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M.Sc. Thesis

Late-stage B-bearing fluid circulation in the Kavala pluton: Evidence from mineralogical, spectroscopic and geochemical data in tourmaline-rich fault-related rocks

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Abstract

The tourmaline-rich rocks in Kavala are the products of juvenile late B-rich hydrothermal fluids exsolved from a granitic magma. In other words, this granitic magma that generated after anatectic processes in a thickened crust, during its emplacement in an ascending core-complex margin was fractionated leading to the exsolution through boiling of an immiscible volatile B-rich phase. The boiling pressure of the fluid exceeded the relatively low lithostatic pressure as it happened in a brittle setting of upper tectonic floors. Hydraulic, almost vertical, fracturing of various degrees and in dispersed places occurred, which mostly located along the NE-SW axial planes of the foliated and folded granitic pluton. This process may have occurred at least two times after further magmatic fractionation and exsolution. Hydrothermal fluid infiltration, triggered metasomatic alteration of the host granodiotite, resulting in the formation of tourmaline-rich rocks. Tourmalinites, in which tourmaline exceeded 50% vol, were formed at high fluid/rock ratios, while tourmaline breccias formed at lower ones. The latter, which comprise abundant angular to sub-rounded clasts of country rock infilled mostly by cryptocrystalline tourmaline, prevailed, indicating that the process was of high temperature and salinity. Progressive enrichment in Boron and other oxides compatible in tourmaline, coupled with depletion in REE's produced a geochemical signature of typical toyrmalinization, suggesting an acidic pH, for the overall proces, which is maybe a dominat factor for the absence of sulfide mineralization within the breccias.

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1. Introduction

1.1 Tourmaline supergroup minerals description and geological significance

Tourmaline supergroup minerals are apparently the most common borosilicate phases in Earth's crust, consisting a major sink and component in Boron geochemical cycle (Anovitz and Grew, 1996, Leeman and Sisson, 1996). Due to its exceptional stability field in terms of pressure, temperature, fluid and host-rock composition tourmaline is found in a wide variety of geological environments, namely as a diagenetic mineral in sedimentary basins, as a gangue mineral in ore deposits, associated with contact, regional and subduction-related metamorphism, in metasomatism and as a significant accessory mineral in fractionated igneous bodies (Van Hinsberg et al., 2011 and references therein).

Tourmaline is a ring-silicate mineral, with its unit cell consisting of a six-fold ring of tetrahedra (T sites) on top of a concentric arrangement of three Y-site and six Z-site octahedra. The Z-site octahedra are somewhat smaller than the Y-site octahedra, whereas the latter are more distorted (Bosi and Lucchesi, 2007). Within the six-fold ring, all tetrahedra point toward the layer of octahedra, and this arrangement results in the polar characteristics of tourmaline, because it prohibits the presence of symmetry elements perpendicular to the long axis. The X site sits in a nine-coordinated polyhedron situated on top of the six-fold ring. Three trigonal boron polyhedra are further present within the layer of octahedra in the unit cell, roughly perpendicular to the c axis. The V and W sites are anion sites that are occupied by OH^- or O^{2-} (or both) at the V site, and OH^- , F^{1-} , or O^{2-} at the W site.

The above structure can be described by a general formula of $XY_3Z_6[T_6O_{18}](BO_3)_3V_3W$, where X = Na, Ca, K, and \Box , Y = Li^{+1,} Mg⁺², Fe⁺², Mn⁺², Al⁺³, and Ti⁺⁴, Z = Al⁺³, Mg⁺², Fe⁺³, V⁺³, and Cr⁺³, T = Si, Al, and B, V = OH, O, and W = OH, O, and F (Dyar et al., 1998; Hawthorne and Henry, 1999). As a result of the great variety of major elements that can be incorporated in tourmaline's structure, there is a wide spectrum of compositions, and consequently of different end-members. In the classification of Hawthorne and Henry (1999) there were 14 IMA-CNMNC recognized end-members, with the number increasing to 18 in the most recent nomenclature review by Henry et al. (2011). The later authors, also proposed a hierarchical "step by step" approach for the tourmaline classification procedure considering that tourmaline investigations have varying levels of available information.

In addition, tourmaline can incorporate numerous trace elements, which combined with the major element content, make tourmaline a very sensitive indicator of the geological environment, as it can record the geochemical signature of the medium from which it crystallizes (e.g. Henry and Guidotti, 1985; Dutrow and Henry, 2000; van Hinsberg et al., 2011). Consequently, the study of tourmaline can provide important information for understanding fluid-related processes, including those in subduction zones, crustal metamorphism and anatexis, magma genesis and evolution, and hydrothermal ore formation (e.g., Marschall and Jiang 2011; Slack and Trumbull 2011).

Although tourmaline abundance is small in the vast majority of the rocks, where it participates, it can locally become the main constituent of particular rock types, such as tourmalinite (e.g. Slack et al., 1984), tourmaline-bearing granite, pegmatite, greisen (e.g. Trumbull and Chaussidon, 1999), tourmaline-quartz breccias and breccias pipes within granites (e.g. London and Manning, 1995, Williamson et al., 2000) and metasomatic blackwalls around eclogite knockers within serpentinite mélanges (e.g. Altherr et al., 2004, Marschall et al., 2006).

In magmatic-hydrothermal systems, commonly associated with granitoid intrusions, tourmaline can be formed as a magmatic mineral, as a subsolidus phase and as a late hydrothermal mineral, especially at the exocontacts of the plutons, indicating high activity of boron. Boron in granitic magmas, particularly in combination with fluorine, increases the solubility of H₂O, and reduces their viscosity. This results in enhanced partitioning of B into the fluid phase, the incremental solubility of silica in the fluid phase and high hydrostatic pressure during final crystallization (Pollard et al., 1987; London, 2009). The circulation of the released B-rich fluids from the crystallizing granitic magma, in the contact aureoles causes metasomatic reactions (tourmalinization and silicification) and/or hydro fracturing in both the granite and the host rocks (Müller and Halls, 2005; Dini et al., 2008; Slack and Trumbull, 2011). When the internal pressure of the fluids exceeds the lithostatic load, the hydro fracturing triggers a breccia pipe and stockwork formation, usually associated with Cu, Au, Mo, Zn and Sn ores and barren types, at the apices of granitic bodies (Derham and Feely 1988; Williamson et al., 2000; Skewes et al., 2003; Dini et al., 2008; Feely et al., 2010). In the hydrofractured

zones the solid rocks are fragmented and cemented by minerals crystallizing from the exsolved fluid, forming tourmaline-bearing breccias (Skewes et al., 2003; Müller and Halls, 2005; Dini et al., 2008).

1.2 Definition of Tourmalinization and worldwide examples

Tourmalinization is geochemically characterized by enrichment in Al, Mg, Ca, Fe, Na, Li, B, H_2O and depletion in SiO₂, CO₂ (Harlov and Austheim, 2013 and references therein). Tourmaline precipitates at the expense of common granitic ferromagnesian minerals like biotite and hornblende, and if the process continues feldspars are also replaced, producing a rock that is mainly composed by tourmaline and quartz.

Tourmalinization phenomena, are well documented from several localities worldwide. In Europe they are associated with the European Variscan collisional orogen including Great Britain (Cornwall), Central Europe (Schwarzwald, Germany) and Iberian Peninsula (Central Iberian Zone in Portugal).

In the Cornish Variscan province, tourmalinization, is associated with the emplacement of evolved crustal magmas, forming the Cornnubian Batholith (Chen et al., 1993; Clark et al., 1993). Tourmaline, is present as an accessory in the entire differentiation series of granitoid phases of the batholiths and the associated pegmatites and aplites (London and Manning, 1995). Locally increased modal abundance of tourmaline (> 50 % vol.) produces specialized kind of tourmaline-rich rock, referred as massive quartz tourmaline rock (MQT) (Müller et al., 2006; Williamson et al., 2000). This kind of rock commonly forms veins to small lenses, whereas a small MQT stock is described in Roche rock formation near St. Austell granite. Several models are proposed for the petrogenesis of MQT's including magma degassing (Smith and Yardley, 1996), magmatic formation from silicate (Badham, 1980) or hydrous borosilicate melts (Driveness et al., 2015), to magmatic-hydrothermal transition regimes (London and Manning, 1995).

In Schwarzwald, tourmaline bearing aplo-pegmatites, coarse grained quartz-tourmaline veins and medium- to fine-grained quartz-tourmaline crack fillings, occur both in the fine-grained granites and the high grade migmatitic gneisses of the Central Schwarzwald Gneiss Complex and the Southern Schwarzwald Gneiss Complex (Eisbacher et al. 1989; Marschall et al., 2003), intruded by the anatectic granitoids (Marks et al., 2013). Marks et al., (2013) discriminated pegmatitic from hydrothermal tourmalines, based on major,

trace elements and REE systematic, highlighting the significance of tournaline trace element compositional record in the discrimination of different sources of crustal derived fluids.

In the Central Iberian zone, massive replacement and breccias tourmalinites are described (Ribeiro da Costa et al., 2014) in the exocontact of the Pencamor-Monsanto pluton (Central Portugal) with the host Ordovician Schist- Greywacke Complex (Sousa, 1985; Ribeiro et al., 1990). The pluton is composed mainly of medium and coarse grained two mica granite, with tourmaline encountered as an accessory mineral in both rock types (Neiva and Campos 1992, 1993). Tourmalinites are developed in the contacts and inside metasediments, due to localized B-rich fluid circulation, with tourmaline formation resulting from alteration of Fe-Mg minerals and/or direct precipitation from the fluid (Ribeiro da Costa et al., 2014). Another well studied example in Northern Portugal is the Panasqueira S-type granite (Kelly and Rye, 1979), associated with the world-class Panasqueira W-Sn-Cu deposit (Shedd, 2016). Tourmalinization is developed as a wall-rock alteration associated with tourmaline bearing mineralized veins and greisens, as a result of fluid cooling combined with various degrees of fluid/rock interaction (Cocedo et al., 2017).

Another important occurrence of Alpine age (Late Miocene) tourmaline veins is found at the contact aureole of Eastern Elba (Italy). There, exsolution of B rich fluids from the aplite in the contact with the hornfels deposited two distinct generations of tourmaline veins, as a result of a two-stage pressure build up and consequent explosive hydrofracturing events (Dini et al., 2008).

1.3 Tourmalinization and tourmaline occurrences in Greece

In Greece, several studies were conducted dealing with tourmaline occurrences in pegmatites in Vavdos (Chalkidiki Peninsula; Laskou, 2005). In the nearby Sithonia tourmaline fracture fillings with an unusual sodian povondraite to hydroxyl uvite-feruvite tourmaline variety, are found within a pegmatite dyke, possibly resulting from complex hydrothermal fluid/host rock interactions (Aurisicchio et al., 2007). In Northern Greece, zoned tourmalines are also present in the graphite-rich metasediments of Polydentri-Kochliko and the migmatitic paragneisses of Riziana, with the complex

metamorphic overgrowths over an initial detrital core of tourmaline, indicating a B-rich aluminous protolith (Michailidis et al., 1994; Michailidis et al., 1996).

In Ikaria, Hezel et al. (2011) studied the evolution of tourmaline in the Miocene S-type granite, aplites, pegmatite and metamorphic host rocks. Besides tourmalines of undoubted magmatic and metamorphic origin, these authors described quartz-tourmaline and tourmalinite formations inside the granite and the matapelites, interpreting the former as fluid segregations after the magmatic-hydrothermal transition and the later as a result of fluid segregations from the metapelites during lower amphibolite phase prograde dehydration. Ikaria is also the place that hosts tourmaline- bearing rhyolites, formed from crustal melts, with an inferred Pliocene age (Baltatzis et al., 2009).

Another interesting case study, deals with hydrothermal tourmaline precipitates forming slickenside fibers in brittle-ductile normal faults in Despotiko Island (Ertl et al., 2011), pointing to the synkinematic tourmaline growth as an indicator of the conditions during the fault activity.

Two alternative but interesting occurrences of metamorphic tourmaline are described from the islands of Syros and Samos in the Atticocycladic Massif. In Syros, tourmaline is found in metasomatic blackwalls around eclogite knockers, and as detrital and metamorphic grains in HP metasediments (Marschall et al., 2006, 2008). In Samos an unusual composition of tourmaline with elevated Ni, Co, Zn contents, associated with micaceous enclaves in marbles and the adjacent metabauxites is described from Henry and Dutrow (2001).

1.4 Purpose and Scope of the present study

In the study area, which is located nearby Kavala city, northern Greece, a previously undescribed in detail system of tourmaline-rich rocks within the Symvolon-Kavala granodiorite, is documented here. Encountered tourmaline-rich rocks are texturally characterized as veins and breccias, with the modal abundance of tourmaline commonly exceeding 15 % vol., which is the limit for classifying a tourmaline-rich rock as a tourmalinite (Slack, 1984). Despite that tourmaline breccias systems are well studied, especially when hosting mineralization (Dill et al., 2012), there is a lack of mineralogical and geochemical data useful for comparison in barren systems, such that of the studied case here. Demirel et al. (2009) described an analogous system within the

Kerkenez granitoid in central Turkey, and proposed an evolutionary trend from calcic to alkali tourmalines based on major element data.

Considering the scarcity of relevant case studies, and the elevated participation of tourmaline in the studied area, this study aims to develop the current knowledge of tourmaline bearing hydrothermal systems, providing new major and trace element data of different tourmaline generations. In addition, new trace element models are proposed to decipher the origin of tourmaline. Last but not least a geochemical study was conducted in order to characterize the chemical element mobility during B metasomatism and constrain the geochemical factors, controlling this process, with special interest on the exact rock types, resulting from different B-rich fluid/ host rock interaction ratios.

2. Geological setting

2.1 Regional Geology

The Symvolon-Kavala granodiorite, the host-rock of the tourmaline-rich rocks, is an elongated Miocene pluton within the Rhodope Zone (RZ), which has also characterized as a metamorphic province. This Zone is a polymetamorphic complex located in NE Greece to SW Bulgaria, in the hinterland of the Hellenic Subduction System (Burg et al., 1990; Bonev et al., 2006; Krenn et al., 2010; Jahn-Awe et al., 2010; Nagel et al., 2011). The discrimination of the different units in the Rhodope, comprises long time debate in international scientific literature. Papanikolaou and Panagopoulos (1981) divided Rhodope in two different tectonic units, namely the Lower Tectonic Unit (LTU) or Pangeon unit and the Upper Tectonic Unit (UTU) or Sidironero unit. Burg et al. (1996) proposed the division in a lower and upper terrain, with the later overlain by the Kimi complex. Kimi is also interpreted as a different unit from Sidironero by Krohe and Mposkos (2002) and Mposkos et al. (2010). The division of Turpaud and Reischmann (2005), introduces the South Thracean (Lower unit) and the North Rhodope (Upper unit) terrains. In a recent interpretation (Krenn et al., 2010), Rhodopean units are considered as a sequence of Alpine nappes, accreted to the European margin form Middle Jurassic to Neogene. In this study a more recent classification was followed, considering that RZ consists of four allochthon tectonic units, namely Lower, Middle, Upper and Uppermost Allochtons (Janak et al., 2011). Three main metamorphic core complexes actually comprise the Lower Allochthon of the RZ (Liati et al., 2016), namely the Core Complexes of Southern Rhodope (SRCC), of Baila Reka/Kechros and of Kesebir/Kardamos. Recently, these core complexes, and hence the Lower Allochthon, have been interpreted to belong to the Pelagonia continental block, which is mostly developed west of Vardar Zone (Brun et al., 2016), leaving the other three allochthons to the Rhodopia continental block. Following this interpretation the Nestos Thrust, which separates the tectonic window of Pelagonia (Lower Allochthon, SRCC) from the overlying nappes, is actually a segment of the Vardar suture zone (Brun et al., 2016).

2.2 Tectonic evolution

RZ is tectonically bordered by Maritza strike-slip fault in the north, by the Vardar suture zone in the western and southern parts and by the Western part of the Thracean basin in the east (Bonev et al., 2006; Kirchenbaur et al., 2012 Froitzhaim et al., 2014) (Fig, 1).

Several ductile-brittle low angle detachment faults resulted to the exhumation of Baila Reka/Kechros and Kesebir/Kardamos gneissic domes from 42 to 30 Ma in Eastern Rhodopes (Bonev et al., 2006, 2010). In the SW part the exhumation and subsequent cooling of the SRCC is a continuous process along the ductile Kerdyllion detachment from 42 to 24 Ma, and the brittle – ductile Strymon valley detachment from 24 to 12 Ma (Brun and Sokoutis, 2007; Wüthrich, 2009; Kounov et al., 2015). Exhumation of the core complexes, along the low angle normal faults led to the formation of several supra-detachment basins from Upper Cretaceous to Miocene (Kilias et al., 2013).

2.2.1 Description of Rhodope Units

The Lower Allochthon (Janak et al., 2011) is composed of a Variscan basement, massive marble with amphibolites and metapelites layers and is metamorphosed from upper greenschist to low amphibolite facies (Pangeon/Pirin complex). Within this unit several anatectic events occurred as indicated from the exposed migmatites at Arda, Byala Reka/Kechros and Kesebir/Kardamos gneissic dome complexes (Kirchenbaur et al., 2012; Kounov et al., 2015), and the plutons occurring in the area e.g. Vrondou, Kavala, Pangeon, Pirin.

In Kechros area prograde high-pressure conditions were established in kyanite eclogite and "common" eclogite; $585 \pm 32^{\circ}$ C / 2.17 ± 0.11 GPa and $619\pm53^{\circ}$ C/ 1.69 ± 0.17 GPa, respectively. Retrograde conditions were $534 \pm 36^{\circ}$ C / 0.77 ± 0.1 GPa. Furthermore, in the same unit, leucocratic rocks within antigorite serpentinite examined in order to constrain the metamorphic evolution. Eclogitic facies metamorphism with conditions of 1.55 ± 0.03 GPA at temperatures of 550 ± 25 °C is considered peak conditions. Subsequently, for the particular unit, an isothermal decompression takes place with P = 1.1 ± 0.03 Gap and T = 580 ± 20 °C, indicating a fast exhumation, followed by an isobaric cooling with final conditions of P 0.55 ± 0.04 Gap and T 430 ± 30 °C (Mposkos et al., 2013).



Figure 1: Geological map of RZ after Kirchenbaur et al. (2012)

The Middle Allochthon corresponds to the Sidironero and Kerdilion Units (Janak et al., 2011), whereas Froitzheim et al (2014) suggest that it belong to the Vardar Zone. Middle Allochthon is composed of metamorphic rocks with continental and oceanic protoliths, interrupted by Eocene granitoids. It was thrusted on the Lower Allochthon along the Nestos Shear Zone during the Paleogene (Jahn-Awe et al., 2010). Amphibolite facies metamorphism is common in this area; moreover, relics of UHP metamorphism are established by several authors, reporting microdiamonds inclusions in garnet of metapelites, in localities at the base of the middle unit (Mposkos and Kostopoulos, 2001; Perraki et al., 2006; Schmidt et al., 2010). Three subduction-related metamorphic events were concluded by Kirchenbaur et al. (2012), at 150 Ma in metapelites and eclogites for timing close to UHP; a 42 Ma age in eclogites are deciphered as the timing of at least HP conditions.

Kerdilion Unit, the southwestern part of the Middle Allochthon, is composed of migmatitic gneisses, amphibolites and marble. Migmatites are also found in Sidironero,

with the time of the partial melting corresponding to 39-40 Ma (Kounov et al., 2015 and references therein).

The Upper Allochthon corresponds to Kimi Complex and Vertiskos Unit (Janak et al., 2011). The rocks exposed at this units are metapelites, gneisses, amphibolites, marble and boudins of eclogites and ultramafic rocks, which can be attributed to melting residues emplaced at the base of the crust (Baziotis et al., 2008). UHP metamorphism has been established by Mposkos and Kostopoulos (2001) as a result of microdiamonds inclusions discovered in Kimi complex and in the base of the upper unit by zircon inclusions (Kirchenbaur et al., 2012 and references therein).

Single crystal zircon dating records at least 3 metamorphic episodes, as indicated by the different overgrowths around the zircon magmatic core. The first episode at 158 Ma recorded in the interior rim is attributed to the time just after the UHP metamorphism with conditions of 1.5 GPa (for T > 670-700 °C, derived by Ti-thermometry). The next overgrowth yields an age of 74 Ma with estimated metamorphic conditions at 650-630 °C (Ti-thermometry) and minimum pressures of 1.5 to 1.7 GPa. The third metamorphic event at ~42 Ma is constrained by pyroxenite layers. The interpretation of the above dates contributes to a complex history with multiple subduction-related metamorphism (Liati et al., 2016 and references therein).

The Uppermost Allochthon is identical to the Circum Rhodope Belt, which comprise the Makri and the Drymos-Melia Units (Janak et al., 2011). These units mostly consist of low grade (up to greenschist facies) volcanic and sedimentary rocks. Metavolcanics and underlying metabasites, plagiogranites and serpentinites are interpreted as an incomplete ophiolitic complex (Evros ophiolite), geodynamically related to a volcanic arc marginal basin of Middle Jurassic age, belonging to the Vardar ocean (Magganas et al., 1991; Magganas, 2002). This Allochthon was overthrusted to the Upper Allochthon as a result of an arc – continent micro-collision from Jurassic to Early Cretaceous, (Bonev and Stampfli, 2003) or during exhumation from shallow depths in an accretionary prism setting later at Cenozoic times (Magganas 2005).

2.3 Tertiary Magmatism

Cenozoic igneous activity in the Rhodope is represented by Oligocene to Miocene volcanic rocks and Upper Eocene to Middle Miocene plutonic rocks. Plutonic rocks,

mainly monzonite, granodiorite and granite with lesser amounts of gabbro, are widespread in Rhodope, although they dominate in the eastern and central parts (e.g., Christofides, 1995; Dinter et al., 1995; Eleftheriadis and Koroneos, 2003). Large plutonic intrusions, namely Symvolon-Kavala, Skaloti-Elatia, Vrondou and Xanthi plutons, dominate in the western and central parts of Rhodope, whereas smaller intrusions are also found in the eastern part, e.g Maronia, Tris Vrises-Halasmata and Leptokarya, with the latter following an E-NE trend (Christofides et al., 1998 and references therein). The vast majority of these intrusions are I-type metaluminous to slightly peraluminous of calc-alkaline to high-K calc-alkaline affinities, displaying a wide compositional spectrum, ranging from granite to monzonite with subordinate amounts of gabbro (Christofides, 1996).

Petrogenesis of Rhodope plutons is considered as a result of evolution of diverse basic and acid melts. Basic plutonic members are derived from metasomatized mantle melting and consequent development of hybrid melts via open system assimilation plus fractional crystallization processes. The acid members represent deep crustal melts, derived by dehydration melting of middle to lower crust (Christofides et al., 1998), whereas Jones et al (1992) stated that in the Rhodope granitoids there is a strong mantle component.

2.4 The Symvolon-Kavala pluton

In Kavala area the metamorphic rocks of the Lower Allochthon of RZ were concordantly to discordantly intruded by the Kavala-Symvolon pluton (Fig. 2) along the SW-NE Kavala–Komotini fault zone (Dimadis and Zachos, 1989). Kokkinakis (1977) suggests that the pluton is mainly consisting of hornblende-biotite granitic and granodioritic blastomylonites, occupying respectively the northern and the southern part of the pluton. Other subordinate lithologies of the pluton include tonalitic, quartz monzonitic and quartz monzodioritic compositions. Both the pluton and the country rocks are penetrated by aplitic, pegmatitic and more basic usually porphyritic dikes, with the latter having an average modal composition of biotite-hornblende quartz monzodiorite, and considered to be of the lamprophyric affinity (Kamvisis, 2010). All the granitic lithologies consist essentially of quartz, plagioclase (An_{16-35}), K-feldspar (Or_{75-99}), amphibole and biotite with lesser amounts of titanite, allanite, apatite, zircon and epidote. Amphibole and biotite participate in equal amounts in granodiorite, but in

tonalite and diorite amphibole dominates over biotite, which is the only mafic phase in the monzogranite (Neiva et al., 1996). Crystallization conditions are presented in detail by Christofides et al. (1995) and Neiva et al. (1996), with a noteworthy feature, that magmatic epidote requires pressures over 6 kb, in order to become stable.

According to Christofides et al. (1995) and Neiva et al. (1996) the pluton is a metaluminous, alpine I-type granodiorite intrusion, with lensoidal enclaves of metaluminous tonalite and diorite particularly towards its margins. These authors also suggest that the observed lithologies are likely a result of a fractional crystallization process, which produced a sequence from biotite-hornblende tonalite to biotite monzogranite, as indicated by major and trace element modeling. High δ^{18} O values (10.4-11.4 $^{0}/_{00}$) and a positive correlation between Sr isotopes ratio and SiO₂ (Kyriakopoulos, 1987; Neiva et al., 1996) constitute evidence of crustal contamination, indicating that an AFC process may played a major role in the differentiation history of the intrusion.

The pluton, suffered intense sub-solidus deformation, as indicated by widespread mylonitic textures (Kokkinakis, 1977). Transitions from protomylonitic granodiorite with K-feldspar and plagioclase porphyroclasts to fine-grained laminated ultra-mylonites are commonly observed, with pseudotachylite development in zones of intense deformation (Christofides, 1995). However, the detailed textural investigation by Kokkinakis (1977, 1980) suggests that the intrusion is dominated by granitic and granodioritic blastomylonites, indicating that most feldspars and in particular K-feldspar megacrysts are actually syn- or meta-tectonic porphyroblasts, due to associated fluid metasomatism.

Interpretation of deformational textures (S-C fabrics, boudins, folds) in the pluton and the country rocks by Kokkinakis (1980), Sokoutis et al. (1993) and Brun and Sokoutis (2007), indicate syn-tectonic emplacement for the intrusion, deep enough to produce ductile deformation, in a regional extensional regime during a core complex growth.

Geochronological data based on U-Pb dating of titanite and ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating of hornblende yielded an emplacement age for Kavala pluton of about 21 Ma (Dinter et al., 1995). These authors also showed that the discordant Mesozoic to Palaeozoic U-Pb ages in zircon obtained by Kokkinakis (1980), are probably erroneous due to inherited Pb content in zircon cores. The K-Ar biotite ages of 15.5±0.5 Ma (Dinter and Royden,

1993) and 17.8 ± 0.8 Ma (Kokkinakis, 1980) along with the 14-16 Ma Rb-Sr biotite age (Kyriakopoulos et al., 1989) originally suggested as reset metamorphic ages that accompanied mylonitization, are in fact the cooling ages related to the deformation during emergence of the SRCC in the footwall of the Strymon valley detachment system.



Figure 2: Simplified geological map of the Symvolon-Kavala pluton (modified after Kokkinakis (1977) and Neiva et al. (1996). Sample locations are shown with the filled star symbol.

2.5 Geological setting of the tourmaline-rich rocks

The dominant rock type in the area of investigation is a blasto-mylonitic granodiorite (Fig, 3a) with K-feldspar megacrysts (porphyroblasts) (up to 5 cm). Progressive transition to finer grained meso- to ultra-mylonitic textures was also observed in the field, spatially associated with shear zones (Fig. 3d). Intense deformational features have also been observed in mafic enclaves in the granodiorite, which are flattened (Fig. 3e) in a direction parallel to the K-feldspar megacrysts. Subordinate rock types, encountered in the area include aplitic (Fig. 3b) and mafic dykes (Fig. 3c) intruding the granodiorite. Aplites display the classic sugary texture with biotite as the main mafic phase observed in the field, and they range in the degree of deformation from undeformed (Fig. 3b) to strongly deformed (Fig. 3f). Mafic dykes are mainly undeformed, porphyritic with biotite, amphibole and feldspar phenocrysts.

The studied tourmaline-rich rocks occur with different frequency in the plutonic and metamorphic rocks occurring nearby Kavala city and the Symvolon Mt (Fig. 2). They are mainly found in three different forms: a) massive veins (Fig.4a, b, c), b) cataclasites/breccias (Fig. 4d, h) and c) injections (Fig. 4e, g). The massive tourmaline veins have a blue-black color and are completely aphanitic with a glassy appearance (Fig. 4f), which makes the discrimination from pseudotachylites extremely difficult without laboratory X-ray diffraction methods. Massive veins display an up to 20 cm width, when found crosscutting the foliation of the host with low angles (up to 40°), whereas in vertical crosscutting structures the width increases an order of magnitude (>1 m). In cataclasites/breccias the angular clasts have a granitic or pure quartz composition, while tourmaline constitutes their matrix. This second rock type also shows a vein or sheeted structure with thickness that varies from few mm to about one meter. Their tourmaline matrix, which also shows a dark blue to black color, is locally disrupted by the grey to white clasts occurring with greater abundance in breccias thicker than 1 cm (Fig. 4c, h). Tourmaline injections (Fig. 4g) are commonly developed into a complicated network, which finally seems to feed/infiltrates the breccias (Fig 4d). Injections are locally associated with micro fault and joint systems, creating a tourmaline-rich crust above the mentioned structures surfaces. It frequently has a thickness not exceeding few cm and a mirror like polished surface with slickensides indicating a movement which is postdating the tourmaline crystallization. It has to be mentioned that the above division of the different tourmaline bearing rock types is strictly based on field observations.

The most important occurrence of the tourmaline-rich rocks is in the area of Mavri Petra in the Symvolon Mt (sample locations KV1-KV5, in Fig. 2). In this area the massive veins and breccias are abundant and are found within the granodioritic blastomylonite, and in close spatial association with aplitic dikes. The tourmaline-rich vein system is mostly developed along a NW-SE to NNW-SSE trend with moderate to steep NW or WNW dip angles.Especially, the observed trending of the tourmaline-rich rocks is almost always subvertical to the main NE-SW regional trending of the B2 and stretching lineation (Kokkinakis, 1977). This trending may have served as the main channel for hydrothermal fluid chanelling, as indicated by the scarcity of tourmaline in fractures with other trending.Crosscutting relationships between the tourmaline-rich cataclasites and the host rock, suggest that the former developed sintectonically in a shallow brittle deformation regime, overprinting the mylonitic foliation of the pluton.



Figure 3:Field photographs of the various rock types encountered in the Symvolon-Kavala pluton.(a) Blasto-mylonitic granodiorite with K-Feldspar megacrysts,(b) Syn-tectonic aplitic dyke intruding the granodiorite parallel to the foliation as indicated by the orientation of K-feldspars(c) porphyritic mafic dyke crosscutting the granodiorite, (d) Blasto-mylonitic granodiorite transition to ultra-mylonite in a shear zone with 2 cm thickness, (e) elongated mafic microgranular enclave within the granodiorite, (f) Deformed (boudinaged) aplitic dyke intruding the metamorphic rocks of the LTU of Rhodope, which are in contact with the pluton.



Figure 4: Outcrop photographs of the studied tourmaline-rich rocks, (a) massive tourmaline veins in the contact of mylonitic granodiorite with aplitic granite, (b) 1 m thick massive tourmaline-quartz vein crosscutting the foliation of the aplitic granite, (c) transition of massive tourmaline vein to breccias with gradual increasing participation of larger sized host rock fragments, (d) typical view of a tourmaline breccias consisting of a dense network of tourmaline veinlets around aplitic granite fragments, (e) Quartz-tourmaline vein crosscutting the mylonitic granodiorite, (f) Close up view of (a) showing the glassy appearance of the tourmaline veins, (g) massive tourmaline injection in the mylonitic granodiorite, (h) Close up view in a tourmaline vein, with rock fragments orientated in a direction parallel to the flow of the hydrothermal fluid.

3. Materials and Methods

3.1 Sample description

A total of 20 representative samples of both tourmaline-rich rocks and the host granitoids were collected during fieldwork. The samples come from six selected sampling locations where the most representative and fresh outcrops occur (Fig.2). The hand-specimen description of the collected rocks was followed by selection of the most representative samples and preparation of 25 polished thin sections, in the laboratories of the Institute of Geological and Mineral Exploration (I.G.M.E) in Athens, for further investigation. In addition, 15 selected samples were pulverized in order to decipher the bulk-rock mineralogy, using a steel-jaw crusher and an agate mill in the laboratories of the Mineralogy-Petrology Department, Faculty of Geology & Geo-environment, of the National and Kapodistrian University of Athens.

3.2 Optical Microscope

Twenty-five polished thin sections were examined in detail using polarized transmitted light microscopy attached with digital camera in plane-polarized and crossed-polarized light in order to identify the minerals and reveal the textural relation between the clasts and the matrix of the rocks under study. Petrographic–study was conducted using a ZEISS AXIOSCOPE 40 polarizing microscope in the I.G.M.E. Microstructure of the samples was determined under ×1.5 magnification, but more powerful objective lenses (up to \times 50) were used for the identification of the participating minerals, especially tournaline.

By the end of this study the most representative five samples were selected to be studied with more advanced analytical techniques.

3.3 X-Ray Diffraction (XRD)

Fifteen samples of tourmaline-rich rocks (both veins and breccias) and host rocks were pulverized for X-Ray Diffraction analysis, obtained using a SIEMENS D-5005 type diffractometer, in order to verify the presence of tourmaline and get some preliminary results in the bulk mineralogy. The diffractometer was operating using CuKa radiation at 40 kV and 40 mA and employing the following scanning parameters: step size 0.020° and step time 2s at room temperature (25° C). The mineralogical phases were determined with the software DIFRAC PLUS 2004, EVA ver. 10 at the laboratories of the NKUA, Faculty of Geology and Geo-Environment. In addition, a first estimation of the modal proportion of the participating phases was obtained by semi-quantitative phase analysis.

3.4 Bulk rock geochemical analysis methods (ICP-ES, ICP-MS)

Four representative samples of tourmaline-rich rocks and one host rock, were selected for major, trace, REE analyses plus Boron estimation. Samples were selected regarding the mode of field occurrence. Sample KV15-13 represents the host mylonitic granodiorite near the tourmaline breccias. Samples KV15-16, KV15-18, KV15-19 represent tourmaline breccias, and sample KV15-9 represents a massive tourmaline vein, which is not disrupted by host rock fragments.

Samples were pulverized using a steel jaw crusher and an agate mortar at the laboratories of the NKUA, Faculty of Geology and Geo-Environment. Following the preparation stage, 30g rock pulp each pulverized sample was sent in ACME Laboratories in Canada for geochemical characterization.

Selected analytical packages included the LF-200 package for major and trace elements and PF370 for Boron estimation. In LF-200 rock powders are fused with lithium borate and then analyzed with ICP-ES and ICP-MS for major and trace element concentrations respectively. Detection limits for major elements oxides are down to 0.01% wt. and for trace elements down to 0.01 ppm.

Boron concentration was determined with ICP-ES with a lower detection limit at 0.01 % wt. after decomposition of the sample powders with the Sodium Peroxide Fusion method. Whole-rock major and trace element compositions of the studied samples are given in Tables 1 and 2, respectively.

3.5 Raman Spectroscopy

Raman Spectroscopy (RS) was performed on two samples in order to distinguish the possible different generations of tourmaline and/or to compare with the available

tourmaline data on different setting. RS spectra were collected using a Renishaw in Via Reflex at the National Hellenic Research Foundation, Institute of Theoretical and Physical Chemistry (Athens, Greece). The RS is equipped with a green excitation source of 633 nm and acquired at the spectrum range 100-1500 cm⁻¹. We used Fityk (ver. 0.9.8), a Levenberg-Marquardt algorithm, and lognormal distributions to optimize deconvolution for the acquired spectra (RS published data from RRUFF database).

3.6 Scanning Electron Microscopy (SEM)

Description of microtexture and tourmaline abundance was additionally examined using a JEOL JSM-6510LA SEM equipped with one energy – dispersive spectrometer (EDS), at the Institute for Mineralogy, University of Münster, Germany. Elemental associations between tourmaline and host rock enriched domains were deciphered, applying high resolution X-ray mapping, in two polished thin sections. Acquisition of the X-ray imaging was conducted under a 20 kV acceleration potential, and a 5 μ m spot size for 2s steps.



Figure 5: JEOL JSM-6510LA SEM at the Institute for Mineralogy, University of Münster, Germany.

3.7 Electron Probe Micro Analysis (EPMA)

Major element compositions of tourmaline were determined in two polished thin sections using a JEOL JXA8530F Field Emission EPMA (FE-EPMA) equipped with five wavelength-dispersive spectrometers (WDS) and one energy - dispersive

spectrometer (EDS) at the Institute for Mineralogy, University of Münster, Germany. A total of 139 tournaline analyses were performed with an accelerating voltage of 15 kV. For minerals, a 20 nA focused beam current, 20 s counting time on peak position and 10 s for each background were used. Natural mineral standards used were albite (Na, Si, Al), wollastonite (Ca), olivine (Mg), almandine (Fe), spessartine (Mn), orthoclase (K), rutile (Ti), chromite (Cr) and Ni-oxide (Ni) with ZAF matrix correction. Representative tournaline compositions are given in Table 3.



Figure 6: JEOL JXA8530F Field Emission EPMA (FE-EPMA) in the Electron Microprobe lab at the Institute for Mineralogy, University of Münster, Germany.

3.8 Laser Ablation - Inductively Coupled Plasma - Mass Spectroscopy (LA-ICP-MS)

Trace element measurements were performed on polished sections after EPMA analysis using LA-ICP MS at the Institute for Mineralogy, University of Münster-Germany. Representative trace element analyses are given in Table 4.

The trace element analyses carried out at University of Münster used a Thermo Fisher Scientific Element 2 sector field ICP-MS coupled to a Photon Machines Analyte G2 Excimer laser system operating with ca. 5 J/cm² laser fluence and a repetition rate of 6-10 Hz. We used a large-volume ablation cell with fast signal response and short washout times (< 1 s) that holds up to 6 conventional thin sections and additional reference materials. Prior to sample analyses, the system was tuned with NIST SRM 612 glass for high sensitivity, stability, and low oxide-interference rates (232 Th 16 O/ 232 Th < 0.2%). Spot sizes for the mineral analysis were between 12 and 60 µm in diameter; in most cases 40 µm was selected as the best compromise between laser signal strength and spatial resolution. The signal ablation time was 40 seconds for the peak and 20 seconds for the background. Wash out time between individual spots was 10 seconds. NIST SRM 612 glass (Jochum et al., 2011) was used as an external standard and the BIR-1G glass (Jochum et al., 2005) as an unknown to monitor precision and accuracy; microprobe derived SiO₂ content in tourmaline was used as internal standard. Five to ten sample measurements were always bracketed by three measurements of NIST SRM 612 glass and two measurements of BIR-IG glass.



Figure 7: Thermo-Fisher Scientific Element 2 sector field ICP-MS coupled to a Photon Machines Analyte G2 Excimer laser system in the LA-ICP MS lab at the Institute for Mineralogy, University of Münster, Germany.

4. **Results**

4.1 Petrography

4.1.1 Host rocks

The rock types found in close spatial association with the tourmaline-rich rocks during this study are granodiorite and aplite. The host granodiorite exhibits a wide textural spectrum from protomylonite to ultramylonite, locally intense recrystallization of quartz and K-feldspars produces blasto-mylonitic textures. The predominant rock-forming minerals in the granodiorites are the following (in decrease mode): K-feldspar, plagioclase, quartz, biotite and hornblende. Titanite, epidote, white mica, allanite, monazite, zircon and magnetite are the most commonly observed accessory phases.

Subhedral K-feldspar is the most common porphyroclast phase with sizes up to 1 cm found in sample KV15-10. Characteristic simple twinning is present, where microcline presence is indicated by its fingerprinting tartan twinning. An often, observed phenomenon is the undulose extinction and the strained twinning plains, indicators of solid state deformation. Plagioclase is in equal amounts with K-feldspar, and is the second commonly encountered porphyroclast phase. Albitic twinning with low extinction angle indicate low content in the anorthitic component of the plagioclase (0-10 An). Deformational features such as kinking of twinning planes and domino fragmented crystals are common. Quartz shows strong recrystallization, forming the ribbon quartz texture, mosaics of fine-grained crystals (average size of 20 µm) with polygonal grain boundaries. Biotite is major mafic mineral and displays strong orientation, parallel to the foliation. Distinctive perfect cleavage is observed, along with an intense brown-green pleochroism. Biotite chloritization, is locally observed as indicated by the characteristic interference color of chlorite. Deformational features such as mica fish and sheet separation parallel to the cleavage are quite common. Hornblende, when present forms euhedral to subhedral prismatic crystals, with green-dark green pleochroism and distinctive 120° angle between cleavage plains. Titanite, epidote and allanite are present in elongated prismatic crystals, whereas epidote is also replacing allanite in the latter's rims. Monazite has been identified as isolated crystals with high relief 4th order interference colors. Zircon crystals are present as isolate grains and as

inclusions in K-feldspar or biotite forming the distinctive pleochroic haloes in the second. White mica is restricted in the foliation plane and displays its greater abundance in the boundaries of K-feldspar porphyroclasts, probably as an alteration product. Magnetite in the form of subhedral to anhedral isolated grains is the only opaque mineral observed in the granodiorites.

The transition between the finer-grained varieties is achieved by grain size reduction of the above described phases, forming finally matrix dominated ultramylonites. The transition from protomylonite to ultramylonite is quite distinct even in thin section scale (sample KV15-6).

Studied sections of aplite mainly consist of (in decrease mode): K-feldspar, quartz, plagioclase, biotite, muscovite, sericite, allanite and zircon. Aplite is less deformed, displaying protomylonitic textures, underlined by the weak orientation of the micas. Characteristic myrmekitic texture is commonly observed.

K-feldspar (orthoclase and/or microcline) is the most abundant mineral, forming porphyroclasts. Apart from the expected magmatic twinning, they also display undulose extinction due to deformation. Quartz is present in interstitial spaces or in ribbon shaped deformation bands, and shows always strong recrystallization with extended subgrain formations. Albitic plagioclase, characterized by polysynthetic twinning, is also present but in much less abundance than quartz and K-feldspar. Biotite is the only ferromagnesian mineral and shows a preferred orientation parallel to the foliation. Muscovite, is also placed parallel to foliation, and is considered of magmatic origin, in contrast with sericite which is widespread as an alteration product in the margins of feldspars. Allanite, which occurs as euhedral prismatic and more often as broken crystals, is a common accessory, whereas zircon occurs only as inclusions in K-feldspar. In the case of KV15-12 sample, garnet enriched zones are present in the aplite.

4.1.2 Tourmaline-rich rocks

All the studied samples are mainly composed of angular host rock fragments, mineral clasts and an aphanitic tourmaline dominated matrix and can be generally classified as cataclasites. The partition of host rock fragments can be broadly correlated with the outcrop-scale distinguished types, classifying the rocks with visible fragments as tourmaline breccias (tur-breccias), while when matrix is dominant as massive veins and

injections, which from herein are referred collectively as tournalinites (see also Discussion – chapter 5.1). Microscopic textures are quite similar to macroscopic-scale textures, and effects of brittle deformation and cataclasis are very clear in most of the samples, regardless the outcrop-scale type distinction. Clear evidence of ductile deformation seems to be absent from the studied samples, in contrast to the host granodiorite, which presents a well-defined gneissic texture, which can be also noticed in the host rock fragments within the breccias (Fig. 9c). However, in few places tourmaline crystals and quartz fragments present orientation of their elongated c-axes, providing the characteristic texture of the foliated cataclasite. The clastic material inside the breccias is mainly composed of angular to subrounded granodioritic fragments and monomineralic clasts, mainly quartz and K-feldspar, derived from the host rocks, giving the rock a poorly sorted appearance (Fig.9a, c). The fragments are characterized by ribbon quartz textures, K-feldspars with deformation twins and domino fragmented porphyroclasts of K-feldspars and plagioclase (Fig. 9b, c). It should be noticed that plagioclase occurs mainly into the clasts, and is nearly absent in the form of isolated grains inside the matrix. Quartz generally displays angular outlines with numerous internal fractures; recrystallization and sub grain formations are visible and undulose extinction is widespread.



Figure 9 :Photomicrographs of the studied samples under the polarizing microscope: a) Typical view of the tourmaline-rich rocks showing abundant angular rock and mineral fragments embedded in the tourmaline matrix (KV15/9, PPL), b, c) Angular fragment of the host granodiorite composed by kinked K-feldspar and plagioclase porphyroclasts and a recrystallized groundmass of quartz with ribbon texture (KV15/9, XPL), d) Micro-crystalline tourmaline in the matrix of the breccias with ultra fine- grained tur crystals appearing in the margins of the host rock fragments (PPL), e) Micro- to crypto-crystalline tourmaline is replacing a primary phase (possibly biotite) forming a pseudomorph. Spots from the LA-ICP-MS analysis are visible (PPL), f) Tabular, subhedral, coarser tourmaline crystal with distinct zoning surrounded by the matrix (KV15/9, PPL).

Between the rock and mineral fragments, an ultrafine-grained to micro-crystalline tourmaline-rich matrix is present covering at least 15% of the surface in the vast majority studied thin sections (see Fig. 9d). The tourmaline-rich matrix appears with a

light- to dark green color under plane polarized light and with a blue-green color in crossed polars, presenting subsequently a weak to moderate green pleochroism (Fig. 10d, e). In some cases, the aphanitic matrix appears nearly isotropic. Euhedral to subhedral tiny (up to 30 μ m long and 5-10 μ m wide) tourmaline crystals are present, forming a nearly equigranular crypto- to microcrystalline matrix (Fig. 10e, f). Within the matrix the presence of neocrystallized quartz and K-feldspar can be optically identified and discriminated from those derived from the host rock by their polygonal grain boundaries and lack of undulose extinction. The major opaque phase, encounterd in the studied samples is pyrite. Pyrite is mainly present in tur-breccias samples (KV15-16), as isolated or patches of crystals within the tourmaline matrix.

Besides the aphanitic matrix, tourmaline is present in two other distinct but rarely occurring forms in the studied thin sections, namely zoned and orbicular tourmalines. Zoned tourmalines are subhedral to anhedral, elongated (up to 120 μ m long), corroded crystals with distinct zonation. They are present within the aphanitic matrix (Fig.4d) forming a microporphyritic texture, resembling clasts in a similar manner with the host rock fragments (Fig.9f; Fig.10a), indicating that these crystals formation may have predated the crystallization of the matrix tourmaline. The orbicular tourmalines consist of light green euhedral matrix tourmaline microcrystals surrounding a core of undeformed quartz grains (Fig. 10b, c).



Figure 10: Photomicrographs of the studied samples under the polarizing microscope: a) Different generations of tournaline, expressed as ultrafine-grained, zoned phenocrysts embedded in a microcrystalline to aphanitic matrix composed by tournaline and quartz (KV15-18 XPL), b) Open- space filling intergrowth of tournaline and quartz (KV15-18 PPL), c) Same as in (b) (KV15-18 XPL) d) Tournaline-flooded domain in the breccias matrix (KV15-16 PPL) e, f) Magnified view of tiny, tabular tournaline grains from the matrix around patches of recrystallized quartz (KV15-16 PPL and XPL respectively).

4.2 Bulk rock powder mineralogy

X-Ray Diffraction (XRD) patterns of -powder mounts revealed the bulk mineralogy of the studied tourmaline-rich rocks. Tourmaline and quartz are essentially present in all the studied samples. Other components are orthoclase, plagioclase and white mica, which represent alongside quartz the granodioritic clasts inside the breccias. Based on XRD patterns morphology and recognized mineral phases, the studied rocks can be divided in two groups (Fig 11): Group 1 rocks are composed only of tourmaline and quartz, while in Group 2 rocks tourmaline coexists with quartz, orthoclase, albite and white mica. The assignment of these groups, shows an expected correlation with the macroscopically distinguished types of tourmaline-rich rocks: Group 1 patterns are the case in massive vein and injection types, whereas Group 2 is representing the breccias.



Figure 11: Representative XRD patterns of tourmaline-rich rocks in the study area (Samples KV15-9 and KV15-16). Semi-quantitative (S-Q) analysis of the patterns results in an estimation of the modal proportions of participating phases. The upper diagram corresponds to a rock composed by quartz and tourmaline mixture, while the lower is a rock composed by quartz + tourmaline + orthoclase + albite + muscovite.

4.3 Bulk Rock Geochemistry

4.3.1 Major elements

The SiO₂ content of the studied samples ranges from 66.88 to 71.72 % wt., Al₂O₃ ranges from 14.38 to 15.59 % wt. with the lowest content observed in KV15-9 (Table 1). The later, shows also the higher Fe₂O₃ and MgO contents, in the observed range of 1.92 – 6.33 % wt. and 0.69 – 2.56 % wt. respectively. CaO, Na₂O and K₂O display a similar geochemical behavior with their lower values observed in KV15-9. The rest of major element oxides, namely TiO₂, P₂O₅, MnO and Cr₂O₃ are present in negligible contents in the studied samples and don't present any noteworthy variation between the different samples.H2O content expressed by Loss of Ignition (L.O.I) ranges from 0.9 to 3.1 % with the lowest value observed in KV15-13.

Boron is commonly treated as a trace element, but as we study tourmaline samples, B concentration can become exceptionally high. In the studied samples B shows ranges from < 0.01 to 1.53 %, with the minimum and maximum values corresponding to the host rock and the massive tourmaline vein respectively. Major element oxide compositions where plotted in Harker diagrams (Fig. 12), in order to investigate the correlations between them. Magnesium oxide was used for the X axis value, as soon as it displays a significant range from the freshest to the completely tourmalinized sample, with the values increasing alongside with alteration intensity.

Magnesium enrichment shows a strong positive correlation with Fe_2O_3 and B, negative correlation with Al_2O_3 , CaO, Na₂O, K₂O, TiO₂ and almost no correlation with SiO₂ content.
Table 1:	Whole rock	major	(in wt%)	and trace	(in ppm)	element	<i>compositions</i>	of the	studied	samples.
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	KV15-13	KV15-16	KV15-18	KV15-19	KV15-09
	Granodiorite	Tur-breccia	Tur-breccia	Tur-breccia	Tourmalinite
SiO_2	69.82	66.88	71.16	71.72	68.60
TiO ₂	0.21	0.25	0.24	0.19	0.18
Al_2O_3	15.59	15.59	15.34	15.01	14.38
Fe_2O_3	2.05	1.92	2.76	2.42	6.33
MnO	0.02	0.04	< 0.01	< 0.01	0.01
MgO	0.69	0.69	1.42	0.86	2.56
CaO	2.50	3.35	0.57	0.89	0.25
Na ₂ O	4.11	3.59	2.66	4.74	1.05
K_2O	3.70	3.63	2.06	1.25	0.04
P_2O_5	0.08	0.10	0.09	0.06	0.07
LOI	0.90	3.10	1.60	1.40	1.40
Sum	99.80	99.19	97.97	98.54	94.88
Cr	75	<1.3	1.4	<1.3	1.4
Ba	891	901	376	327	8
Ni	<20	<20	<20	<20	<20
Sc	3	3	3	2	3
Mo	0.2	7.1	0.1	0.3	0.4
Cu	5.0	1.1	0.4	1.0	4.1
Pb	6.0	2.7	3.4	4.1	2.6
Zn	9	7	15	26	5
Ni	6.3	1.8	0.6	1.2	0.8
As	1.7	5.7	1.5	2.6	2.0
Cd	<0.1	<0.1	<0.1	<0.1	<0.1
Sb	0.2	0.9	0.6	0.6	0.3
Bi	0.1	0.5	<0.1	<0.1	< 0.1
Ag	<0.1	<0.1	<0.1	<0.1	<0.1
Au	<0.5	1.6	<0.5	<0.5	<0.5
Hg	*	*	0.03	*	< 0.01
11 G	0.3	0.1	<0.1	<0.1	<0.1
Se	<0.5	<0.5	<0.5	<0.5	<0.5
В	<100	1800	5900	4000	15300
Ве	3	4	4	3	5
	01.9	44.2	10.4	41.4	12.3
Cs	4./	4.5	2.2	0.0	0.1
Ga	10.1	15.8	20.9	15.5	24.0
	5.9	4.0	5.0	3./ 10.0	3.0
IND Dh	9.0	11.0	11.5	10.0	2.3
KU Sn	129.0	124.1	13.3	23.3	1.0
SII Sr	590.2	5	د 7 202	125.2	206.6
ы Та	J07.2 1 A	1 0	507.7 1 2	433.2 1 <i>C</i>	320.0 1 2
ra Th	1.4 17.0	1.0	1.3	1.0	1.2
111	17.9	19.0	20.3	12.9	1.8

Table 1 continued...

.

	KV15-13	KV15-16	KV15-18	KV15-19	KV15-09
	Granodiorite	Tur-breccia	Tur-breccia	Tur-breccia	Tourmalinite
U	6.4	7.6	2.9	1.6	2.1
V	32	30	32	25	36
Zr	127.3	154.7	157.5	121.4	96.0
Y	13.0	15.0	15.5	7.3	8.1
La	28.8	39.7	52.5	22.6	2.1
Ce	54.6	74.6	92.0	39.0	3.5
Pr	5.64	7.93	10.80	4.53	0.46
Nd	19.1	28.4	36.4	15.2	2.0
Sm	3.17	4.65	5.75	2.30	0.44
Eu	0.74	1.13	1.42	0.46	0.14
Gd	2.66	3.68	4.16	1.70	0.73
Tb	0.38	0.49	0.59	0.25	0.16
Dy	2.20	2.57	2.91	1.38	1.14
Но	0.46	0.54	0.53	0.28	0.30
Er	1.37	1.48	1.75	0.92	0.95
Tm	0.22	0.27	0.27	0.16	0.19
Yb	1.48	2.00	2.11	1.15	1.51
Lu	0.25	0.33	0.38	0.22	0.28
TOT/					
С	0.09	0.51	0.04	0.10	0.05
TOT/S	< 0.02	0.38	< 0.02	< 0.02	< 0.02



Figure 12: X-Y correlation diagrams of the bulk rock major element oxide concentration (%wt.) in the studied samples. Major element oxides and B (% wt.) are plotted against MgO. Green circle represents the host rock sample, blue rectangles the tourmaline breccias and red triangle the intensively tourmalinized vein sample

4.3.2 Trace elements and REE

Trace elements and REE's display a variable behavior, characterized by selective enrichments and depletions from the least altered samples towards the massive tourmalinite. The previously assigned groups are quite obvious regarding the trace elements and the REE's with Group 1 including the tourmaline breccias samples and Group 2, representing the massive quarz-tourmaline rock (tourmalinite).Large Ion Lithophile Elements (LILE) are among the trace elements which dsplay the most significant ranges in their concentration (Rb 1 - 129 ppm; Cs 0.1 - 4.7 ppm; Ba 8 - 891

ppm; Sr 612.5 - 326.6 ppm). High Field Strength Elements (HFSE) display much more limited ranges (Zr 96.0 – 157.5 ppm; Nb 2.3 – 11.6 ppm; Ta 1.2 – 1.8 ppm; Y 7.3 -15.5 ppm; Hf 3.0 – 5.0 ppm; Th 7.8 – 20.5 ppm;U 1.6 – 7.6 ppm).

The REE patterns of tur-breccias are characterized by a pronounced concave upward chondrite-normalized profile, with a slight negative Eu anomaly. In contrast tourmalinite displays a smoothed U-shaped pattern with descending LREE's, negative Eu anomaly and positive slopes in the HREE (Fig. 13). Tourmalinite also shows a depletion of an order of magnitude in REE compared to breccias, except the HREE, which are almost ideal. This fractionation is better constrained considering the (La/Yb)_N and Σ REE values between the two groups. Breccias has an average (La/Yb)_N =14.13, where this ratio is significantly lower in Group 2 with (La/Yb)_N = 0.94. Likewise, tourmalinite has lower Σ REE than breccias with values 13.9 and 147.64 respectively.

Clear distinction between the groups is also present regarding the trace element compositions where Cs, Rb, Ba, Nb, that are also significantly depleted in tourmalinite. Zr, Y, Hf, Th and U are also slightly depleted in contrast with tur-breccias and the host rock (Fig. 14). Transition metal group elements show a variable behavior with increasing Ga, V, Co, Cu and decreasing Zn Ni from the tur-breccias to the tourmalinite, where the KV15-16 tur-breccia shows elevated Mo, As, Bi, Sb and Au content.



Figure 13: Chondrite normalized (Boynton 1984) REE element spidergram for host rock, tourmaline breccias and tourmaline veins compositions.



Spider plot - Bulk Continental Crust (Taylor and McLennan 1995)

Figure 14: Bulk Continental Crust normalized trace element spidergram (Taylor and McLennan, 1995) for host rock, tourmaline breccias and tourmaline veins compositions.

4.3.3 Isocon analysis

Changes in major, trace elements and REE concentrations between the studied samples have been quantified, using the isocon method (Grant 1986). Three samples were used, two end-members from the unaltered (KV15-13) to pervasively altered (KV15-9), with a third sample, comprising an average tourmaline breccias (average breccias) composition, between the two end-members. Isocons were calculated for three pairs of the selected samples in order to investigate elemental mobility in the continuum of the tourmalinization process.

Pair 1 KV15-13/average breccias

Pair 1 consists of the fresh granodiorite sample (KV15-13) and the average tourmaline breccias sample (Fig. 15). Major element mobility is characterized by a significant gain in B, slight gains in Fe₂O₃, MgO, MnO, TiO₂, and loses in K₂O,Na₂O,CaO,SiO₂,Al₂O₃ and Cr₂O₃. Trace element concentrations are characterized by significant enrichment in Mo, Bi, Au, Sb, Cd, Zn, As, slight enrichment in REE, Sn, Be, Zr, Ga, depletion in V, Sc, Sr, Rb, U, Th, Pb, Co, Cs, Tl, Cu, where Ho and Y remain immobile.

Pair 2 average breccias/KV15-9

Pair 2 consists of the intermediate composition of the average breccias and the pervasively altered sample KV15-9 (Fig. 16). Major elements display significant gains in B, Fe₂O₃ and MgO, constant contents of Cr₂O₃, SiO₂, Al₂O₃, P₂O₅, and minor depletion in TiO₂ and significant loss of Na₂O, MnO, CaO and K₂O. Trace elements display a quite diverse behavior with gains in Co, Cu, Ga, V, Zn, and Sc and slight to strong depletion in the rest of the elements remain immobile.

Pair 3 KV15-13/KV15-9

Pair 3 represents the two end-member compositions of the fresh (KV15-13) and pervasively altered (KV15-9) samples (Fig. 17). B is characterized by 2 orders of magnitude enrichment, followed by moderate gains in Fe₂O₃. MgO, SiO₂, Al₂O₃ and P₂O₅ remain quite constant on the isocon line, whereas TiO₂, MnO, Na₂O, Cr₂O₃, CaO and K₂O seem to be leached from the protolith. Trace elements are characterized by gains in Mo, Ga, Be, Sb, As, V, constant Ag, Se, Sn and slight to moderate depletion in Th, Cu, Zr, Zn and LREE to MREE. Strong depletion is observed in Cs, Rb and Ba.



Figure 15: Relative gain-loses and isocon diagrams for major and trace elements in Pair 1.



Figure 16: Relative gain-loses and isocon diagrams for major and trace elements in Pair 2.



Figure 17: Relative gain-loses and isocon diagrams for major and trace elements in Pair 3.

4.4 Raman Spectroscopy

Identification of tourmaline from the studied thin sections was achieved by comparing the acquired spectrums with published Raman Spectrums for tourmalines from the RRUFF database (reference sample R110133). Acquired spectrums from matrix tourmalines of the sample KV15-19 (tu-breccia) were in the range of 100-1300 cm⁻¹, with five major peaks appearing in 147.9-168.7, 359-364, 529-533.4, 698.4-701.4 and 950-1125 cm⁻¹ corresponding to the Mg-O-Fe bond stretching, Al-O stretching, O²⁻ vibrations in Si-O rings, B-O stretching & B-O-Al bend, and Si-O stretching respectively (Gasharova et al., 1997). Different intensities in the spectrums could be attributed to impurities, due to the complex tourmaline quartz intergrowths and the small size of tourmaline. Representative Raman spectrums of the studied tourmalines are demonstrated in Fig.18.



Figure 18: Representative Raman spectrums of the studied tourmalines.

4.5 Mineral chemistry

4.5.1 Major elements

The analyzed tourmalines from KV15-9 (tourmalinite) and KV15-18 (tur-breccia) samples (Table 3) show a narrow compositional range in their major element composition (in wt. %) SiO₂ 34.65-37.31, TiO₂ 0.05-1.21, Al₂O₃ 26.41-31.54, FeO 7.76-12.32, MgO 4.64-7.46, CaO 0.14-1.88, Na2O 1.77-2.64 and K₂O 0-0.71 MnO 0-0.22, Cr_2O_3 0-0.05.

Processing of the microprobe data in order to calculate the atomic proportions and the site allocations in the studied tournalines was performed using the WinTcac software (Yavuz et al., 2014). WinTcac offers quite enough options for tournaline recalculation based on the normalizations schemes included in the review of Henry et al. (2011 and references therein). The software also calculates light elements which cannot be measured by microprobe such as B, Li and H. B₂O₃ is automatically calculated by the assumption that B= 3 a.p.f.u. (atoms per formula unit). Li can be calculated by the equation: (Li (a.p.f.u.) = 15 - (Y site cations + Z site cations + tetrahedral site cations (a.p.f.u.). As Z and T sites are fully occupied, Li was estimated by subtracting the sum of the Y-site cations from 3 (Li=3- Σ Y), assuming no vacancies in the octahedral sites (Henry and Dutrow, 1996).

For the classification of the analyzed tourmalines we followed the procedure proposed by Henry et al. (2011). The 15 cations (T+Z+Y-side) normalization scheme of Henry and Duthrow (1996), which was followed in this study, assumes that there are no vacancies in the Y, Z and T sites, a valid assumption based on a majority of crystal structure refinement data. This is the recommended normalization approach for tourmaline with low Li contents and minor B in the tetrahedral site. Studied tourmalines contain Mg> 0.02 a.p.f.u. and coexist with sericite, so they match the criteria of Henry and Duthrow (1996), who proposed that tourmaline containing even a moderate amount of Mg (>0.02 a.p.f.u.) and coexists with minerals such as biotite, muscovite and staurolite typically have minor-to-insignificant amounts of Li due to the preferential partitioning of Li into these coexisting minerals. B was assumed to be stoichiometric (3 a.p.f.u), whereas H₂O and Li content was calculated with the OH +F +Cl =4 normalization in the WinTcac routine.



Figure 19: Representative FE-SEM Backscattered electron images of the KV15-18 and KV15-9 samples: a) Massive tourmaline quartz intergrowth alongside some K-feldspar relics. Note that the cracks in the image divide the mesocataclasite from ultracataclasite in respect to grain size reduction (KV15-18), b) Tourmaline vein within the cataclasite (KV15-9), c) Void filled by matrix tourmaline (KV15-9), d) Tourmaline healing cracks along the margins of quartz. Note the small size of tourmaline (1-2 μ m and the distinct zoning)(KV15-9), e) Micro-crystalline zoned tourmalines displaying a growth zoning from a Ca-rich core to a Ca-poor rim(KV15-18), f) Ultra-fine grained unzoned Ca-rich tourmaline(KV15-18).

Table 3: Representative EPMA major element concentrations in the studied tournalines. Analyses 56-64 are from the KV15-9 sample and 65-74 from the KV15-18. Atomic proportions and site allocations were calculated on the basis of T+Y+Z=15 cations normalization (Henry and Duthrow, 1996).

	56rim	57core	58core	59core	60rim	61rim	62core	63core	64rim	65rim	66core	67rim	68rim	69rim	70rim	71core	72core	73core	74core
Wt.%																			
SiO ₂	35.78	34.91	35.05	35.15	35.67	35.47	35.28	34.81	35.22	35.89	35.03	35.70	35.68	35.51	35.73	34.65	34.76	36.50	35.30
TiO_2	0.09	0.33	0.38	0.25	0.29	0.70	0.47	0.62	0.58	0.21	0.45	0.06	0.15	0.14	0.11	0.20	0.07	1.00	0.21
Al_2O_3	30.11	26.94	27.34	27.65	30.78	29.21	27.54	27.48	29.53	30.12	27.39	30.59	29.96	30.54	30.15	27.29	27.16	27.59	30.00
Cr_2O_3	0.00	0.00	0.00	0.00	0.04	0.02	0.00	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.04	0.00
FeO	9.14	12.21	11.90	11.53	11.41	11.45	11.72	12.32	9.91	8.53	11.71	8.61	8.53	8.49	8.62	11.82	11.43	10.01	8.94
MnO	0.06	0.14	0.19	0.11	0.04	0.00	0.17	0.18	0.01	0.02	0.12	0.06	0.05	0.05	0.03	0.14	0.20	0.05	0.01
MgO	6.73	7.21	6.67	6.54	4.64	5.30	7.13	6.73	6.29	7.26	6.69	7.24	7.16	7.28	7.20	7.05	7.10	6.75	6.81
CaO	0.57	1.65	1.53	1.39	0.22	0.25	1.38	1.40	0.39	0.26	1.52	0.14	0.23	0.15	0.21	1.79	1.66	0.79	0.27
Na_2O	2.10	1.98	2.04	1.98	2.16	2.46	2.18	2.02	2.45	2.43	1.92	2.30	2.37	2.32	2.25	2.03	1.93	2.34	2.39
K ₂ O	0.00	0.06	0.02	0.03	0.04	0.05	0.04	0.05	0.01	0.02	0.06	0.02	0.03	0.04	0.02	0.04	0.07	0.71	0.03
Total	84.58	85.43	85.12	84.63	85.29	84.89	85.91	85.64	84.42	84.74	84.89	84.72	84.17	84.52	84.31	85.03	84.37	85.78	83.96
							I	Formulae o	n the basis	of T+Z+Y	'= 15 catio	ns							
В	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
T-site																			
Si	6.027	5.951	6.001	6.032	6.033	6.052	5.969	5.922	5.993	6.014	6.004	5.961	6.016	5.945	6.001	5.940	5.984	6.202	5.986
Al	0.000	0.031	0.000	0.000	0.000	0.000	0.02	0.063	0.007	0.000	0.000	0.027	0.000	0.043	0.000	0.049	0.004	0.000	0.009
<u>Z-site</u>																			
Al	5.977	5.381	5.517	5.592	6.000	5.874	5.472	5.447	5.915	5.948	5.533	5.993	5.954	5.983	5.968	5.465	5.507	5.525	5.987
Mg	0.023	0.619	0.483	0.408	0.000	0.124	0.528	0.549	0.082	0.052	0.467	0.007	0.046	0.017	0.032	0.532	0.493	0.470	0.013
Cr	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.004	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.005	0.000
<u>Y-site</u>																			
Al	0.000	0.000	0.000	0.000	0.135	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.011	0.042	0.049	0.032	0.037	0.089	0.06	0.079	0.074	0.027	0.058	0.007	0.019	0.017	0.013	0.025	0.008	0.128	0.026
Fe	1.287	1.741	1.704	1.655	1.614	1.634	1.658	1.753	1.410	1.195	1.678	1.202	1.203	1.189	1.211	1.695	1.646	1.422	1.268
Mg	1.667	1.214	1.219	1.265	1.17	1.224	1.127	1.158	1.514	1.762	1.242	1.795	1.754	1.8	1.771	1.27	1.329	1.24	1.708
Mn	0.008	0.020	0.027	0.016	0.005	0.000	0.024	0.026	0.002	0.002	0.017	0.009	0.007	0.007	0.004	0.021	0.029	0.008	0.002
Li	0.024	0.000	0.000	0.018	0.069	0.096	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.404	0.000
ΣY X-site	2.997	3.017	2.999	2.986	3.036	3.044	3.012	3.015	3.006	2.986	2.996	3.013	2.984	3.012	2.999	3.011	3.012	3.202	3.005
Ca	0.103	0.301	0.281	0.255	0.04	0.045	0.25	0.255	0.072	0.046	0.279	0.025	0.042	0.027	0.037	0.329	0.306	0.143	0.049
Na	0.686	0.654	0.677	0.659	0.708	0.814	0.715	0.666	0.808	0.789	0.638	0.745	0.775	0.753	0.733	0.675	0.644	0.771	0.786
K	0.001	0.013	0.005	0.005	0.007	0.010	0.010	0.011	0.003	0.005	0.013	0.004	0.006	0.008	0.005	0.008	0.015	0.155	0.006
X _{vac}	0.21	0.031	0.037	0.081	0.244	0.131	0.025	0.067	0.117	0.159	0.07	0.226	0.177	0.212	0.225	0.000	0.035	0.000	0.158
, ac																			V-site
OH	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000	3.000
W-site																			
0	0.280	0.900	0.040	0.164	0.330	0.268	0.941	0.857	0.099	0.196	0.080	0.122	0.220	0.065	0.228	0.827	0.993	0.455	0.122
OH	0.720	0.100	0.960	0.836	0.670	0.732	0.059	0.143	0.901	0.804	0.920	0.878	0.780	0.935	0.772	0.173	0.007	0.545	0.878
#Mg	0.567	0.513	0.500	0.503	0.420	0.452	0.520	0.493	0.531	0.603	0.505	0.600	0.599	0.604	0.598	0.515	0.525	0.546	0.576
#Ca	0.130	0.315	0.293	0.279	0.054	0.053	0.259	0.277	0.082	0.055	0.304	0.032	0.052	0.034	0.048	0.327	0.322	0.157	0.060

Primary tourmaline group was determined by plotting the data on the Ca -Xvac-Na+ (K) ternary diagram (Fig. 20) of Henry et al. (2011), where all the tourmalines belong to the Alkali Group as Na is the dominant cation on the X-site. It should be mentioned that in this diagram two different populations can be distinguished on the basis of different Ca content: a Ca-rich group (Ca> 0.20 a.p.f.u.) and a Ca poor. This distinction coupled with petrographical observations supports the presence of two diverse tourmaline groups. The Ca-rich group consists of the core (Group I) of coarser crystals (>50 μ m), and the Ca poor group includes the rims of the later and the unzoned tourmalines in the matrix of the rocks (Group I).



Figure 20: (Na + K) - Ca - X-Site Vacancy ternary diagram for the classification in the primary Tournaline Group (Henry et al., 2011). All tournalines plot in the Alkali group field with two distinct populations in regard to Ca content. Symbols are assigned in respect to the textural discrimination of each tournaline group: circles represent fine-grained to microcrystalline tournalines, green for core vs blue for rims and red squares for cryptocrystalline homogenous tournalines in the matrix.

After the primary group definition, tourmalines have to been classified in the general tourmaline species in respect to the W site occupancy. OH^- and O^{-2} are in the absence

of F^{-1} the dominant anions in this site characterizing the samples as hydroxyl- and oxy- species respectively. V-site is also assumed to be occupied by OH⁻, which are the most common situation for the majority of tournalines except buergerite and some olenitic tournalines (Ertl et al., 2005; Cempírek et al., 2006; Bosi and Lucchesi, 2007). The major trivalent cation in the V site is Al^{3+,} as Cr amounts are negligible and V was under detection limit of the microprobe.

Following the later site allocations tourmalines were subdivided to the dominant subgroups (Subgroup 1 & Subgroup 3; Fig.21) of the alkali group, concerning that Y-site is mainly occupied by Fe^{2+} and Mg^{2+} .



Figure 21: Determination of subgroups 1-4 for alkali- and calcic-group tournalines using parameters $YZR^{2+}/(YZR^{2+} + 2Li^{1+})$ vs. $Ca^{2+}/(Ca^{2+} + Na^{1+} + K^{1+})$ together with the dominant valence anion(s) in the W site i.e., $(OH^{1-} + F^{1-})$ vs. O^{2-} . YZR^{2+} represents the total number of divalent cations in the Y and Z site.

The determination of the subgroups, allows us to proceed to the final classification using the Y-site Li - Mg - Fe ternary diagrams for individual subgroups and determine the studied tourmaline species as schorl, dravite with two analyses classified as oxyschorl (Fig. 22), because OH is the dominant anion in the W-site.



Figure 22: Ternary diagrams for plotting and classifying alkali-group tourmaline species (with Al^{3+} dominance at the Z site and OH^{1-} dominance at the V site (Henry et al., 2011). In the diagram the W site dominant anion is OH.

Pronounced differences in their chemical compositions are present regarding the major element contents (in a.p.f.u) in the structural formula of the assigned tourmaline groups. Group 1 tourmalines are Ca-richer (0.34-0.18 a.p.f.u) in comparison with Group 2 (0.14-0.02 a.p.f.u). The opposite is observed in Na, where Group 1 has the lower content (0.58-0.74 a.p.f.u), as the other group present relatively higher Na content (0.62-0.85 a.p.f.u). Group 2 shows also larger vacancies in the X-site (0.06-0.28 vacancy p.f.u), in contrast with Group 1 (0-0.09 p.f.u). Iron content decreases from Group 1(1.78-1.38 a.p.f.u.) to Group 2 (1.66-1.05 a.p.f.u), which is also the case

for Li (calculated). Magnesium content show a strong overlap between Group 1 (1.88-1.57 a.p.f.u) and Group 2 (1.83-1.16 a.p.f.u) but presents a slight negative correlation among them. Aluminum increases from Group 1 (5.26-5.77 a.p.f.u) to Group 2 (5.31-6.01 a.p.f.u). Overlaps are also noticed in the Mg/(Mg+ Fe) and Na(Na +Ca) ratios (Figs 23, 24). Group 1 has a Mg/(Mg+ Fe) range between 0.48-0.55, in contrast to Group 2 (0.42-0.61). Relations become clearer concerning the Na/ (Na+ Ca) ratio, ranging from 0.63-0.79 in Group 1, and from 0.84-0.97 and from 0.79-0.97 in Group



Figure 23: Variation diagrams of selected major elements (in a.p.f.u.) plotted against Na/(Na+ Ca) ratio for the assigned tourmaline groups.



Figure 24: Variation diagrams of selected major elements (in a.p.f.u) plotted against Mg/(Mg+Fe) ratio for the assigned tourmaline groups.

4.5.2 Trace elements and REE

Trace elements and REE composition of the studied tournalines were determined using LA-ICP-MS. Due to the small size of tournaline crystals, relatively to the beam diameter, it was impossible to acquire core-rim analyses. Instead we analyzed finegrained tournaline aggregates, after selecting the most homogenous and densely tournalinized surfaces, in order to avoid contamination from other mineral phases.

Group 1 is characterized by low REE content ($\Sigma REE = 49.83$), especially in LREE, positive Pr, negative Nd and strong positive Eu anomaly (Eu/Eu*=1.72). Group 1 also shows stronger HREE fractionation, compared to Group 2, as indicated by a stronger positive slope from Er to Lu. Group 2 is enriched in REE ($\Sigma REE = 322.96$) relatively to Group 1, forming a subparallel pattern which is characterized by a gently negative slope in LREE, slight positive Eu anomaly (Eu/Eu*=1.72), and a generally positive slope from MREE to HRRE. Normalized La/Yb ratio is also a discriminator among the two groups with (La/Yb)_N = 0.49 and (La/Yb)_N = 0.61 for core and matrix tourmalines respectively (Fig. 25).

Trace elements concentrations are highly variable, with the observed variation comprising several orders of magnitude. Li concentration spans from 76.59 -142.99 ppm, verifying the assumption that Li content in the studied tourmalines is negligible. Transition metals Co, Ni, Zn, Cr show relatively good small variance and display two diverse populations, with absence of any correlation when plotted against Σ REE showing a clear enrichment in Group 2 tourmalines.

Element	KV19-T15	KV19-T9	KV19-T5	KV19-T6	KV19-T4	KV19-T13	KV19-T2	KV19-T14	KV19-T8	KV19-T1	KV16-T7	KV19-T12	KV19-T10	KV19-T3	KV19-T11
Li7	76.59	122.95	132.19	124.41	192.49	113.55	77.74	132.81	100.86	<68.72	<111.48	<94.23	89.74	100.21	83.06
Sc45	506.82	1152.05	773.23	1369.22	759.29	671.12	572.41	1414.37	911	1762.35	2471.88	422.39	1158.12	1425.4	1214.6
V51	3991.02	4807.9	4311.29	4822.87	4367.62	3836.89	3697.97	4808.81	4576.33	4840.84	5303.22	2848.21	3863.76	4004.15	4053.03
Cr53	156.68	227.2	162.67	280.23	179.65	193.79	158.53	169.47	195.29	155.27	203.86	<72.60	113.48	187.61	146.17
Co59	179.01	147.88	155.76	142.32	155.33	117.08	131.42	120.72	130.78	144.23	138.14	96.97	110.8	107.16	98.27
Ni60	156.19	144.46	173.13	142.01	152.7	149.71	182.11	295.39	<96.98	<90.91	<145.74	<123.58	116.86	188.99	128.45
Zn66	688.15	567.4	652.92	629.79	612.24	528.14	546.44	647.79	543.78	433.52	461.43	391.11	533.39	658.27	430.98
Ga69	799.35	912.54	838.56	944.88	875.2	795.69	785.41	999.17	943.79	935.08	1035.62	596.42	801.25	948.56	868.74
Rb85	12.11	<8.01	7.5	8.94	<7.18	37.53	35.88	69.19	<8.12	44.83	<12.35	57.41	61.36	258.12	112.7
Sr88	2953.37	3414.32	3105.91	3197.53	3058.58	3273.43	2896.49	3428.85	3824.73	3083.72	3420.91	2532.02	2885.5	2842.38	3120.72
Y89	97.65	377.07	335.35	323.87	327.23	45.29	40.26	438.32	41.81	177.8	207.66	25.17	234.51	257.38	49.48
Zr90	<7.29	601.05	14.27	26.24	7.7	<7.40	<7.75	31.79	<8.53	<7.68	<12.70	18.87	12.64	<7.54	<8.02
Nb93	11.84	23.17	22.44	31.73	24.42	7.56	4.46	28.07	3.8	11.95	15.34	2.61	15.05	20.62	5.08
Cs133	<1.67	<1.89	<1.60	<1.52	<1.65	<1.82	<2.08	<3.16	<1.94	2.01	<3.17	<2.39	2.56	2.39	<2.02
Ba137	292.29	233.96	286.55	298.34	235.54	512.08	566.1	1441.62	143.18	646.36	160.86	795.1	487.39	3091.84	1706.42
La139	25.93	45.34	54.63	58.94	53.63	7.88	3.86	71.5	5.62	28.13	44.02	2.99	40.6	40.55	6.38
Ce140	44.22	147.74	119.23	148.8	120	12.08	6.54	163.02	10.35	62.14	90.21	7	84.49	81.24	12.91
Pr141	5.78	13.45	15.1	17.21	14.6	2.19	0.82	20.06	1.7	8.26	10.58	0.99	10.46	11.9	2.01
Nd146	21.22	58.57	64.72	70.27	64.88	5.9	4.86	83.99	5.62	36.09	49.61	3.04	46.84	45.99	4.12
Sm147	6.58	18.06	16.93	20.03	20.09	1.75	<2.11	23.93	2.9	12.24	12.66	2	12.87	19.21	2.38
Eu153	1.36	6.06	6.28	5.76	4.94	1.39	1.42	7.91	1.84	4.17	5.51	<0.86	5.24	6.61	1.71
Gd157	8.3	27.86	22.17	25.03	20.66	3.34	<2.32	28.66	<3.30	11.56	13.66	3.58	12.37	21.34	2.65
Tb159	1.75	6.02	5.06	5.54	5.09	0.74	0.50	7.18	0.8	3.31	4.38	0.63	3.84	5.64	0.7
Dy163	15.29	54.12	42.89	55.79	44.01	7.28	6.81	64.16	6.81	30.59	31.74	4.2	35.34	38.9	4.58
Ho165	2.57	12.45	10.2	11.21	9.44	1.32	1.12	14.49	1.39	7.69	5.6	0.68	7.19	7.91	1.41
Er166	11.3	41.11	31.76	38.73	35.87	5.51	4.03	43.43	5.03	20.68	22.08	2.28	25.05	26.83	3.89
Tm169	2.37	6.39	6.23	7.12	6.9	1.21	0.74	8.93	0.98	4.62	4.9	0.36	5.41	5.4	1.12
Yb172	15.9	56.43	54.4	61.57	50.62	10.35	6.19	81.19	7.28	35.59	36.75	4.28	41.94	41.84	7.87
Lu175	2.17	9.88	8.89	9.99	8.32	2.05	1.09	13	1.94	6.37	7.75	1.19	5.17	7.29	2.41
Hf178	0.49	14.43	1.13	1.86	1.47	<0.55	0.139	2.08	<0.61	0.72	0.85	1.01	0.74	0.83	<0.41
Ta181	0.48	0.96	0.99	1.33	1.15	<0.26	0.167	0.93	1.05	0.54	0.37	<0.48	0.84	0.91	0.184
Pb208	39.86	90.74	75.35	91.25	84.68	30.7	26.73	105.94	128.95	47.82	57.67	23.66	78.44	75.83	31.41
Th232	21.81	165.14	62.98	428.54	69.69	20.64	15.66	87.03	18.7	676.42	40.68	12.47	94.98	791.37	14.31
U238	3.76	25.79	8.08	614.39	11.51	0.96	0.72	13.97	0.81	128.51	3.51	1.32	48.14	154.26	0.67

Table 4: Representative LA-ICP-MS trace element and REE compositions (ppm) of studied tourmalines.



Figure 25: Chondrite normalized REE patterns (normalization after Boynton, 1984) for tourmalines from this study.

5. Discussion

5.1 Characterization of the tourmaline-rich rocks

The term tourmalinite is used for rocks that contain modal tourmaline in a percentage equal of higher than 15% vol. of the total modus, in general association with exhalative ore deposits in rift settings (Slack, 1984, Plimer, 1987). This kind of rocks are commonly found along with sediment-hosted massive sulfide deposits in Proterozoic and Palaeozoic sedimentary sequences, such as Broken Hill areas (Australia), and in Namaqualand (South Africa) and were interpreted as a result of submarine exhalations of basinal brines in rift environments (Slack, 1996; Slack et al., 1984; Plimer, 1987). As in most of the studied rocks in Kavala area tourmaline modal abundance exceeds 15 % vol. as indicated by the results of semi-quantitative analysis in XRD patterns and petrography, the tourmaline-rich rock under study can be named tourmalinite. However, field relations suggest that, most of this rock follows NW-SE up to NNW-SSE directed high angle towards SE or WSW fractures of the host rock the circulation of B-rich fluids had a strong structural control. Hence, previous foliation planes and mainly later developed almost vertical fractures have served as a conduit for fluid infiltration. The overall geometry of the conduits, combined with different fluid/rock interaction intensity, seems to be a dominant control on the tourmaline abundance in the studied rocks. In low fluid/rock ratio regimes, formation of tourmaline breccias is favored, combined with elevated partitioning of host rock fragments. In contrast massive tournaline veins and injections are indicative of high fluid/rock ratio, with scarce host rock material embedded in a micro- to cryptocrystalline tournaline matrix, pinpointing a direct precipitation of the latter from a Brich solution. Textural features such as the presence of angular host rock fragments, tourmaline injections in the host rocks which form a complex vein network, jig-saw puzzle textures and the overall perpendicular development of the system to the foliation of the pluton, indicate a fluid assisted brecciation in a brittle deformation regime Additionally, geochemical data, concerning tourmaline major element composition, preclude a formation in metamorphic (stratiform) tournalinite associated settings. Regarding these, the studied tourmaline rich rocks could be characterized as tourmaline breccias and massive replacement tourmalinite veins.

5.2 Tourmaline chemistry as origin indicator of the tourmaline-rich rocks

Tourmaline composition, in respect to major and trace element concentrations, is a powerful tool, in order to decipher the geological environment and the origin of the medium, from which tourmaline crystallized (Henry and Guidotti, 1985; Dutrow and Henry, 2000; van Hinsberg et al., 2011). A first good approach on the origin of the tourmaline-rich rocks within the Symolon-Kavala pluton can be obtained by plotting the studied tourmaline compositions in the ternary Al-Fe-Mg diagram (Fig. 27) of Henry and Guidotti (1985), where tourmaline composition is correlated with different types of possible host lithologies.

All the studied tourmalines, plot in the field 6 of the Al-Fe-Mg ternary, which corresponds in tourmaline compositions from ferric-iron rich quartz-tourmaline rocks, calc-silicate rocks and metapelites. The plotted values show also a strong overlap, so any distinction of the previously assigned groups is not feasible. In addition, studied tourmalines were plotted, against published compositions of hydrothermal quartztourmaline breccias (Demirel et al., 2009), tourmalines recording the magmatichydrothermal transition (Yang et al., 2015), tourmalinites (Yucel-Qzturk et al., 2015) and selected tourmaline occurrences in Greece (Hezel et al., 2011; Michaillidis et al., 1994). The outcome of this comparison is a clear distinction of tourmalines from this study from tourmalines from metamorphic settings associated with stratiform tourmalinites, as well from early formed magmatic tourmalines. Unfortunately, no distinction can be inferred with tournalines from magmatic-hydrothermal transitional settings, as they display a broad compositional spectrum, (fields 2, 3, 6 of the Al-Fe-Mg ternary). According to Hawthorne et al. (1999) tournaline compositions falling below the Schorl (-Buergerite) - Dravite joint are commonly Al-deficient and either Fe or Ca-Mg rich, which is observed in both tourmaline generations in the tourmalinerich rocks of Kavala.



Figure 27: Ternary Al–Fe–Mg and Ca–Fe–Mg diagram showing compositions of tourmaline from the studied tourmaline veins and breccias within the Symvolon-Kavala pluton. Shaded fields represent tourmaline compositions from the published records for comparison reasons. The regions define the compositions of tourmaline from different rock types (Henry and Guidotti 1985). 1 = Li-rich granitoids and associated pegmatites and aplites; 2 = Li-poor granitoids and associated pegmatites and aplites; 3 = Fe^{3+} -rich quartz–tourmaline rocks (hydrothermally altered granites); 4 = metapelites and metapsammites coexisting with an Al-saturating phase; 5 = metapelites and metapsammites not coexisting with an Al-saturating phase; 6 = Fe^{3+} rich quartz–tourmaline rocks, calc silicate rocks, and metapelites; 7 = low Ca metaultramafics and Cr, V-rich metasediments; 8 = metacarbonates and metapyroxenites.

Pirajno and Smithies (1992) showed that Fe/Mg ratio in tourmaline can be used as a proximity index to a granitic source, as it tends to decrease with increasing distance from it. Studied tourmalines Fe/(Fe+ Mg) ratio vs MgO indicate that both Group 1 and Group 2 formed in an intermediate to distal granitoid related magmatic-hydrothermal system, pinpointing an environment located in the apices of the host granitoid(Fig. 28).



Figure 28 : Proximity index of tournaline to granitic source using the tournaline FeO/(FeO + MgO) vs MgO (Pirajno and Smithies, 1992).

Another quite interesting outcome from this approach is that the Group 1 tournalines, plot only in the "distal field" of the proximity index, whereas the rims and the matrix tournaline plot following a linear trend from the "proximal-intermediate to distal field", indicating that the observed tournaline compositions have been likely developed within a two-stage magmatic-hydrothermal process, rather than a single hydrothermal pulse.

This hypothesis is further examined by considering the major element core-rim zoning patterns and the possible cation substitution mechanisms, which govern the compositional variations among the different groups (Fig. 29). Ca-rich cores and Capoor rims of zoned crystals (Group 1 and Group 2), display an irregular contact and are characterized by the absence of any systematic difference in major elements concentrations between core and rim. Furthermore, the observed trends for Group1 suggest that FeAl₋₁ is the dominant substitution mechanism controlling the tourmaline composition, and FeMg₋₁ exchange vector controls the compositions of Group 2. The proposed diverse substitution mechanisms, among the tourmaline groups coupled with other observed geochemical features such as and Al deficiency, Mg content lower or equal to 2 a.p.f.u. are also described from other authors (Bakhseev et al., 2011 and references therein; Bakhseev et al., 2015) for tourmalines from hydrothermal settings, enriched in Fe³⁺. Due to the absence of Fe³⁺ estimation in tourmalines of this study, the presence of significant amounts of Fe³⁺ in Group 1, can only be inferred by the homovalent FeAl₋₁ substitution dominant trend, and the Al³⁺ content which is lower in Group 1, in contrast with later generations.



Figure 29: Fe-Mg correlation diagrams for different tourmaline groups. Vectors indicate the dominant cation substitution mechanism.

These differences could lead to the conclusion that Group 2 tourmaline is an overgrowth, and the Group 1 cores may represent a previously formed tourmaline, but it's yet unclear if Group 1 has a magmatic origin or it represents an older

hydrothermal pulse, before the episode which is responsible for the contemptuous formation of the Ca-poor rims and matrix tourmalines, as indicated by the similarities in mineral chemistry in Group 2.

5.3 REE composition of tourmaline as a recorder of magmatichydrothermal evolution

Concerning the above interpretation of tourmaline major element chemistry, two different models could be proposed for the formation of the observed compositions.

Model 1 suggests that the detrital cores of Group 1 have crystallized from magma and Group 2 represent a later hydrothermal episode. In contrast Model 2 implies that precipitation from hydrothermal fluids is responsible for the formation of both groups, and the observed textural and compositional differences developed due to a sharp change in the composition or the physicochemical conditions of the fluid. For the evaluation of the above scenarios, assessment of LA-ICP-MS REE and trace element composition is necessary, as tourmaline obtains the geochemical signature of the medium from which it crystallizes (e.g., Henry and Guidotti, 1985; Jolliff and Papike, 1987; Dutrow and Henry, 2000; van Hinsberg et al., 2011). Of particular interest is its potential to record the trace-element signature of the medium (e.g., Neiva, 1974; Jolliff and Papike, 1987; Jiang et al., 2002; 2004; Galbraith et al., 2009; Novák et al., 2011; Yavuz et al., 2011; Marks et al., 2013).

5.3.1 Model 1 – Magmatic core + Hydrothermal rims and matrix

Group 1 tourmalines are characterized by low REE content, especially in LREE, positive Eu anomaly and strong HREE fractionation, as indicated by a stronger positive slope from Er to Lu. In contrast REE pattern of the host granodiorite displays higher LREE content lower HRRE's, and slight negative to absent Eu anomaly (Fig. 30). Supposing a magmatic origin for Group 1 the positive Eu anomaly can be attributed to the preferential partitioning of Eu^{2+} over Eu^{3+} in tourmaline when the melt is dominated by Eu^{2+} (Van Hinsberg, 2011) or in late stage Eu^{2+} release due to feldspar replacement (Yang et al., 2015).

The observed enrichment in HREE relatively to the host rock can be attributed to early crystallization to magmatic tourmaline, predating the crystallization of common granitic accessories such as zircon, apatite and allanite, which control the REE budget in this kind of rocks.

A major concern in this approach, regards the enrichment of both groups in REE relatively to host rock. Yang et al. (2015) showed that early magmatic disseminated tourmalines and late magmatic nodular tourmalines in the Qitianling magmatic-hydrothermal system are generally depleted in REE in contrast with the host, but they are also displaying the positive Eu anomaly observed in our samples.



Spider plot – REE chondrite (Boynton 1984)

Figure 30: Chondrite normalized REE concentrations of Group 1 and 2 tourmalines, compared with the REE pattern of the host granodiorite. Interpretation of pattern morphology and observed anomalies provide insights for the discrimination of magmatic vs hydrothermal origin of tourmaline.

In addition, there are some other observed petrographical features and geochemical data precluding the magmatic origin of tourmaline in Kavala. Experimental data from Wolf and London (1997) suggest that tourmaline is stable as a liquidus phase only in moderately to strongly peraluminous melt compositions such as pegmatites, two-mica leucogranites, F-rich leucogranites, etc. at a moderate temperature of 750 °C (200 MPa_(H2O), fO_2e_{Ni-NiO} , and $a_{(H2O)} = 1$). Tourmaline was found to be unstable in

metaluminous melts regardless the B content, as there is not sufficient alumina for tourmaline stabilization. In contrast subsolidus hydrothermal tourmalines can form with lower boron contents and a wider range of granitic compositions (Weisbrod et al., 1986; Morgan and London, 1989). Previous work on the geochemistry of Kavala granitic rocks classifies the intrusion as I-type metaluminous to slightly peraluminous with ASI in the range of 0.94-1.04. These values are lower than the ASI 1.2, which is demonstrated by Wolf and London (1997) as the sill of tourmaline stability in this kind of melts. In addition, biotite is dominant in Kavala intrusive, which is a preventing factor for the presence of tourmaline, regarding the antepathetic relation of this phases proposed by Pesqueira et al. (2013). Our petrographic observations are consistent with previous workers (Kokkinakis, 1977, Neiva, 1996), as no tourmaline was present even in the most evolved fractions of the melt (e.g. aplites). Tournaline is restricted in the matrix of the breccias displaying a blue green pleochroism, which is quite far from the khaki-brown homogenous tourmalines of igneous origin (London and Manning, 1995). The later authors also, propose that the occurrence of quartztourmaline veins and tourmaline breccias within granitoids indicate rather a hydrothermal than a magmatic origin.

Regarding the above consideration and the inconsistent REE patterns of Group 1 tourmalines compared to the host rocks, the hypothesis of magmatic origin for these tourmalines is strongly doubted, although there are some common features with magmatic tourmalines.

5.3.2 Model 2 – Hydrothermal core + Hydrothermal rims and matrix

Both tourmaline groups display a concave upwards shaped REE pattern, with major differences including the smoother Eu anomaly and the REE enrichment in Group 2 (Fig. 30). Concave upward-shaped REE patterns in tourmaline have also been found in other hydrothermal tourmalines, such as the Houxianyu borate deposit in eastern Liaoling, China (Jiang et al., 1997); the Yunlong tin deposit in Yunnan, China (Jiang et al., 2004); the Martinamor Antiform in the Central Iberian zone, Salamanca, Spain (Pesquera et al., 2005); the Asarcik vein-type Pb–Zn–Cu \pm U deposit in NE Turkey (Yavuz et al., 2011); the pegmatitic and hydrothermal system in Schwarzwald, Germany (Marks et al., 2013). Most of these studies suggested that the shape of the

REE patterns of hydrothermal tourmalines reflects the REE patterns of the medium from which they precipitated.

Marks et al. (2013) presented two major differences in pegmatitic and hydrothermal tourmalines from Schwartzwald. Pegmatitic tourmalines have flat REE patterns and no Eu anomalies, whereas hydrothermal tourmalines display asymmetric concave-upward patterns with a strong HREE enrichment and positive Eu anomaly.

Furthermore, Möller et al. (1997) and Shibata et al. (2006) showed that plagioclase dissolution releases more HREE than LREE and Yavuz et al. (2011) found evidence for HREE fractionation between tourmaline and granitic host-rock due to hydrothermal mobilization of HREE during tourmaline formation, implying that plagioclase destruction is a major control in the REE budget in the hydrothermal fluid.

REE systematics of the studied tourmaline groups can be successfully correlated, with the above interpretation, as plagioclase dissolution is well established from the absence of plagioclase in the studied sections and seems to be responsible for the HREE enrichment and the positive Eu anomaly of Group 1. Enrichment of Group 2 in REE, can obviously be result of a renewed hydrothermal pulse as indicated by the elevated content of transition metals group elements, whereas a reasonable explanation for the reduction of Eu anomaly is the neocrystallization of albite in the matrix of the breccias.

Following these consideration, the hypothesis made in Model 2, seems to produce a much more robust scenario, for the formation of tourmaline in the studied breccias, within the frames of an evolving magmatic-hydrothermal system, where changes in fluid-rock interaction and cooling of the fluid are responsible for the observed compositions and textures in a similar situation as described by Cocedo et al. (2017) for hydrothermal tourmaline from the Panasqueira W-Sn-Cu deposit in Portugal.

5.4 Reconstruction of the Hydrothermal fluid composition using tourmaline chemistry – Estimation of formation conditions

Tourmaline chemistry and stability are strongly dependent on the chemistry of the fluid phase (Morgan and London 1987). Consequently, tourmaline can provide valuable insights in the composition and the properties of the coexisting fluids. Tourmaline stability is well constrained from the pH of the hydrothermal fluid,

matching the formation conditions in acidic to neutral fluids, but not in alkaline (Henry and Duthrow 1996), as the coordination of boron changes from triangular to tetrahedral with increasing pH.

X-site occupation in tourmaline can provide information about the composition of the fluids, especially for the Ca-Na contents, as there is a correlation in the partitioning of these elements in tourmaline and a coexisting fluid (Von Goerne et al., 2001, 2011). In tourmaline with intermediate Ca-Na contents, the Ca/(Ca + Na) ratio in the solution is proportional to the Ca/(Ca + Na) ratio of the associated tourmaline, and temperature independent (von Goerne et al., 2011). The Ca and Na concentrations in a fluid in equilibrium with tourmaline can be approximated using the equations:

 $Na_{fluid(mol/l)=}\,1.59$ x $^{\rm X}Na-1.33$ x $^{\rm X}Na^2\,(1),$ and

 $Ca_{fluid(mol/l)} = 0.64 \text{ x}^{X}Ca - 0.48 \text{ x}^{X}Ca_{2}(2).$

Appling those equations in the different tourmaline groups from the tourmaline veins and breccias from Symvolon - Kavala pluton, resulted in the following concentrations of Na and Ca in the hydrothermal fluid. Group 1 is quite distinct from the other as it is assumed that it is in equilibrium with a fluid with 0.47 mol/l Ca and 0.14 mol/l, where Group 2, precipitated from fluids carrying 0.45 mol/l Na plus 0.04 mol/l Ca

A reconstruction of the trace element concentration of the hydrothermal fluid, was attempted using the partition coefficient (Kd) equation (Table 5), combining the median values of the trace element contents of the studied tourmalines, with the available published tourmaline/fluid Kd values (van Hinsberg et al., 2017 and references therein).

Resulted fluid compositions, are quite similar for both groups in terms of trace element budget in the order of 0.1 to 10000 ppm (Fig. 31), with an expected enrichment in Group 2.

Element	Group 1	Group 2
Li	246.83	325.88
\mathbf{V}	21.48	26.92
Cr	1.67	1.89
Mn	723.88	727.68
Rb	87.22	123.40
Cs	6.36	7.53
Sr	449.68	447.54
Ba	10149.18	5348.71
Ti	126.90	135.80
Nb	14.92	75.08
Ta	0.18	0.63
Zr	5.91	14.92
La	5.23	42.17
Се	9.85	113.45
Sm	1.41	12.05
Lu	0.69	2.95
Y	6.91	53.53
Pb	3.04	7.77
Th	17.86	108.34
U	0.48	15.23

Table 5: Calculated trace element hydrothermal fluid concentrations combining LA-ICP-MS tourmaline trace element content and published Kd values, concentration in fluid is given by the equation $C^{i}_{Fluid} = C^{i}_{Tour}/K_{d}$; K_d from Van Hinsberg et al.(2017).



Figure 31: Trace element concentrations of reconstructed fluids for Group 1 and Group 2 tournalines based on LA-ICP-MS tournaline trace element contents.

The minor differences observed in the calculated fluid composition, could result in a scenario that both groups out came from the same hydrothermal fluid, affected by a rapid change in physicochemical conditions responsible for the different tourmaline compositions.

Formation temperature can't result from the zoned Group 1 and Group 2 tournalines, as the observed zoning is not the inter-sector zoning requited for the application of the single crystal tournaline geo-thermometer (van Hinsberg and Schumacher, 2007). Instead cooling of the hydrothermal fluid can be inferred as Na partitioning in tournaline, provides an excellent evidence of cooling of the fluids as it increases with temperature decrease (Von Goerne et al., 2001). Another evidence of super cooling of the hydrothermal fluid includes the elevated abundance and small size of Group 2 tournalines, suggesting high nucleation and low crystal growth rates.

Tourmaline K-content has been suggested as a pressure-indicator based on characteristically high K-contents in UHP tourmalines (*e.g.*, Shimizu and Ogasawara, 2013), thermodynamic considerations (van Hinsberg and Schumacher, 2007) and experimental studies (Berryman et al., 2014, 2015). However, this correlation between K-content and P is not always consistent (e.g., Marschall et al., 2009), as it also

depends on the exchanging mineral phases and bulk K-content (Berryman et al., 2015). Above discussed uncertainties and the qualitative results of this method, were regarded enough to avoid pressure estimation in this study, but decompression can be carefully suggested concerning the brittle features of the studied formations.

In addition, petrography and tourmaline chemistry, suggest a change in the redox conditions of the system. Pyrite precipitation along with Group 2 tourmaline and the change of dominant substitution mechanism from Fe/Al to Fe/Mg from Group 1 to Group 2 indicate a shift in O^{2-} fugacity, enough to diminish the availability of ferric iron in the system.

5.5 Chemical element mobility due to tourmalinization process

Overall characterization of chemical element mobility through the tourmalinization process could be approached by combining the results of petrography, mineral chemistry and whole rock geochemistry. Tourmalinization is geochemically characterized by enrichment in Al, Mg, Ca, Fe, Na, Li, B, H₂O and depletion in SiO₂ and CO₂ (Harlov and Austheim 2013 and references therein). In the case of Kavala tourmaline-rich rocks, concerning whole rock compositions, some divergences can be observed from the typical geochemical signature. Significant enrichment in B, Fe and Mg is present, verified by the positive correlations between them and isocon diagrams. In contrast Ca and Na show depletion in every stage of the process, additionally Si and Al remain constant or show slight depletions. Enrichment in H₂O can be inferred by the higher L.O.I. value of the tournalinized samples in contrast with the host rocks. The observed diversities can be explained, if tourmaline chemistry is concerned, and especially the influence of host rock composition in tourmaline, which may be significant (van Hinsberg et al., 2011). Encountered tourmalines belong to the Alkali Group, and have been classified as intermediate members of the schorl-dravite solid solution series, dominated by a Fe-Mg substitution in the Y-site, pointing a control of tourmaline chemistry and abundance in the distribution of these elements in the bulk rock analyses. Concerning Ca depletion, a reasonable interpretation could be resulted, as calcic tournalines are absent from the analyzed compositions, where Ca-plagioclase and hornblende, seem to be vanquished from the studied sections as a result of the tourmalinization. Sodium depletion is quite erroneous, as Na is the dominant X-site cation in tourmaline from Kavala. In a similar

manner as Ca, Na depletion could be attributed in the gradual reduction of plagioclase presence from the host to intensively altered rocks, resulting in a negative trend, as tourmaline Na content is low compared with albite and neocrystallized albite modal abundance is negligible in order to affect the bulk rock composition. Potassium progressive depletion is expected, as K-feldspar participation is diminished with increasing presence of tourmaline, and the later don't favors K incorporation in its formula, except rare cases of K-rich tourmalines (e.g., Grice et al., 1993; Ota et al., 2008), but this is not our case. Al depletion and Si immobility interpretation, is a challenging issue as the small number of analyzed bulk samples may be insufficient to produce results with a statistically significant level of confidence. Limited feldspar presence and quartz neocrystallization, out coming from petrography could be a reasonable assumption, but in this case uncertainty is high.

In order to deal with the present issues and verify the rest of the geochemical results, a detailed μ m scale investigation using EDS X-ray mapping was applied. High resolution X-ray maps in the matrix of the breccias (KV15-19) revealed the elemental distribution in the studied samples (Fig. 31). The matrix of the breccias consists of tournaline dominated micro-domains, disrupted by scarce patches consisted of quartz, K-feldspar and white mica. Tournaline-rich domains show the expected elemental association of tournalinization, displaying the observed enrichment in Fe and Mg from the whole rock data. In addition, Al and Na enrichment are present, with higher content observed only in the K-feldspar and white mica rich domains, where potassium is also enriched. Depletion in Si is also present in the tournaline rich domains, resulting in an alteration geochemical pattern that resembles that of a typical tournalinization.


Figure 31:X-ray maps of major elements distribution in the matrix of the vein/breccias (KV15-19). Tourmaline rich domains represent the low Si areas, marked by increase in Fe, Mg, Al, Na, and Ca. The second plate verifies the above results in higher resolution.



Regarding trace element content in the bulk rock samples, Rb, Ba, and Cs depletion is a common phenomenon in high flux zones due to primary devolatilization (Ague, 2017). Feldspar destruction seems to control the depletion in Ba, Sr, Pb, while hornblende breakdown is responsible for deceasing Nb and Ta values. Enrichment in Be, Ga, V, Co and Sn can be attributed in the preferential partitioning of these elements in tournaline (van Hinsberg, 2011). Elevated contents in Au, As, Sb, Mo and Bi are present in the tourmaline-breccias and may be correlated with the presence of pyrite intergrown with tourmaline and other unidentified sulfide or sulfosalt minerals, point a possible connection of the studied breccias to Kavala sheeted vein intrusion related mineralized system (Fornadel et al., 2011). Positive correlations between Zr, Hf, U and Th could be explained to the presence of refractory zircon crystals from the host rock. REE elements patterns of the tourmaline-breccia rocks display a match with the host rocks pattern in terms of morphology and concentration. This indicates that the chemistry of these rocks is highly dependent to the host rock composition (Taylor and Slack 1984; Cavarretta and Puxeddu 1990; Steven and Moore 1995), especially in a rock dominated, fluid-rock interaction system. In the continuum of the process, marked by dominant B-rich fluid presence in the fluid/rock system, REE leaching is characteristic due to pH decrease (Morgan and London 1989), producing the depleted REE pattern of tourmalinite.

5.6 Petrogenetic history

The Kavala-Symvolon tourmaline brecciated system represents the manifestation of late stage B-rich hydrothermal fluid circulation in at least two separate pulses in the host granitoid. Direct geochronological data for the tourmaline-rich rocks formation are currently not available. Instead, from the fact that the cataclasis of the tourmaline-rich rocks is overprinting the mylonitic texture of the granodiorite and that the breccias formed above the ductile-brittle transition zone, indirectly is implied that the rocks under study formed during emplacement of the pluton in a late stage during the exhumation of the Southern Rhodope Core Complex following an earlier thickening stage. Transition from compressional to extensional regime practically recorded in Kavala tourmaline rocks, has also been recently described in the Comanja Granite, Mexico (Angeles-Moreno et al., 2017). Exhumation of the solidified pluton in lower pressure regime, in the footwall of the Strymon valley detachment, triggered the

explosive injection of an overpressured B-rich hydrothermal fluid resulting in fluid assisted brecciation and consequent tourmaline precipitation as suggested by Demirel et al. (2009) for the tourmaline rich rocks in the Kerkenez granitoid. The model proposed by these authors, regarding focused fluid flow within shear zones parallel to the regional trending, seems to be the case for Kavala as the studied system consists of an elongate zone parallel to the regional NE-SW trending, explaining also the lack of breccias pipes in the studied area. The system can be broadly classified as magmatic-hydrothermal breccias, as they match distinguishing criteria such as the presence of angular to sub rounded rock fragments and high temperature cementing phases (Sillitoe, 1985; Lawless et al., 1998). Lawless et al. (1990) suggested that this kind of breccias is likely formed by the release of juvenile magmatic volatiles derived from fractionated exsolved felsic magmas ascending from the lower crust.

Penetrative B-rich fluid circulation triggered metasomatic reactions that resulted in the precipitation of tourmaline in the expense of biotite, hornblende, plagioclase and K-feldspar, marked by the decreasing participation of the later in the continuum of alteration process. The decomposition of the later phases could have probably contributed to the offer of the essential elements for the tourmaline crystallization, underlining the host rock control in tourmaline composition, which is characterized by a narrow intermediate compositional range in the schorl-dravite solid solution series. Tourmalines in the studied rocks can be divided in two generations, consisting of the cores (Group 1), and (Group 2) the rims of zoned tourmalines and the tourmaline matrix. Discrimination of tourmaline, regarding host rocks from different environments, using the Al-Fe-Mg provenance diagram (Henry and Guiddoti,1985), and Fe/Mg ratio proximity index (Pirajno and Smithies, 1992), conclude that all the tourmaline groups formed in an intermediate to distal granitoid related magmatichydrothermal system, pinpointing an environment located in the marginal parts of a granitic intrusion. Such an environment, coupled with petrographical features and tourmaline chemistry, could result in further insights about the nature of the fluid phase. Irregular contacts and absence of any systematic relation in major element contents between Group 1 and 2 suggest that the latter is an overgrowth on a previously formed hydrothermal tourmaline. The observed variations between the two tourmaline generations should be attributed in an evolving fluid phase, characterized by a change in physiochemical conditions, enough rapid to produce the observed compositional and textural diversities among the two groups.

Reconstruction of the fluid phase using X- site cation occupancy in tourmaline (Von Goerne et al., 2001, 2011) and tourmaline LA-ICP-MS trace element concentrations using tourmaline/fluid partition coefficients (van Hinsberg et al., 2017 and references therein), suggest that observed tourmalines formed by an acidic solution with Na concentration ranging from 0.14 mol/l in Group 1 to 0.45 mol/l in Groups 2 a, and Ca between 0.47 to 0.03 mol/l respectively, with quite similar trace elements concentrations in the order of 0.1 to 10000 ppm. The change in fluid composition, resulted to the observe changing in physicochemical conditions of the fluid such as temperature, pressure and redox state.

In the absence of secure estimations of the P-T conditions of the system formation, the change in the redox state of the fluid, is the only factor that can be inferred to affect the compositional evolution of the diverse tournaline groups. Further work must be carried out, in order to constrain the exact P-T-X conditions of the formation. Upcoming work, includes thermobarometry in equilibrium assemblages with the matrix tournaline and estimation of Fe³⁺ content in tournaline directly via Mossbauer spectroscopy, or indirectly via EPMA correction methods (Fyalin et al., 2004), in order to evaluate the change in redox state hypothesis.

Another question outcoming, regards the origin of B, and consequently the source of the hydrothermal fluids. Lacking B isotope analyses only assumptions cane me made for the origin of the fluid. Possible sources include B-rich metasedimentary rocks in the source region and/or the wall-rocks of the pluton, the pluton itself, the aplites in the area or degassing of highly fractionated unexposed magma, but more petrogenetic and comparative isotopic investigation should be carried out in order to reach in a possible scenario.

6. References

Ague, J. J. (2017). Element mobility during regional metamorphism in crustal and subduction zone environments with a focus on the rare earth elements (REE). *American Mineralogist*, *102*(9), 1796-1821.

Altherr, R., Topuz, G., Marschall, H., Zack, T., & Ludwig, T. (2004). Evolution of a tourmaline-bearing lawsonite eclogite from the Elekdağ area (Central Pontides, N Turkey): Evidence for infiltration of slab-derived B-rich fluids during exhumation. *Contributions to Mineralogy and Petrology*, *148*(4), 409-425.

Angeles-Moreno, E., Nieto-Samaniego, A. F., Ruiz-Gonzalez, F. J., Levresse, G., Alaniz-Alvarez, S. A., Moya, M. D. J. P. O., ... & Miranda-Aviles, R. (2017). The transition between shortening and extensional regimes in central Mexico recorded in the tourmaline veins of the Comanja Granite. Journal of South American Earth Sciences, 73, 65-77.

Anovitz, L.M. & Grew, E.S. (1996): Mineralogy, petrology and geochemistry of boron: an introduction. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 1-40.

Aurisicchio, C., Bartolomei, A., Κυριακόπουλος, K., & Μαγγανάς, A. K. (2007). An unusual tournaline composition from Sithonia Peninsula (northern Greece). Δελτίον της Ελληνικής Γεωλογικής Εταιρίας, 40(2), 641-652.

Badham, J.P.N., 1980. Late magmatic phenomena in the Cornish batholith – useful field guids for tin mineralization. Proc. Ussher 5, 44–53.

Baksheev IA, Prokof'ev VY, Yapaskurt VO, Vigasina MF, Zorina LD, Solov'ev VN (2011) Ferric-iron-rich tourmaline from the Darasun gold deposit, Transbaikalia, Russia. Can Mineral 49:263–276

Baksheev, I. A., Prokofiev, V. Y., Trumbull, R. B., Wiedenbeck, M., & Yapaskurt, V. O. (2015). Geochemical evolution of tournaline in the Darasun gold district, Transbaikal region, Russia: evidence from chemical and boron isotopic compositions. *Mineralium Deposita*, *50*(1), 125-138.

Baltatzis, E., Kostopoulos, D., Godelitsas, A., Zachariadis, P., & Papanikolaou, D. (2009). Pliocene tourmaline rhyolite dykes from Ikaria Island in the Aegean back-arc region: geodynamic implications. *Geodinamica Acta*, 22(4), 189-199.

Baziotis, I., Mposkos, E., & Asimow, P. D. (2008). Petrogenesis of ultramafic rocks from the ultrahigh-pressure metamorphic Kimi Complex in Eastern Rhodope (NE Greece). *Journal of Petrology*, *49*(5), 885-909.

Berryman, E. J., Wunder, B., Wirth, R., Rhede, D., Schettler, G., Franz, G., & Heinrich, W. (2015). An experimental study on K and Na incorporation in dravitic tourmaline and insight into the origin of diamondiferous tourmaline from the Kokchetav Massif, Kazakhstan. *Contributions to Mineralogy and Petrology*, *169*(3), 28.

Berryman, E., & Wunder, B. (2014). Synthesis of K-dominant tourmaline. *American Mineralogist*, *99*(2-3), 539-542.

Bonev, N., J.-P. Burg, and Z. Ivanov (2006), Mesozoic-Tertiary structural evolution of an extensional gneiss dome—The Kesebir-Kardamos dome, eastern Rhodope

(Bulgaria-Greece), Int. J. Earth Sci. (Geol Rundsch), 95(2), 318–340, doi:10.1007/s00531-005-0025-y.

Bonev, N., Moritz, R., Marton, I., Chiaradia, M., & Marchev, P. (2010). Geochemistry, tectonics, and crustal evolution of basement rocks in the Eastern Rhodope Massif, Bulgaria. *International Geology Review*, *52*(2-3), 269-297.

Bonev, N. G., & Stampfli, G. M. (2003). New structural and petrologic data on Mesozoic schists in the Rhodope (Bulgaria): geodynamic implications. *Comptes Rendus Geoscience*, 335(8), 691-699.

Bosi, F. & Lucchesi, S. (2007): Crystal chemical relationships in the tournaline group: structural constraints on chemical variability. *Am. Mineral.* **92**, 1054-1063.

Boynton, W. V. (1984). Geochemistry of the rare earth elements: meteorite studies. W: Rare earth element geochemistry.(red. P. Henderson): 63–114.

Brun, J.-P., Sokoutis, D., 2007. Kinematics of the Southern Rhodope core complex (North Greece). International Journal of Earth Science 96, 1079–1099.

Brun, J. P., Faccenna, C., Gueydan, F., Sokoutis, D., Philippon, M., Kydonakis, K., & Gorini, C. (2016). The two-stage Aegean extension, from localized to distributed, a result of slab rollback acceleration. *Canadian journal of earth sciences*, *53*(11), 1142-1157.

Burg, J.-P., Z. Ivanov, L.-E. Ricou, D. Dimov, and L. Klain (1990), Implications of shear-sense criteria for the tectonics evolution of the Central Rhodope massif, southern Bulgaria, Geology, 18, 451–454, doi:10.1130/0091-7613(1990)018.

Burg, J. P., Ricou, L. E., Ivano, Z., Godfriaux, I., Dimov, D., & Klain, L. (1996). Syn-metamorphic nappe complex in the Rhodope Massif. Structure and kinematics. *Terra Nova*, 8(1), 6-15.

Cavarretta G, Puxeddu M (1990) Schorl-dravite-ferrodravite tourmalines deposited by hydrothermal magmatic fluids during early evolution of the Larderello geothermal field, Italy. Econ Geol 85:1236–1251

Cempírek, J., Novák, M., Ertl, A., Hughes, J. M., Rossman, G. R., & Dyar, M. D. (2006). Fe-bearing olenite with tetrahedrally coordinated Al from an abyssal pegmatite at Kutná Hora, Czech Republic: structure, crystal chemistry, optical and XANES spectra. *The Canadian Mineralogist*, 44(1), 23-30.

Chen, Y., Clark, A.H., Farrar, E., Wasteneys, H.A.H.P., Hodgson, M.J., Bromley, A.V.,1993. Diachronous and independent histories of plutonism and mineralization in the Cornubian Batholith, southwest England. J. Geol. Soc. 150, 1183–1191.

Clark, A.H., Chen, Y., Farrar, E., Wasteneys, H.A.H.P., Stimac, J.A., Hodgson, M.J., Willis-Richards, J., Bromley, A.V., 1993. The Cornubian Sn-Cu (-As, W) metallogenetic province: product of a 30 M.Y. history of discrete and concomitant anatectic, intrusive and hydrothermal events. Proc. Ussher 8,112–116.

Christofides, G., 1996. Tertiary magmatism in the Greek Rhodope Massif, northern Greece: Granitic plutons. In, Knezevic, V. and Krstic, B. eds., Terranes of Serbia: The Formation of the Geologic Framework of Serbia and the Adjacent Regions. University of Belgrade, Belgrade, 155–160.

Christofides, G., Neiva, A., Soldatos, T. and Eleftheriadis, G., 1995. Petrology of the Kavala plutonite (Eastern Macedonia, Greece). Proc. XV Congress CBGA, Athens. Bull. Geol. Soc. Greece, Spec. Publ., 4(2), 489-494.

Christofides, G., Soldatos, T., Eleftheriadis, G., & Koroneos, A. (1998). Chemical and isotopic evidence for source contamination and crustal assimilation in the Hellenic Rhodope plutonic rocks. *Acta Vulcanologica*, *10*, 305-318.

Codeço, M. S., Weis, P., Trumbull, R. B., Pinto, F., Lecumberri-Sanchez, P., & Wilke, F. D. (2017). Chemical and boron isotopic composition of hydrothermal tourmaline from the Panasqueira W-Sn-Cu deposit, Portugal. *Chemical Geology*, *468*, 1-16.

Demirel, S., Göncüoğlu, M. C., Topuz, G., & Isik, V. (2009). Geology and chemical variations in tourmaline from the quartz-tourmaline breccias within the Kerkenez granite-monzonite massif, Central Anatolian Crystalline Complex, Turkey. *The Canadian Mineralogist*, 47(4), 787-799.

Derham, J.M. and Feely, M. 1988. A K-feldspar breccia from Mo–Cu stockwork deposit in the Galway granite, west of Ireland. J. Geol. Soc., London, 145, 661–667.

Dill, H. G., Garrido, M. M., Melcher, F., Gomez, M. C., & Luna, L. I. (2012). Depthrelated variation of tournaline in the breccia pipe of the San Jorge porphyry copper deposit, Mendoza, Argentina. Ore Geology Reviews, 48, 271-277.

Dimadis, E., Zachos, S., 1989. Geological and tectonic structure of the metamorphic basement of the Greek Rhodope. Geologica Rhodopica, 1, 122–130.

Dini, A., Mazzarini, F., Musumeci, G. and Rocchi, S. 2008. Multiple hydrofracturing by boron-rich fluids in the Late Miocene contact aureole of eastern Elba Island (Tuscany, Italy). Terra Nova, 20: 318–326

Dinter, D. A. and Royden, L, 1993. Late Cenozoic extension in northeastem Greece: Strymon Valley detachment and Rhodope metamorphic core complex. Geol., 21, 45-48.

Dinter, D., MacFarlane, A., Hames, W., Isachsen, C., Bowring, S. and Royden, L., 1995. U–Pb and 40Ar/39Ar geochronology of the Symvolon granodiorite: implications for the thermal and structural evolution of the Rhodope metamorphic core complex, northeastern Greece. Tectonics, 14, 886–908.

Drivenes, K., Larsen, R.B., Müller, A., Sørensen, B.E., Wiedenbeck, M., Raanes, M.P., 2015. Late-magmatic immiscibility during batholith formation: assessment of B isotopes and trace elements in tourmaline from the Land's End granite, SW England. Contrib. Mineral. Petrol. 169, 1–27.

Dutrow, B. L., & Henry, D. J. (2000). Complexly zoned fibrous tourmaline, Cruzeiro mine, Minas Gerais, Brazil: a record of evolving magmatic and hydrothermal fluids. *The Canadian Mineralogist*, 38(1), 131-143.

Dyar, M. D., Taylor, M. E., Lutz, T. M., Francis, C. A., Guidotti, C. V., & Wise, M. (1998). Inclusive chemical characterization of tourmaline: Mössbauer study of Fe valence and site occupancy. *American mineralogist*, *83*(7-8), 848-864.

Eisbacher, G.H., Lüschen, E., Wickert, F., 1989. Crustal-scale thrusting and extension in the Hercynian Schwarzwald and Vosges, central Europe. Tectonics 8, 1–21.

Eleftheriadis, G. and Koroneos, A., 2003. Geochemistry and petrogenesis of postcollisonal Pangeon granitoids in central Macedonia, northern Greece, Chemie der Erde 63, 364–389.

Ertl, A., Rossman, G. R., Hughes, J. M., Prowatke, S., & Ludwig, T. (2005). Mnbearing "oxy-rossmanite" with tetrahedrally coordinated Al and B from Austria: Structure, chemistry, and infrared and optical spectroscopic study. *American Mineralogist*, *90*(2-3), 481-487.

Ertl, A., Draganits, E., Grasemann, B., Ntaflos, T., Giester, G., & Tillmanns, E. (2011). Synkinematic growth of tourmaline on brittle–ductile normal faults, Despotiko Island, Aegean Sea, Greece. *The Canadian Mineralogist*, *49*(1), 105-116.

Feely, M., Selby, D., Hunt, J. and Conliffe, J. 2010. Long-lived granite-related molybdenite mineralization at Connemara, western Irish Caledonides. Geol. Mag., 147: 886–894

Froitzheim, N., Jahn-Awe, S., Frei, D., Wainwright, A., Maas, R., Georgiev, N., Nagel, T.J., Pleuger, J., 2014. Age and composition of meta-ophiolite from the Rhodope Middle Allochthon (Satovcha, Bulgaria): a test for the maximum-allochthony hypothesis of the Hellenides. Tectonics 32.

Galbraith CG, Clarke DB, Trumbull RB, Wiedenbeck M (2009) Assessment of tourmaline compositions as an indicator of emerald mineralization at the Tsa da Glisza Prospect, Yukon Territory, Canada. Econ Geol 104:713–731

Grant, J. A. (1986). The isocon diagram; a simple solution to Gresens9 equation for metasomatic alteration. *Economic geology*, 81(8), 1976-1982.

Grice, J. D., & Ercit, T. S. (1993). Ordering of Fe and Mg in the tourmaline crystal structure: The correct formula. *Neues Jahrbuch für Mineralogie Abhandlungen*, *165*(3), 245-266.

Harlov D.E. and H. Austrheim, 2013. Metasomatism and the Chemical Transformation of Rock, Lecture Notes in Earth System Sciences. DOI 10. 1007/978-3-642-28394-9_1, Springer-Verlag, Berlin, Heidelberg.

Hawthorne, F.C. & Henry, D.J. (1999): Classification of the minerals of the tourmaline group. *Eur. J. Mineral.* **11**, 201-215

Henry, D. J., & Dutrow, B. L. (1996). Metamorphic tournaline and its petrologic applications. *Reviews in Mineralogy and Geochemistry*, 33(1), 503-557.

Henry, D. J., & Dutrow, B. L. (2001). Compositional zoning and element partitioning in nickeloan tournaline from a metamorphosed karstbauxite from Samos, Greece. *American mineralogist*, *86*(10), 1130-1142.

Henry, D.J. & Guidotti, C.V. (1985): Tourmaline as a petrogenetic indicator mineral: an example from the staurolite-grade metapelites of NW Maine. *Am. Mineral.* **70**, 1-15.

Henry, D.J., Novák, M., Hawthorne, F.C., Ertl, A., Dutrow, B.L., Uher, P. & Pezzotta, F. (2011): Nomenclature of the tourmaline supergroup minerals. *Am. Mineral.* **96**,

Hezel, D. C., Kalt, A., Marschall, H. R., Ludwig, T., & Meyer, H. P. (2011). Majorelement and Li, Be compositional evolution of tourmaline in an S-type granite– pegmatite system and its country rocks: an example from Ikaria, Aegean Sea, Greece. *The Canadian Mineralogist*, 49(1), 321-340. Jahn-Awe, S., N. Froitzheim, T. J. Nagel, D. Frei, N. Georgiev, and J. Pleuger (2010), Structural and geochronological evidence for Paleogene thrusting in the western Rhodopes, SW Bulgaria: Elements for a new tectonic model of the Rhodope Metamorphic Province, Tectonics, 29.

Janák, M., Froitzheim, N., Georgiev, N., Nagel, T. J., & Sarov, S. (2011). P–T evolution of kyanite eclogite from the Pirin Mountains (SW Bulgaria): implications for the Rhodope UHP Metamorphic Complex. *Journal of Metamorphic Geology*, 29(3), 317-332.

Jiang SY, Palmer MR, Peng QM, Yang JH (1997) Chemical and stable isotopic compositions of Proterozoic metamorphosed evaporates and associated tourmalines from the Houxianyu borate deposit, eastern Liaoning, China. Chem Geol 135:189–211

Jiang SY, Palmer MR, Yeats CJ (2002) Chemical and boron isotopic compositions of tourmaline from the Archean Big Bell and Mount Gibson gold deposits, Murchison Province, Yilgarn Craton, Western Australia. Chem Geol 188:229–247

Jiang SY, Yu JM, Lu JJ (2004) Trace and rare-earth element geochemistry in tourmaline and cassiterite from the Yunlong tin deposit, Yunnan, China: implication for migmatitic–hydrothermal fluid evolution and ore genesis. Chem Geol 209:193–213

Jochum, K. P., Nohl, U., Herwig, K., Lammel, E., Stoll, B., & Hofmann, A. W. (2005). GeoReM: a new geochemical database for reference materials and isotopic standards. *Geostandards and Geoanalytical Research*, 29(3), 333-338.

Jochum, K. P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., ... & Günther, D. (2011). Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines. *Geostandards and Geoanalytical Research*, *35*(4), 397-429.

Jolliff, B. L., Papike, J. J., & Shearer, C. K. (1987). Fractionation trends in mica and tourmaline as indicators of pegmatite internal evolution: Bob Ingersoll pegmatite, Black Hills, South Dakota. *Geochimica et Cosmochimica Acta*, *51*(3), 519-534.

Jones, C. E., Tarney, J., Baker, J. H., & Gerouki, F. (1992). Tertiary granitoids of Rhodope, northern Greece: Magmatism related to extensional collapse of the Hellenic Orogen?. *Tectonophysics*, *210*, 295-314.

Kelly, W.C., Rye, R.O., 1979. Geologic, fluid inclusion, and stable isotope studies of the tin-tungsten deposits of Panasqueira, Portugal. Econ. Geol. 74, 1721–1822.

Kilias, A., Falalakis, G., Sfeikos, A., Papadimitriou, E., Vamvaka, A., & Gkarlaouni, C. (2013). The Thrace basin in the Rhodope province of NE Greece—A tertiary supradetachment basin and its geodynamic implications. *Tectonophysics*, 595, 90-105.

Kirchenbaur, M., Pleuger, J., Jahn-Awe, S., Nagel, T. J., Froitzheim, N., Fonseca, R. O. C., & Münker, C. (2012). Timing of high-pressure metamorphic events in the Bulgarian Rhodopes from Lu–Hf garnet geochronology. *Contributions to Mineralogy and Petrology*, *163*(5), 897-921.

Kokkinakis, A.: Das Intrusivgebiet des Symvolon-Gebirges und yon Kavala in Ostmakedonien, Griechenland. -- Diss. Univ. München. -- 255 + XIII S., 208 Abb., 29 Tab., 8 Kt., 1 B1.; München, 1977.

Kokkinakis, A. (1980): Altersbeziehungen zwischen Metamophosen, mechanischen Deformationen und Intrusionen am Südrand des Rhodope-Massivs (Makedonien, Griechenland), Geol. Rundschau 69, 726-144.

Kounov, A., Wüthrich, E., Seward, D., Burg, J. P., & Stockli, D. (2015). Low-temperature constraints on the Cenozoic thermal evolution of the Southern Rhodope Core Complex (Northern Greece). *International journal of earth sciences*, *104*(5), 1337-1352.

Krenn, K., C. Bauer, A. Proyer, U. Klötzli, and G. Hoinkes (2010), Tectonometamorphic evolution of the Rhodope orogen, Tectonics, 29, TC4001,

Krohe, A., Mposkos, E., 2002. Multiple generations of extensional detachments in the Rhodope Mountains (N. Greece): evidence of episodic exhumation of high-P rocks. In: Blundell, D.J., Neubauer, G., Von Quadt, A. (Eds.), The Timing and Location of Major Ore Deposits in an Evolving Orogen. Geological Society of London, Special Publication 204, pp. 151–178

Kyriakopoulos, K., Pezzino, A. and Del Moro, A. 1989. Rb-Sr geochrological, petrological and structural study of the Kavala plutonic complex (N. Greece). Bull. Geo1. Soc. Greece, 23, 545-560.

Kyriakopoulos, K.G., 1987. A geochronological, geochemical and mineralogical study of some Tertiary plutonic rocks of the Rhodope massif (northern Greece) and their Rb/Sr, K/Ar isotopic characteristics. Unpublished Ph.D. Thesis, University of Athens, Greece, 434 pp.

Lafuente B, Downs R T, Yang H, Stone N (2015) The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography, T Armbruster and R M Danisi, eds. Berlin, Germany, W. De Gruyter, pp 1-30

Laskou, M. D. (2005). Chemical and mineralogical characteristics of tourmaline in pegmatites from Vavdos, Chalkidiki peninsula, N Greece. In *Mineral Deposit Research: Meeting the Global Challenge*(pp. 769-772). Springer Berlin Heidelberg.

Leeman, W.P. & Sisson, V.B. (1996): Geochemistry of boron and its implications for the crustal and mantle processes. *In* Boron: Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 645-708.

Liati, A., Theye, T., Fanning, C. M., Gebauer, D., & Rayner, N. (2016). Multiple subduction cycles in the Alpine orogeny, as recorded in single zircon crystals (Rhodope zone, Greece). *Gondwana Research*, *29*(1), 199-207.

London D, Manning DAC (1995) Chemical variation and significance of tourmaline from southwest England. Econ Geol 90:495–519

London, D. 2009. The origin of primary textures in granitic pegmatites. Canad. Mineral, 47, 697–724.

London, D., & Manning, D. A. (1995). Chemical variation and significance of tourmaline from Southwest England. *Economic geology*, 90(3), 495-519.

Magganas, A. C. (2002). Constraints on the petrogenesis of Evros ophiolite extrusives, NE Greece. *Lithos*, 65(1), 165-182.

Magganas A. (2005). Sub-greenschist to Greenschist Facies Metamorphism of Metavolcanics of Circum-Rhodope Belt in Thrace. Bulletin of the Geological Society of Greece, vol. XXXVII, 78-89.

Magganas, A., Sideris, C., & Kokkinakis, A. (1991). Marginal basin—volcanic arc origin of metabasic rocks of the Circum-Rhodope Belt, Thrace, Greece. *Mineralogy and Petrology*, 44(3), 235-252.

Marks MA, Marschall HR, Schóhle P, Guth A, Wenzel T, Jacob DE, Barth M, Markl G (2013) Trace element systematics of tournaline in pegmatitic and hydrothermal systems from the Variscan Schwarzwald (Germany): the importance of major element composition, sector zoning, and fluid or melt composition. Chem Geol 344:73–90

Marschall, H.R., Kalt, A., Hanel, M., 2003. P–T evolution of a Variscan lower crust segment: a study of granulites from the Schwarzwald, Germany. Journal of Petrology 44,227–253.

Marschall HR, Ludwig T, Altherr R, Kalt A, Tonarini S (2006) Syros metasomatic tourmaline: Evidence for very high- δ 11B fluids in subduction zones. Journal of Petrology 47: 1915-1942.

Marschall, H. R., Altherr, R., Kalt, A., & Ludwig, T. (2008). Detrital, metamorphic and metasomatic tourmaline in high-pressure metasediments from Syros (Greece): intra-grain boron isotope patterns determined by secondary-ion mass spectrometry. *Contributions to Mineralogy and Petrology*, *155*(6), 703-717

Marschall, H. R., Korsakov, A. V., Luvizotto, G. L., Nasdala, L., & Ludwig, T. (2009). On the occurrence and boron isotopic composition of tourmaline in (ultra) high-pressure metamorphic rocks. *Journal of the Geological Society*, *166*(4), 811-823.

Marschall, H. R., & Jiang, S. Y. (2011). Tourmaline isotopes: no element left behind. *Elements*, 7(5), 313-319.

McDonough, W. F., & Sun, S. S. (1995). The composition of the Earth. *Chemical geology*, *120*(3-4), 223-253.

Michailidis, K., & Kassoli-Fournaraki, A. (1994). Tournaline concentrations in migmatitic metasedimentary rocks of the Riziana and Kolchiko areas in Macedonia, Northern Greece. *European journal of mineralogy*, 6(4), 557-569.

Möller, P., Stober, I., Dulski, P., 1997. Seltenerdelement-, Yttrium-Gehalte und Bleiisotope in Thermal- und Mineralwässern des Schwarzwaldes. Grundwasser 3, 118–132

Morgan, G.B. and London, D., 1989. Experimental reactions of amphibolite with boron-bearing aqueous fluids at 200 MPa: implications for tournaline stability and partial melting in mafic rocks. *Contributions to Mineralogy and Petrology*, *102*(3), pp.281-297.

Mposkos, E. D., & Kostopoulos, D. K. (2001). Diamond, former coesite and supersilicic garnet in metasedimentary rocks from the Greek Rhodope: a new ultrahigh-pressure metamorphic province established. *Earth and Planetary Science Letters*, 192(4), 497-506.

Mposkos, E., Baziotis, I., & Proyer, A. (2010). Metamorphic reprocessing of a serpentinized carbonate-bearing peridotite after detachment from the mantle wedge: A P–T path constrained from textures and phase diagrams in the system CaO–MgO–Al 2 O 3–SiO 2–CO 2–H 2 O. *Lithos*, *118*(3), 349-364.

Mposkos, E., & Perraki, M. (2013). Metamorphic record in metalherzolite pockets within the Virsini metaharzburgite from the Kechros HP metamorphic complex in

Eastern Rhodope, Greece. Bulletin of the Geological Society of Greece, 47(1), 397-406.

Mposkos, E., Baziotis, I., Leontakianakos, G., & Barry, P. H. (2013). The metamorphic evolution of the high-pressure Kechros complex in East Rhodope (NE Greece): Implications from Na–Al-rich leucocratic rocks within antigorite serpentinites. *Lithos*, *177*, 17-33.

Müller A and Halls, C. (2005). Rutile – the tin–tungsten host in the intrusive tourmaline breccia at Wheal Remfry, SW England. In: Jingwen, M and Bierlein, F.P., eds., Mineral Deposit Research: Meeting the Global Challenge, 441–444

Müller, A., Seltmann, R., Halls, C., Siebel, W., Dulski, P., Jeffries, T., Spratt, J., Kronz, A., (2006). The magmatic evolution of the Land's End pluton, Cornwall, and associated pre-enrichment of metals. Ore Geol. Rev. 28, 329–367.

Nagel, T. J., S. Schmidt, M. Janak, N. Froitzheim, S. Jahn-Awe, and N. Georgiev (2011), The exposed base of a collapsing wedge: The Nestos Shear Zone (Rhodope Metamorphic Province, Greece), Tectonics, 30, TC4009, doi:10.1029/2010TC002815

Neiva AMR (1974) Geochemistry of tourmaline (schorlite) from granites, aplites and pegmatites from Northern Portugal. Geochim Cosmochim Acta 38:1307–1317

Neiva AMR, Campos TFC (1992) Genesis of the zoned granitic pluton of Penamacor-Monsanto, Central Portugal. Memo'rias eNoti'cias, Publ Mus Lab Mineral Geol Univ Coimbra 114:51–68

Neiva AMR, Campos TFC (1993) The zoned granitic pluton of Penamacor-Monsanto, Central Portugal: hydrothermal alteration.Memo'rias e Noti'cias, Publ Mus Lab Mineral Geol Univ Coimbra 116:21–47

Neiva, A., Christofides, G., Eleftheriadis, G., Soldatos, T., (1996). Geochemistry of granitic rocks and their minerals from the Kavala pluton, northern Greece. Chemie der Erde, 56, 117–142.

Novak M, Škoda R, Filip J, Macek I, Vaculovic^{*} T (2011) Compositional trends in tourmaline from intragranitic NYF pegmatites of the Trebic pluton, Czech Republic: an electron microprobe, Mφssbauer and LA–ICP–MS study. Can Mineral 49:359–380

Ota, T., Kobayashi, K., Katsura, T., & Nakamura, E. (2008). Tourmaline breakdown in a pelitic system: implications for boron cycling through subduction zones. *Contributions to Mineralogy and Petrology*, *155*(1), 19-32.

Papanikolaou, D., Panagopoulos G. (1981). On the structural style of Southern Rhodope (Greece). Geol. Bale., 11, 13-22.

Perraki, M., Proyer, A., Mposkos, E., Kaindl, R., & Hoinkes, G. (2006). Raman micro-spectroscopy on diamond, graphite and other carbon polymorphs from the ultrahigh-pressure metamorphic Kimi Complex of the Rhodope Metamorphic Province, NE Greece. *Earth and Planetary Science Letters*, 241(3), 672-685.

Pesquera A, Torres-Ruiz J, Garcia-Casco A, Gil-Crespo PP (2013) Evaluating the controls on tourmaline formation in granitic systems: a case study on peraluminous granites from the Central Iberian Zone (CIZ), Western Spain. J Petrol 54:609–634

Pesquera A, Torres-Ruiz J, Gil-Crespo PP, Jiang SY (2005) Petrographic, chemical and B-Isotopic insights into the origin of tourmaline-rich rocks and boron recycling in

the Martinamor Antiform (Central Iberian Zone, Salamanca, Spain). J Petrol 46:1013-1044.

Pirajno, F., & Smithies, R. H. (1992). The FeO/(FeO+ MgO) ratio of tourmaline: a useful indicator of spatial variations in granite-related hydrothermal mineral deposits. *Journal of Geochemical Exploration*, 42(2-3), 371-381.

Plimer, I. R. (1987). The association of tourmalinite with stratiform scheelite deposits. *Mineralium Deposita*, 22(4), 282-291.

Pollard, P.J., Pichavant, M. and Charoy, B. (1987). Contrasting evolution of fluorineand boron-rich systems. Miner Depos, 22, 315–321.

Ribeiro A, Quesada C, Dallmeyer RD (1990) Geodynamic evolution of the Iberian massif. In: Garcia Martinez, Dallmeyer RD (eds) Pre-Mesozoic Geology of Iberia. Springer-Verlag, Berlin,pp 399–409

Ribeiro da Costa, I.R., Mourão, C., Récio, C., Guimarães, F., Antunes, I.M., Ramos, J.F., Barriga, F.J.A.S., Palmer, M.R., Milton, J.A., (2014). Tourmaline occurrences within the Penamacor-Monsanto granitic pluton and host-rocks (Central Portugal): genetic implications of crystal-chemical and isotopic features. Contrib. Mineral. Petrol. 167, 1–23.

Schmidt, S., Nagel, T. J., & Froitzheim, N. (2010). A new occurrence of microdiamond-bearing metamorphic rocks, SW Rhodopes, Greece. *European Journal of Mineralogy*, 22(2), 189-198.

Shedd, K.B., (2016). Tungsten 180–181.

Shibata, S.-N., Tanaka, T., Yamamoto, K., (2006). Crystal structure control of the dissolution of rare earth elements in water–mineral interactions. Geochemical Journal 40, 437–446.

Shimizu, R., & Ogasawara, Y. (2013). Diversity of potassium-bearing tourmalines in diamondiferous Kokchetav UHP metamorphic rocks: A geochemical recorder from peak to retrograde metamorphic stages. *Journal of Asian Earth Sciences*, *63*, 39-55.

Skewes, M.A., Holmgren, C. and Stern, C.R., (2003). The Donoso copper-rich, tourmaline-bearing breccia pipe in central Chile: petrologic, fluid inclusion and stable isotope evidence for an origin from magmatic fluids. Miner Depos, 38, 2–21

Slack, J. F., & Trumbull, R. B. (2011). Tourmaline as a recorder of ore-forming processes. *Elements*, 7(5), 321-326.

Slack, J. F., Herriman, N., Barnes, R. G., & Plimer, I. R. (1984). Stratiform tourmalinites in metamorphic terranes and their geologic significance. *Geology*, *12*(12), 713-716.

Slack, J. F., Passchier, C. W., & Zhang, J. S. (1996). Metasomatic tourmalinite formation along basement-cover décollements, Orobic Alps, Italy. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 76(2), 193-207.

Smith, M.P., Yardley, B.W.D., (1996). The boron isotopic composition of tournaline as a guide to fluid processes in the southwestern England ore field: an ion microprobe study. Geochim. Cosmochim. Acta 60, 1415–1427.

Steven NM, Moore JM (1995) Tourmaline mineralization in the Late Proterozoic Kuiseb Formation of the Damara Orogen, Central Namibia: evidence for a replacement origin. Econ Geol 90:1098–1117

Sousa MB (1985) Perspectiva sobre os conhecimentos actuais doComplexo Xisto-Grauva'quico de Portugal. Memo'rias e Noticias, Publ Mus Lab Mineral Geol Univ Coimbra 100:1–16

Trumbull, R. B., & Chaussidon, M. (1999). Chemical and boron isotopic composition of magmatic and hydrothermal tournalines from the Sinceni granite–pegmatite system in Swaziland. *Chemical geology*, *153*(1), 125-137

Turpaud, P., & Reischmann, T. (2005). Relationships between crustal blocks and UHP relics, an example from Northern Greece. In *Geophysical Research Abstracts* (Vol. 7, p. 04353).

van Hinsberg VJ (2011) Preliminary experimental data on traceelement partitioning between tourmaline and silicate melt. Can Mineral 49:153–163

van Hinsberg, V. J., & Schumacher, J. C. (2007). Intersector element partitioning in tourmaline: a potentially powerful single crystal thermometer. *Contributions to Mineralogy and Petrology*, 153(3), 289-301.

van Hinsberg, V. J., Henry, D. J., & Marschall, H. R. (2011). Tourmaline: an ideal indicator of its host environment. *The Canadian Mineralogist*, 49(1), 1-16.

van Hinsberg, VJ., Franz, G., Wood, B.J. (2017) Determining subduction-zone fluid composition using a tourmaline mineral probe. Geochem. Persp. Let. 3, 160-169.

von Goerne, G., Franz,G., & Heinrich, W. (2001) Synthesis of tourmaline solid solutions in the system $Na_2O-MgO-Al_2O3-SiO_2-B_2O_3-H_2O-HC1$ and the distribution of Na between tourmaline and fluid at 300 to 700 °C and 200 MPa. Contributions to Mineralogy and Petrology 141, 160–173.

von Goerne, G., Franz, G., & van Hinsberg, V.J. (2011) Experimental determination of Na-Ca distribution between tournaline and fluid in the system CaO–Na₂O–MgO–Al₂O₃–SiO₂–B₂O₃–H₂O. Canadian Mineralogist 49, 137–152.

Weisbrod A, Polak C, Roy D (1986) Experimental study of tourmaline solubility in the system Na–Mg–Al–So–B–O–H. Applications to the boron content of natural hydrothermal fluids and tourmalinization processes. In: International Symposium on Experimental Mineralogy and Geochemistry (Nancy), Abstracts volume: 140–141

Williamson, B. J., Spratt, J., Adams, J. T., Tindle, A. G., & Stanley, C. J. (2000). Geochemical constraints from zoned hydrothermal tournalines on fluid evolution and Sn mineralization: an example from fault breccias at Roche, SW England. *Journal of Petrology*, *41*(9), 1439-1453.

Wolf, Michael B., and David London. "Boron in granitic magmas: stability of tourmaline in equilibrium with biotite and cordierite." *Contributions to Mineralogy and Petrology* 130.1 (1997): 12-30.

Wüthrich, E., 2009. Low temperature thermochronology of the Northern Aegean Rhodope Massif. Ph.D. thesis, Swiss Federal Institute of Technology Zurich.

Yang, S. Y., Jiang, S. Y., Zhao, K. D., Dai, B. Z., & Yang, T. (2015). Tourmaline as a recorder of magmatic-hydrothermal evolution: an in situ major and trace element

analysis of tourmaline from the Qitianling batholith, South China. *Contributions to Mineralogy and Petrology*, 170(5-6), 42.

Yavuz F, Jiang SY, Karakay N, Karakaya MH, Yavuz R (2011) Trace element, rareearth element and boron isotopic compositions of tourmaline from a vein-type Pb– Zn–Cu \pm U deposit, NE Turkey. Int Geol Rev 53:1–24

Yavuz, F., Karakaya, N., Yıldırım, D. K., Karakaya, M. Ç., & Kumral, M. (2014). A Windows program for calculation and classification of tourmaline-supergroup (IMA-2011). *Computers & Geosciences*, *63*, 70-87.

Yücel-Öztürk, Y., Helvacı, C., Palmer, M. R., Ersoy, E. Y., & Freslon, N. (2015). Origin and significance of tourmalinites and tourmaline-bearing rocks of Menderes Massif, western Anatolia, Turkey. *Lithos*, 218, 22-36