied ("tur2") in nine points (RTR1- RTR9). b.d. = below detection; $H_2O(c)$, $B_2O_3(c)$, $Li_2O(c)$ = counted; OH^* , O^* = counted

the crystallographic Z-site dominance criteria, the Al³⁺ subgroup resulted.

The determination of the species inside the tourmaline alkali group with OH⁻ dominance at the crystallographic Z-site is made by plotting the cations (Fe²⁺, Mg²⁺, in an ordered structural formula) in the 2Li-Fe-Mg ternary diagram (Fig. 5c). The resulting species are schorl and dravite. Determination of the occupancy of the crystallographic Y-site (considering an ordered structural formula, for classification purpose), makes possible the establishment of the dominant subgroup. The dominant subgroup can be roughly outlined graphically from Figure 5d: alkali group, dominant alkali subgroup 1 and dominant subgroup 1, the dominant species in that subgroup can be identified

by occupancy at the crystallographic W-site (in Tabs 1 and 2): hydroxyl dominated schorl and dravite species in dominant subgroup 1 of alkali group tourmalines.

3.3 White micas and chlorite

Representative chemical analyses of white micas, together with structural formulae, are reported in Table 5. The micas analysed are dioctahedral, chemically more or less zoned, and include an important quantity of celadonitic component.

The H_2O + OH contents of micas were determined according to Loucks (1991), (model 1). The proportions of tetrahedral, octahedral, and interlayer cations have been calculated on the basis of 11 oxygen using the method proposed by Rieder et al. (1998). The analysed mica revealed an octahedral occupancy M = 2.03-2.05,

Sample /Wt%	8m	8r	9c	9m	9r	9r1	10c	10m	10r	11c	11c1	11m	11m1
SiO ₂	34.81	34.81	35.1	34.85	35.6	35.28	35.02	34.55	35.39	34.73	34.65	34.95	35.21
TiO ₂	1.63	1.09	0.84	0.88	0.72	1.06	1.00	1.23	1.08	0.67	1.04	1.15	1.14
Al ₂ O ₃	30.16	30.14	30.52	30.3	31.24	30.62	30.35	30.15	30.65	30.9	31.19	30.41	30.72
FeO	11.43	12.27	12.25	12.66	10.00	10.66	11.74	12.36	10.14	12.18	12.64	10.7	10.44
MnO	0.13	0.39	0.32	0.15	0.07	0.07	0.24	0.22	0.12	0.39	0.38	0.17	0.15
MgO	4.43	3.79	3.91	3.9	5.32	5.19	4.39	3.95	5.16	3.62	3.83	4.97	5.23
CaO	0.43	0.24	0.24	0.46	0.29	0.31	0.38	0.37	0.33	0.22	0.29	0.29	0.32
Na ₂ O	2.56	2.67	2.67	2.51	2.51	2.56	2.61	2.52	2.5	2.58	2.78	2.53	2.54
K ₂ O	0.07	0.09	0.06	0.09	0.04	0.05	0.08	0.08	0.06	0.09	0.08	0.05	0.05
F	0.03	0.07	0.09	0.06	0.12	0.05	0.04	0.05	0.04	0.03	0.08	0.02	0.08
O=F	0.01	0.03	0.04	0.03	0.05	0.02	0.02	0.02	0.02	0.01	0.03	0.01	0.04
$H_20(c)$	3.5	3.46	3.48	3.48	3.51	3.53	3.5	3.47	3.52	3.49	3.51	3.52	3.52
$B_2O_3(c)$	10.18	10.13	10.2	10.17	10.35	10.3	10.21	10.13	10.27	10.14	10.29	10.22	10.3
$Li_2O(c)$	0.17	0.17	0.16	0.14	0.15	0.13	0.14	0.14	0.16	0.14	0.12	0.12	0.13
Total	99.54	99.35	99.88	99.68	99.97	99.83	99.72	99.24	99.44	99.19	99.91	99.11	99.87
			Crystalloc	hemical fo	ormulae/ 3	1 (O, OH,	F) anions,	3B, 4(OH	I, F). T+Z	+Y=15			
Si(T)	5.9	5.93	5.94	5.92	5.94	5.92	5.93	5.89	5.95	5.91	5.82	5.92	5.91
Al(T)	0.1	0.07	0.06	0.08	0.06	0.08	0.07	0.11	0.05	0.09	0.18	0.08	0.09
Total T site	6	6	6	6	6	6	6	6	6	6	6	6	6
Al(Z)	5.92	5.98	6	5.98	6	5.98	5.98	5.95	6	6	6	5.98	5.98
Mg(Z)	0.08	0.02	0	0.02	0	0.02	0.02	0.05	0	0	0	0.02	0.02
Total Z site	6	6	6	6	6	6	6	6	6	6	6	6	6
Al(Y)	0	0	0.02	0	0.08	0	0	0	0.02	0.11	0	0	0
Ti(Y)	0.21	0.14	0.11	0.11	0.09	0.13	0.13	0.16	0.14	0.09	0.13	0.15	0.14
Mg(Y)	1.04	0.94	0.99	0.97	1.32	1.28	1.09	0.95	1.29	0.92	0.95	1.24	1.29
Mn(Y)	0.02	0.06	0.05	0.02	0.01	0.01	0.03	0.03	0.02	0.06	0.05	0.03	0.02
$Fe^{2+}(Y)$	1.62	1 75	1 73	1.8	14	1.5	1.66	1 76	1 43	1 73	1 78	1 51	1 47
Li(Y)	0.12	0.12	0.11	0.1	0.1	0.09	0.09	0.09	0.11	0.09	0.08	0.08	0.09
Total V site	3.01	3.01	3.01	3	3	3.01	3	2.99	3.01	3	2.99	3.01	3.01
	0.08	0.04	0.04	0.08	0.05	0.06	0.07	0.07	0.06	0.04	0.05	0.05	0.06
$\operatorname{Va}(X)$	0.00	0.04	0.04	0.00	0.05	0.00	0.07	0.07	0.00	0.04	0.05	0.05	0.00
$K(\mathbf{X})$	0.04	0.00	0.00	0.03	0.01	0.05	0.00	0.03	0.82	0.03	0.91	0.85	0.03
	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.01
Total A site	0.94	0.94	0.95	0.95	0.87	0.9	0.95	0.92	0.89	0.91	0.98	0.89	0.9
X _{vac}	0.06	0.06	0.07	0.07	0.13	0.1	0.05	0.08	0.11	0.09	0.02	0.11	0.1
OH*	3.49	3.48	3.48	3.48	3.47	3.49	3.49	3.49	3.49	3.49	3.48	3.50	3.48
0*	30.98	30.97	30.95	30.97	30.94	30.98	30.98	30.97	30.98	30.98	30.96	30.99	30.96
F	0.017	0.035	0.048	0.032	0.064	0.024	0.022	0.029	0.023	0.018	0.041	0.010	0.044
B	3	3	3	3	3	3	3	3	3	3	3	3	3
^Y Mg/(Fe+Mg)) 0.39	0.35	0.363	0.350	0.487	0.460	0.395	0.351	0.475	0.346	0.350	0.449	0.467
Y(Fe/Mg)	1.45	1.82	1.76	1.82	1.05	1.15	1.50	1.76	1.10	1.89	1.85	1.21	1.12
	8m	8r	9c	9m	9r	9r1	10c	10m	10r	11c	11c1	11m	11m1
V site (OH)	3	3	3	3	3	3	3	3	3	3	3	3	3
W site	0.49+	0.48+	0.48+	0.48+	0.47+	0.49+	0.49+	0.49+	0.49+	0.49+	0.48+	0.50+	0.48+
(OH+F+O)	0.02	0.04	0.05	0.03	0.06	0.02	0.02	0.03	0.02	0.02	0.04	0.01	0.04
	+0.23	+0.23	+0.21	+0.23	+0.21	+0.23	+0.23	+0.22	+0.23	+0.23	+0.22	+0.24	+0.21

 Table 2: Chemical composition of four tourmaline grains.

 Samples 8, 9, 10, 11, in core (c), middle (m) and rim (r) points and corresponding crystallochemical formulae. Xvac= X site vacancy.

	Altot	^y Al	^y Fe ²⁺	Mg _{tot}	^y Mg	Ca	Na	\mathbf{X}_{vac}	Si
Al tot	1								
^y Al	0.8344	1							
^y Fe ²⁺	-0.9067	-0.5083	1						
Mg _{tot}	0.6312	0.3103	-0.8744	1					
^y Mg	0.0735	0.3927	-0.9849	0.9914	1				
Ca	0.9793	0.6316	-0.9158	0.6723	0.6355	1			
Na	-0.9945	-0.7844	0.8864	-0.5900	-0.4866	-0.9756	1		
X_{vac}	0.9745	0.7947	-0.8323	0.4965	0.3985	0.9305	-0.9864	1	
Si	0.8623	-0.1400	0.8048	-0.6919	0.4351	-0.8263	0.8424	-0.8248	1

Table 3: Correlation matrix of main cations from studied tourmalines.

Site substitutions	Corresponding exchange vectors					
$^{\rm Y}{\rm Fe} = {}^{\rm Y}{\rm Mg}$	MgFe ₋₁					
$^{\mathrm{Y}}\mathrm{Mg} = {^{\mathrm{Y}}\mathrm{Fe}}$	FeMg-1					
^Y Mn ^{= Y} Fe	FeMn-1					
$2^{\mathrm{Y}}\mathrm{Fe} = {}^{\mathrm{Y}}\mathrm{Al} + {}^{\mathrm{y}}\mathrm{Li}$	LiAlFe-2					
$^{X}Na + ^{Y}Mg = ^{X}\Box + ^{Y}Al$	□Al Na-1Mg-1					
$^{\mathrm{Y}}\mathrm{Fe} + ^{\mathrm{T}}\mathrm{Si} = ^{\mathrm{Y}}\mathrm{Al} + ^{\mathrm{T}}\mathrm{Al}$	Al ₂ Fe ₋₁ Si ₋₁					
$^{\mathrm{Y}}\mathrm{Mg} + ^{\mathrm{T}}\mathrm{Si} = ^{\mathrm{Y}}\mathrm{Al} + ^{\mathrm{T}}\mathrm{Al}$	Al ₂ Mg ₋₁ Si ₋₁					
$^{X}Na + ^{Y}Al = ^{X}Ca + ^{Y}Fe$	CaFeNa-1Al-1					

 Table 4: Site substitutions and corresponding exchange vectors, established for investigated tourmalines.

meaning dioctahedral micas (Rieder et al., 1998). In the studied samples, white micas show Si values between 3.1 apfu (core) and 3.2 apfu (rim), in interlayer sheet (I-site) K⁺ > 0.8, I-site occupancy > 0.9 and Si^{IV}/Al^{VI} is around 3.1:1.7. Other important parameters are Al^{VI}/octahedral occupancy > 0.8 and Mg/(Mg + Fe²⁺) = 0.4 - 0.5.

The analysed chlorite flake is oriented along the mylonitic C-foliation and its microprobe analysis was included in the Table 5, last column. The structural formula of chlorite is based on 14 oxygens and with Fe²⁺/ Fe³⁺ and OH calculated assuming full site occupancy. In the Table 5, last column, Fe²⁺ = 2.4 apfu, calculated Fe³⁺ = 0.05 apfu, octahedral vacancy (Vac) = 0.02 and OH = 8 apfu and its crystallochemical formula calculated after Wiewióra and Weiss (1990): (Fe²⁺_{2.4}Mg_{2.06}Fe³⁺_{0.05}Al_{1.34} $\chi_{0.02}$)₆ (Si_{2.76}Al_{1.24})₄ O₁₀ (OH)₈.



Figure 5: Studied tourmaline classification. (a) Primary tourmaline groups, based on the dominant occupancy of the crystallographic X-site; (b) General series of tourmaline species, based on anion occupancy of the crystallographic W-site. Our samples are hydroxy species of alkali group; (c) Ternary diagram for plotting and classifying alkali-group tourmaline species with Al³⁺ dominance at the crystallographic Z-site and OH–dominance at the crystallographic V-site, by plotting crystallographic Y-site cations (Fe²⁺ and Mg²⁺). Blue triangles are core compositions of tur2, black squares are rim compositions of tur2, green diamonds are core compositions of other tourmaline grains and red circles their rim compositions; (d) Determination of dominant subgroups for alkali-group tourmalines (the case of: crystallographic X-site = Na+K dominant, crystallographic Z-site = A dominant, crystallographic W-site = measured, inferred or calculated), using parameters ${}^{YZ}R^{2+}/({}^{YZ}R^{2+} + 2Li^{+})$ vs. $Ca^{2+}/(Ca^{2+} + Na^{+} + K^{+})$ together with the dominant valency anion(s) in the W site. (${}^{YZ}R^{2+}$ represents the total number of divalent cations – Fe, Mg, Mn- in the crystallographic Y- and Z-site.). Our tourmaline samples have (OH⁻ + F⁻) rich crystallographic W-site (Tabs 1 and 2) and are (Na + K)-R²⁺ species of dominant subgroup 1.

Samples Wt%	3c	3m	3r	3r1	2c	6m	7r	8r1	Chl
SiO2	46.44	46.35	46.45	46.13	47.75	48.89	47.81	47.26	25.80
TiO ₂	0.95	0.84	0.86	0.85	0.38	0.71	0.84	0.68	0.17
Al ₂ O ₃	32.34	31.96	31.89	32.89	32.33	32.38	32.64	33.51	20.35
FeO	2.74	2.98	2.83	2.60	2.21	2.63	2.81	2.71	27.39
MnO	0.01	0	0.01	0	0.05	0.11	0.08	0.06	0.0
MgO	1.09	1.14	1.11	0.98	1.36	1.55	1.17	1.21	12.91
CaO	0	0	0	0	0	0.08	0	0	0
Na ₂ O	0.29	0.15	0.33	0.36	0.45	0.33	0.27	0.25	0
K ₂ O	10.98	11.18	10.92	11.10	10.08	10.72	10.53	10.98	0.39
BaO	0	0	0	0	0.08	0.14	0	0.16	0
Subtotal	94.84	94.6	94.4	94.91	95.10	97.54	96.15	96.81	98.23
H_2O+OH*	4.44	4.42	4.42	4.44	4.47	4.58	4.52	4.53	
H_2O^*									11.16
	Cr	ystalloche	emical for	mula of mi	cas/ based	on 11 O			14 O
apfu/ samples	3c	3m	3r	3r1	2c	6m	7r	8r1	Chl
Si	3.140	3.149	3.156	3.118	3.188	3.201	3.174	3.128	2.76
Al iv	0.860	0.851	0.844	0.882	0.812	0.799	0.826	0.872	1.24
T _{total}	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.00
Al vi	1.717	1.707	1.710	1.738	1.763	1.700	1.727	1.742	1.34
Ti	0.048	0.043	0.044	0.043	0.019	0.035	0.042	0.034	0.02
Fe	0.155	0.169	0.161	0.147	0.124	0.144	0.156	0.150	2.4 + 0.05
Mn	0.001	0	0.001	0	0.003	0.006	0.004	0.003	0
Mg	0.110	0.115	0.112	0.099	0.135	0.151	0.116	0.119	2.06
M _{total}	2.030	2.033	2.028	2.026	2.040	2.038	2.045	2.050	Vac 0.02
Ca	0	0	0	0	0	0.005	0	0	0
Na	0.038	0.020	0.043	0.047	0.058	0.021	0.035	0.033	0
K	0.947	0.969	0.947	0.953	0.859	0.895	0.892	0.927	0.11
Ba	0	0	0.001	0	0	0	0	0	0
I _{total}	0.985	0.989	0.991	1.000	0.917	0.922	0.927	0.960	Total 6.0
Al _{total}	2.577	2.559	2.554	2.620	2.575	2.500	2.554	2.614	2.58
Mg/(Fe+Mg)	0.415	0.405	0.411	0.402	0.523	0.512	0.426	0.441	0.46
Fe/(Fe+Mg)	0.585	0.595	0.589	0.598	0.477	0.488	0.574	0.559	0.54
Al vi/M _{tot}	0.845	0.839	0.843	0.857	0.833	0.835	0.811	0.818	
Fe/Mg	0.912	0.834	0.976	0.952	0.911	0.954	1.349	1.266	1.19
OH	2.22	2.21	2.21	2.22	2.23	2.29	2.26	2.26	8

Table 5: Chemical composition and crystallochemical formula of studied micas and chlorite (in rim - r, core - c, and mid - m points).

4. Discussion

In the studed area the described rocks from Bretila and Rebra terranes contain tourmaline as accesory mineral. In the previous papers investigating East Carpathians metamorphics tourmaline was not mentioned as petrogenetically important mineral. The studied rocks were involved in Prealpine and Alpine shear zones (Fig. 2) and present a polymetamorphic feature with metamorphic peak and retrograde mineral assemblages. The last metamorphic event was imprinted dynamically with S-C fabric, mechanical twins in feldspars and neoblasthesis of micas 2, chlorite and albite, the rocks turning into low grade mylonitic schists of Alpine age (Gröger et al., 2013).

The tourmaline-bearing mylonitic schist of Rebra terrane (described in chapter 3.1) contain two mineral assemblages: first is of medium grade peak conditions (microcline and oligoclase porphyroclasts, quartz, fishshaped micas 1 and accesoric minerals as tourmaline, zircon, apatite), the second is of retrogression conditions (albite, chlorite, micas 2, carbonates, opaque minerals oriented along C-mylonitic foliation). Chemically studied "tur2" tourmaline grain presents a core zone of prograde origin and two metamorphic overgrowth zones (inner rim 1 and outer rim 2). At microscopic scale also observed asymmetrically developed pressure shadows around "tur2" porphyroblast parallel with extension lineation, hinting the tourmaline prekinematic or synkinematic genesis. The porphyroblast presents irregular outer boundaries in contact with quartz, whereas the inner zone boundaries remain idiomorphical (Fig. 4). The irregular boundaries could be interpreted in two ways. A first explanation may be that this boundary is a corrosion effect due to pressure release and fluid activity operating under differential stress along the C foliation plane. The other interpretation assumes the presence of metamorphic fluids (H₂O, CO₂, B₂) and stressinduced prekinematic blastesis along the boundaries of the quartz grain. (Vernon, 2018; Passchiere and Trouw, 2005). The tourmaline porphyroblasts with spiralshaped inclusion trails of quartz (Fig. 3e) presents decreasing grain size towards the tourmaline rim zone, but with grain sizes in the core smaller than in the rock matrix. Such microstructural relationships evidence the change in thermodynamic conditions during tourmaline rotational blastesis. (Vernon, 2019 and therein references).

Tourmalines show chemical growth zoning (Fig. 6), frequently associated with specific mineral inclusions (such as ilmenite, zircon, quartz or other boron minerals). The grain "tur2" belongs to the dravite–schorl solid solution series, with a more dravite component in the core than in the rim zone, and relatively Ca enriched in the rim compared to the core (Fig. 4b). Considering that in thin sections cut diagonally to the c-axis of tourmaline, the chemical growth zoning profiles could have very different patterns (Henry and Dutrow, 1992; Bridge et al., 1977). From the chemical zoning profiles of tourmaline in Figure 6a negative correlation between Fe and Mg or Si and Al results, caused by important substitutions (described in the section 3.2, Tab. 4).

In the Al, Fe and Na profiles from Figure 6a, three main composition zones could be delimited on "tur2" grain from Figure 6b: a core zone (microprobe point RTR 3, RTR4, RTR 5) and two asymmetric overgrowth zones ("rim2" with RTR1, RTR2, RTR8, RTR9 points and "rim1" with RTR6 and RTR7 points). The Al content drops from 5.8 to 5.5 apfu from the core boundary into the rim zone, but in the core zone it shows a reverse bell-shaped zoning profile. The Mg/(Mg+Fe) ratio in Figure 6c also revealed a reversed bell-shaped zoning in the core and an asymmetric appearance in the rim. In the 'rim1' zone, the Mg/(Mg + Fe) ratio reaches its maximum at 0.69 apfu (more dravite in solid solution) and decreases in 'rim2'. The composition profile of Ti (Fig. 6a) obviously outlined the same zones with a higher Ti-content at the core.

Compared to the Henry and Dutrow (1992) data, our tourmalines (based on Mg/(Mg + Fe) ratio and Ti-content) and coexisting with ilmenite or rutile may suggest medium grade tourmalines in metapelites. Tourmaline growth and stability is influenced by Fe, Mg, Ca, and fluid composition of the system. Its growth is inhibited by low B content or solutions with high contents of Fe, Mg, and Ca relative to those of Al and Si. Fluids with high levels of Na and Mg will determine stabilization of the dravite component (Dutrow and Foster, 1992; Henry and Dutrow, 1992; Spánitz et al., 2018).

Micas compositions correspond to a solid solution between muscovite and ferro-alumino celadonite endmembers. Chlorite is a tri- trioctahedral group chlorite. The ($Fe^{2+} + Fe^{3+}$) of 2.45 apfu and tetrahedral Si = 2.76 apfu corresponds to the chlorite of ripidolite variety (Hey, 1954). The low K content (0.11 apfu) appears due to dark mica origin.

4.1 Geothermobarometry

The X_{Mg} versus X-site vacancy diagram for tourmalines in metapelite rocks, and X_{Mg} versus Ca-diagram for tourmalines from calcareous metasediments and pelites (Henry and Dutrow, 1992) helped us to constrain metamorphic conditions for analysed tourmalines. Their core and rim zones overlap mainly (Fig. 7) and indicate medium-grade metamorphic conditions for tourmalines and their host metasedimentary rocks.

Forthe computations of the metamorphic peak condition of the Rebra terrane, the following geothermometers/ geobarometers were used: tourmaline- plagioclase (12 % An), tourmaline-muscovite (Hinsberg and Schumacher, 2009), and phengite geobarometer (Massonne, Schreyer, 1987) which indicated a temperature of 589 \pm 8 °C, respectively 575 to 582 °C \pm 22 °C, and the later one a pressure of 5.5 to 6 kb at 575 °C.

Alpine retrogressive conditions were also deduced, taking into account dynamically recrystallized quartz (subgrain rotation mechanism), feldspar microstructures, and quartz paleopiezometry (Passchier and Trouw, 2005). The microstructures showed a temperature around $350 - 400 \,^{\circ}$ C and a differential stress ($\sigma_1 - \sigma_3$) around 1.5 kb. The retrogression conditions appear to not have greatly affected the tourmaline prograde metamorphic composition, the last evidenced by increasing Ca- and Mg- content and occupancy of X site from core into the rim (mentioned also by Sperlich et al. (1996) in Luckmanier zone from Alps).

4.2 Tourmaline-bearing rock protolith

The AI-Fe-Mg discrimination diagram (Henry and Guidotti, 1985) evidenced the composition of tourmaline derived mainly from metapelites and metapsammites (fields 4 and 5 in Fig. 8a). Exceptions are the core compositions (tur10c, tur11c, tur11c1) (Table 2.) which plot into the Lipoor granitoid field.

Taking into account the core (circle symbols) and rim compositions (squares symbols) of the same grains (Fig. 8a), it can be seen that the grains evolved from the Li-poor granitoid field (boundary zone of field 2) into the metasedimentary field (field 5) or evolved in the metasedimentary environment (from field 4 and 5 boundary zone into the field 5). In the Fe-Ca-Mg discrimination diagram (Henry and Guidotti, 1985) (Fig. 8b), the tourmaline analyses plot mainly in field 4 (Ca-poor metapelites), exceptions are some core compositions (tur9, tur10, tur11) (Tab. 2), which are from Li-poor granitoids and their associated pegmatites and aplites. Observing the composition of the core and overgrowth rim compositions of the same grain (Fig. 8b), it may be noticed that the grains evolved from the Li-poor granitoid field (2) into the Ca-poor metasedimentary field (4) or in the same metasedimentary environment. The Li-poor granitoid field environment of few tourmaline core compositions could be explained by north-eastern Gondwana craton origin of tourmaline host rock protolith but Anorogen type Varican Li-poor granitoids were



Figure 6: Chemical composition of "tur2" grain. (a) Chemical profiles of "tur2" grain. The "+c" pole position was estimated at around point RTR6 (the thin section position is mainly normal to the "c" axis); (b) BSE image of "tur2". Arrow= measurement profile position; (c) Mg/(Mg+Fe) profile in "tur2" grain.



Figure 7: Tourmalines metamorphic grade. (a) X_{Mg}-X_{vacancy} diagram for tourmalines in metapelitic rocks (Henry and Dutrow, 1992, modified); (b) X_{Mg}-Ca diagram for calc-silicate rocks and metapelites (Henry and Dutrow, 1992, modified).

presented in Bohemian massif – from basement unit of European plate margin, by Breiter (2020).

4.3 Other tourmaline descriptions in Alpine -Carpathian zone

Alpine metamorphic conditions from Alpine -Carpathian orogen (Fig. 1) vary from west into east, these being characterized by high pressure (locally up to ultrahigh pressure, eclogitic conditions) in western part, but into east the pressure is lowering. The temperatures are also changing both in east-west direction and south-north from subgreenschist facies to upper amphibolite facies). (resulted from different correlations made by Linzer et al., 1998; Schmid et al., 2004; Miller et al., 2005; Schmid et al., 2008; Schmid et al., 2020). In all these conditions tourmaline is forming in metamorphic rocks either as accesoric mineral or as tourmaline-rich rock mineral, depending on rock protolith compositions, boron source in phyllosilicates beside fluor mobilized along brittle- ductile/ ductile shear zones. In the Carpathians Crystalline-Mesosoic Zone (Median Dacidic unit) Alpine type metamorphism took place during Cretaceous (Austrian and Laramian phase) tectonic nappe stacking, along thick shear zones, index minerals being chloritoid, stilpnomelane, phengitic mica, chlorite, albite (ex. Hîrtopanu, 1986; Seghedi et al., 1995; Balintoni, 1997; Dallmeyer et al., 1998; Kräutner and Bindea, 2002; Mosonyi, 1999;

Mosonyi, 2003; Munteanu and Tatu, 2003; Gröger, 2006; Sabău and Negulescu, 2016).

Few tourmalines, mainly with Alpine metamorphic evolution, were described from the other parts of Alpine - Carpathian orogen (see map in Fig. 1 with tourmaline locations). Chemical data of centimetrical sized tourmaline hosted in garnet-bearing orthogneisses from Sopron area (Western Hungary, tectonically from Grobgneiss Series of the Lower Austroalpine nappe system, corresponding to Bihor autochton unit from Apuseni Mountains) were analysed by Spánitz et al., (2018). Chemically zoned tourmaline presents a Variscan magmatic schorlitic core zone, overgrown by 2 metamorphic ones Fe-rich and Mgrich, formed due to high salinity, B-bearing fluids which metasomatised an Alpine shear zone. The associated Alpine phengitic micas have X_{Mg} of 0.4 - 0.6.

From Central Western Carpathians Bačik et al. (2011), analyzed Vanadium-bearing tourmaline that is in association with V-bearing micas in Paleozoic metacherts from the pre- Alpine (Variscan) basement with medium to high grade metamorphism, representing a westeast prolongation of Apulia- derived allochton unit (in Strážovské Vrchy Mountains, as part of Tatra - Fatra Belt core mountains, near the village of Chvojnica, Slovakia). The Chyoinica tourmaline appears to belong to a series between dravite and vanadiumdravite, and is the product of several processes, including sedimentation of the protolith and subsequent polystage pre-Alpine regional metamorphism. The crystals display a color zoning and a strong chemical zoning, with a core (magnesio-foitite, of low grade metamorphism), an intermediate zone, and two rim zones of prograde metamorphic events from amphibolite up to upper amphibolite facies conditions.

Sperlich et al. (1996) studied Alpine monometamorphic evolution and zoning in tourmaline with detrital Li-poor core in Lukmanier zone (at boundary between Helvetic and Penninic nappes). The authors evidenced 3 stage in prograde metamorphic evolution around tourmaline core with 2 metamorphic overgrowth zones (from greenschist up to amphibolite facies conditions), and conclude that in the Central Alps, increasing metamorphic grade is showed by increases in Ca/(Ca + Na) and Mg/(Mg + Fe²⁺), and an increase in the occupancy of the crystallographic X-site of tourmaline.

High-pressure tourmaline hosted by Eoalpine Austroalpine basement ultrahigh pressure rocks, Fe-Tirich eclogites from the Kreuzeck Mountains, (southeast of the Penninic Tauern Window, Eastern Austria) was studied by Konzett et al. (2012). The eclogite was encapsulated in quartzo- feldspathic schists of the Polinik unit. The analyzed tourmaline is essentially a schorl-dravite- uvite solid solution. The tourmalines show compositional zoning of two types with respect to Ca, ${}^{\rm Y}\!X_{_{\rm Ma}}$ and Ti. First type is a concentric zoning with sharp boundaries and the outermost zone being enriched in schorl in compare to inner zones. The other type is a patchy zoning and may be present as core in the larger tourmalines with first type of zoning. Most of the tourmalines are crosscut by very

fine vein-like schorl-rich tourmaline of later generation (712 and 658 °C counted based on Zr concentration in titanite for chosen pressure of 10 and 5 Kb).

Krenn et al. (2021) checked fluid inclusions trapped by different minerals from the polymetamorphic Koralpe-Wölz nappe system with a Permo-Triassic LP/T imprint and an Eoalpine HP/T overprint. In pegmatite fields of Permian origin were reported tourmalines, but these are part of Permian magmatic mineral assemblages, not metamorphic ones and these were not tested by electron microprobe.

Ertl et al. (2010a) analysed Li-tourmalines from the contact zone of Permian pegmatites to mica schists and marbles from different localities of the Austroalpine basement units in Styria, (Austria). They established Al-Mg disorder between the crystallographic Y- and the Z-sites in tourmalines of dravitic species, the later having X_{Mg} in the range 0.84 – 0.95.

Tourmaline from UHP rocks from few location in Alps were analysed by Ertl et al. (2010b) to find any properties related to P-T conditions. For dravitic tourmaline from Parigi and Dora Maira, the counted peak P-T conditions were ~ 37 Kb, 750 °C. Dravite from Lago di Cignana, (Western Alps, Italy) formed at ~ 27 - 29 Kb, 600 - 630 °C. The authors concluded, that: there is no significant substitution of Si^T by Al^T or B^T in the UHP tourmaline; tourmaline formed at LP/HT typically has significant amounts of Al^T; was established positive correlation between total AI apfu (i.e., $AI^{Y} + AI^{Z}$) and the determined temperature conditions of tourmaline formation from the different localities; was also observed negative correlation between F-content and the temperature conditions of UHP tourmaline formation and between F and Al^Y content; finally was conlude that the Al-Mg disorder between the crystallographic Y- and Z-sites is possibly dependent on the crystallization/blasthesis temperature.

From presented tourmaline examples it appear that Alpine metamorphic tourmalines could grow mainly at UHP-HP/MT conditions (all tourmaline zones or only overgrowth zone of tourmalines around sedimentary or magmatic core) and the Maramures tourmalines are different by age and *P-T* conditions. In case of our studied tourmalines the evolution is somehow like those mentioned at west from Apuseni Mountains (AM), in the Sopron area (in Fig. 1) by Spanitz et al., (2018), a schorlitic and dravitic tourmaline compositions beside phengitic micas with $X_{Mg} = 0.4 - 0.6$) but in our case both core and rim zones of tourmalines appear to be of Prealpine prograde metamorphic genesis in a metasedimentary environment sometimes with Li-poor granitoid provenance.

5. Conclusions

On the west part of the Vaser Valley basin (Maramureş Mountains) the Median Dacides of the East Carpathians crop out, being represented by the Rebra and Tulgheş rock sequences, which are separated by a pre-Alpine overthrust involved in an Alpine imbricated structure.



Figure 8: Discrimination diagrams for tourmaline host rocks. (a) AI-Fe_{tot}-Mg discrimination diagram (in molecular proportions) for tourmalines from different rock types. Statistically delimited compositional fields: 1 = Li-rich granitoids, pegmatites and aplites, 2 = Li-poor granitoids and their associated pegmatites and aplites, 3 = Fe-rich quartz-tourmaline rocks (hydrothermally altered granites, 4 = metapelites and metapsammites coexisting with an AI-saturating phase, 5 = metapelites and metapsammites not coexisting with an AI-saturating phase, 5 = metapelites and metapsammites and Cr, V-rich metasediments, 8 = metacarbonates and metapyroxenites. Fields 4, 5 are partially overlapping with field 7. (Henry and Guidotti, 1985, modified). Samples marked as circles = core compositions, squares-rim compositional fields: 1 = Li-rich granitoid pegmatites and aplites, 2 = Li-poor granitoids and aplites, 2 = Li-poor granitoids and essociated pegmatites and metapyroxenites. Fields 4, 5 are partially overlapping with field 7. (Henry and Guidotti, 1985, modified). Samples marked as circles = core compositions, squares-rim compositional fields: 1 = Li-rich granitoid pegmatites and aplites, 2 = Li-poor granitoids and associated pegmatites and aplites, 3 = Ca-rich metapelites, metapsammites and calc-silicate rocks, 4 = Ca-poor metapelites, metapsammites and quartz-tourmaline rocks, 5 = Metacarbonates, 6 = metaultramafics. Field 4 and 6 are partially overlapping (Henry and Guidotti, 1985, modified). Samples marked as circle = core compositions, squares- rim compositions. Same colored symbols - same grain.

The shear zone is marked by mylonitic schists containing as an accessory mineral prekinematic metamorphic tourmaline of the alkali group (Na dominant) and with hydroxyl dominating W site. These tourmalines can be assigned to schorl and dravite.

The investigated Rebra terrane rocks contain at least two generations of minerals: relics from the Variscan prograde and products of the Alpine retrograde dynamic metamorphism. Both tourmalines and white micas (solid solution between muscovite and ferro-alumino celadonite end-members) show chemical zoning. Tourmalines have a complex chemical zoning, with core and asymmetrically developed inner and outer rims. The polar chemical zoning was only slightly evidenced due to either thin section orientation or chemical homogenization during staurolite isograde metamorphic peak conditions. The dravite-schorl solid solutions were conditioned mainly by the sedimentary environment (metapelitic and metapsammitic). Tourmaline porphyroblasts with passive inclusion trails grew during the prograde metamorphism (up to medium grade).

In the Alpine shear zone, the tourmaline porphyroblasts were broken, sometimes rotated and corroded under depression during progressive simple shear, and new phengitic mica ($X_{Mg} = 0.42 - 0.44$), chlorite (ripidolit) could grow along the penetrative C mylonitic foliation. The metamorphic peak conditions, based on geothermobarometric calculations, gave a temperature between 589 and 620 °C and pressure around 5.5 to 6 kb (i.e., staurolite zone, similar to those counted by garnet-biotite and garnet-amphibole geothermometry in the neighbour Rodna Mountains, Mosonyi, 1999) for Rebra terrane rocks, on which mylonitic structures (~ 350 - 400 °C and differential stress of 1.5 kb) were overprinted.

Tourmalines of metamorphic origins were also identified in the other Prealpine and Alpine metamorphics from Alpine - Carpathian orogen: either as tourmaline' sedimentary core zone or all tourmaline grain zones as product of prograde Variscan metamorphism. In Alpine events tourmaline formed either as UHP mineral in prograde monometamorphic, polydeformed rocks or as overgrowth zones of tourmaline around sedimentary/ magmatic core. In Maramures Mountains, tourmalines from Alpine shear zone appear to have suffered only breaking, rotation by progressive shearing and depression corrosion, under greenschist facies conditions, that determined only minor Ca depletion in the tourmaline rim zone.

Acknowledgements

A. Gaweda, P. Dzierżanowski and L. Jeżak are deeply acknowledged for the help during microprobe analyses. Andreas Ertl and Simon Schorn gratefully acknowledged for their constructive reviews, comments and corrections that substantially improved the manuscript. Kurt Stüwe also kindly acknowledged for his thoughtful reading of the manuscript and for the observations and suggestions. The study was supported by a CEEPUS A-105 scholarship for E. M.

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Received: 4.5.2022 Accepted: 6.9.2022 Editorial Handling: Kurt Stüwe

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Zeitschrift/Journal: Austrian Journal of Earth Sciences

Jahr/Year: 2022

Band/Volume: 115

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Artikel/Article: <u>Metamorphic tourmaline and its petrogenetic significance from the</u> <u>MaramureÈ™ Mountains (East Carpathians, Romania) 146-166</u>