

Composition of Tourmaline in Leucogranite, Pegmatite, Quartz Veins and their Country Rocks from Hajiabad area, Boroujerd, NW Iran

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ABSTRACT: Tourmaline occurs as an accessory mineral in a variety of rocks including leucogranite, pegmatite, quartz veins and their country rocks in Haji abad area in SE Broujerd. Therefore, four types of tourmaline were distinguished based on its geological occurrences. Except the tourmaline in pegmatite, which is represented by Fe-rich schorl ($Al = 6.62-6.85$ apfu, $Fe/(Fe + Mg) = 0.86-0.95$), the rest of tourmalines from leucogranite, quartz veins and hornfels are of schorl-dravite solid-solution composition ($Al = 6.41-6.77$ apfu, $Fe/(Fe + Mg) = 0.31-0.61$), and they are richer in Zn (0.13 apfu on average) than the tourmaline from pegmatite (0.02 apfu on average). Tourmaline shows textural and compositional variations in relation with pegmatite type. Subhedral to euhedral prismatic, very fine- to medium-grained (<6 mm - 10 μ m), zoned grains are most common. In the country rock, tourmaline appears as prismatic-euhedral very fine grained (<6 mm) crystals. Their Fe/Mg value changes considerably amongst the different pegmatite types providing insight into the degree of evolution of the associated pegmatites Fe and poorest in Mg are associated with the most evolved bodies. Tourmaline from the country rocks shows compositional characteristics inherited from the host schists: similarity of the shape of the REE patterns for tourmaline and the schists, and a high content in Cr, Lf, Th and U. The Jurassic Boroujerd Granitoid Complex, located in Sanandaj-Sirjan zone in west of Iran, consists essentially of quartz diorite, granodiorite and monzogranite which are cut by aplitic and pegmatitic and quartz-tourmaline veins of a few centimetres to 3 meters in thickness. Tourmaline forms one of major minerals in the pegmatite and hydrothermal veins. It also occurs as nodules in the monzogranite. The tourmalines are alkali-rich, with Na being the dominant alkali element present and having small amounts of X-site vacancy. The dominant variability in composition seems controlled by the exchange vector $CaMgOn \text{ Al}(\text{OH})_1$. Chondritenormalized patterns of the rare-earth elements point out the possible contribution of hydrothermal processes to tourmaline formation. The composition of tourmaline indicates the involvement of coupled substitutions i.e., alkali-defect and proton-deficient substitutions, which the latter one is more effective.

Keywords: Tourmalines , Schorl , Dravite ,Hajiabad ,Granite field.

INTRODUCTION

Tourmaline is the most common borosilicate mineral, with the general formula of $XY_3Z_6T_6O_{18} (BO_3)_3V_3W$, occurring in a variety of rock types including igneous, metamorphic and sedimentary rocks. As it can be seen from its formula a wide variety of cation sizes and charges can occupy the X, Y, and Z sites, therefore, it is one of the most chemically variable silicates, comprising 14 recognized mineral species of which the most common ones are elbaite, schorl and dravite (Hawthorne and Henry, 1999).

Other properties include its large P-T stability up to amphibolite facies (Henry and Dutrow 1996), its resistance to alteration and weathering as it preserves its primary composition, its tendency to develop and maintain chemical zoning, and it hence is considered as an outstanding mineral record.

It has been shown that tourmaline composition reveals the bulk chemistry of the rock in which it forms, and also it can be used as a petrogenetic indicator (e.g., Henry and Guidotti 1985, Kassoli-Foumaraki 1990, Pirajno and Smithies 1992, Kassoli-Fournaraki and Michailidis 1994; Hellingwerf et al. 1994). This study looks at igneous-related tourmaline occurrences in the Boroujerd Granitoid Complex and Astanceh granitoids in the Sanandaj-Sirjan metamorphic-plutonic zone, a part of Central Iran microplate.

This paper presents the results of the first study on the chemical compositions of igneous-related tourmaline occurrences in Boroujerd Granitoid Complex and Astanceh granitoids in the central part of Sanandaj-Sirjan zone in the west of Iran.

In this article we report tourmalines that possess intermediate composition between 'oxy-dravite' and povondraite in an 'oxy-dravite'–povondraite series from a Cu–Au deposit of the Ghagri area in southeast Rajasthan and discuss the genesis of the deposit.

In this paper" we present chemical and textural data on tourmaline in granite, pegmatite, quartz veins and country rocks cropping out in NE of broujerd, to provide a petrogenetic interpretation of different types of occurrences. In this study, geological, mineralogical and geochemical data on tourmaline-rich rocks obtained from the tourmalinized rocks are presented to determine their genesis including the nature of the tourmalinite protholith and the possible source of boron.

Tourmaline is a complex borosilicate mineral with a general formula of $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_4$. In this study, petrographic and chemical data on representative samples of tourmaline selected from the various groups of pegmatites in the Fregeneda area and their extensively tourmalinized country-rock are given. The chemical variations are discussed in order to determine whether these different types of pegmatite 1) are related by a common path of fractionation, and 2) are related to them nearby Lumbrales granite.

Geological setting

The study area is located in the northern part of the Sanandaj-Sirjan metamorphic-magmatic zone, west-central Iran (Fig. 1). The Sanandaj-Sirjan zone, trending NW-SE with a length of about 1500 km and a width up to 200 km consist of metamorphic and complexly deformed rocks associated with abundant deformed and undeformed plutons in addition to widespread Mesozoic volcanic rocks. The development of this zone resulted from the opening and closure of the Neotethys Ocean between Eurasia and Arabia (Mohajjel, 2003; Ghasemi and Talbot, 2006). The plutonic bodies outcropping in the NW part of the zone are considered as arc-related calc-alkaline rocks generated during the Mesozoic due to the subduction of Neotethys beneath the Iranian plate (Ahmadi-Khalaji, 2007). and its subsequent destruction during Cretaceous and Tertiary convergence and continental collision between the Afro-Arabian and the Eurasian plates (1, 12, 26). The rocks of this zone are mostly of Mesozoic age with Paleozoic rocks rarely exposed except in the southeast where they are common [6]. This

zone is characterized by This zone is distinguished from Central Iran by nearly total lack of Tertiary volcanism and the poor development of Tertiary deposits in general (32).

Geology of the study area consists mainly of a leuco-cratic granite surrounded by hornfels and Jurassic phyllites. Pegmatite dykes and quartz-tourmaline veins intersect the leucogranite and Jurassic phyllites-slates-schists.

We have studied tourmaline from a Miocene leucogranite intrusion from Boroujerd Granitoid Complex. The granite intruded a lower green schistfacies metapelite complex. Pegmatitic and aplitic dykes from the intrusion cross-cut the metapelite and the granite itself. Tourmaline occurs in various proportions in all these rocks. It is also present in quartz–tourmaline veins and isolated quartz–tourmaline-rich rocks in the granite and the metapelite.

Boroujerd Granitoid Complex is one of the suites of the several granitoid suites occurring within the 1500 km-long, NW-SE trending Sanandaj-Sirjan zone in western Iran . This zone is considered as a complex tectonic zone including metamorphosed and multiply-deformed volcanic rocks, metasediments, ophiolite sequences and granitoid bodies of mainly Mesozoic age. The Sanandaj-Sirjan zone was affected by various stages of metamorphism and magmatism related to subduction of the Paleo- and Neotethyan lithosphere under Central Iran, which ceased in the Neogene with the closure of the Neotethys and collision of Arabia and Central Iran. The detailed geochronological and geochemical studies of the Boroujerd Complex by Khalaji et al. (2007) showed that the granitoids correspond to metaluminous or slightly peraluminous, high-K calc-alkaline rocks of I-type related to the mid-Jurassic subduction setting.

The Boroujerd Complex is a NW–SE elongate body covering an outcrop area of about 200 km². The complex comprises three main units: quartz diorite, granodiorite and monzogranite. Zircon U-Pb ages for these three plutonic units overlap, with a total spread from 169.6 ± 0.2 to 173.7 ± 1.5 Ma (Khalaji, 2006). The youngest intrusive phases in

the area are scattered dykes of silicic (aplite), intermediate and basic compositions. An example of an aplite dyke cutting quartz diorite in the Nezamabad area is shown in Fig. 2.

The granodiorite, the dominant rock type by volume in the BGC is medium to coarse grained consists of plagioclase, biotite, quartz, alkali feldspar and accessory minerals like apatite, zircon, allanite and magnetite. Secondary minerals are muscovite, sericite, chlorite, epidote and prehnite.

The quartz diorite occurs as small stocks within the granodiorite unit, comprise a granular to porphyritic texture with plagioclase megacrysts, and consists mainly of plagioclase, biotite, amphibole, quartz and alkali feldspar. Zircon, titanite and apatite are conspicuous accessory minerals and sericite, epidote, calcite, prehnite and chlorite are secondary minerals replacing plagioclase, biotite and amphibole.

The monzogranitic unit outcrops along the western margin of the complex, consists of fine to coarse-grained, porphyritic texture including quartz, alkali feldspar, plagioclase, biotite with minor secondary muscovite. Zircon, allanite and apatite are common accessory minerals.

A series of NW-trending aplite and pegmatite veins from a few meters to tens of meters in length and a few metres wide, occur in the study area, commonly in the granodiorite unit. Aplites are characterized by a fine grained equigranular assemblage of quartz, alkali-feldspar, some muscovite and opaque minerals. The petrology and geochemistry of the pegmatites have been described by Masoudi (1997). The pegmatites have a simple mineralogy with graphic texture and are characteristically composed of quartz, feldspar, muscovite and minor zircon and apatite, as well as local andalusite and garnet.

Tourmaline Occurrences

Four modes of tourmaline occurrence on the basis of its host rock are identified in the study area: (1) very coarse-grained crystals (up to 2.5 cm in length) in pegmatite accompanied mainly by large crystals of quartz, feldspars, and muscovite. In this rock, euhedral to sub-hedral tourmaline forms skeletal crystals, cores of which consist of the quartz, microcline. This texture probably formed through early nucleation and growth of tourmaline, followed by simultaneous crystallization of quartz, microcline. (2) Disseminated and patches of tourmaline in leucogranitic host rock. (3) quartz-tourmaline veins, and (4) tourmaline in metamorphic halo.

Quartz, plagioclase, microcline, minor muscovite and tourmaline constitute the pegmatite contents. In thin section, quartz is anhedral, polycrystalline and shows wavy distinction. Tourmaline crystals are euhedral and color-zoned. The cores are homogeneous and surrounded by a narrow rims. Pleochroism changes from light blue to dark blue in the core, and to olive-brown in the narrow zone surrounding the core. Tourmaline grains are usually segmented by cracks and filled with quartz, and microcline. In some cases, tourmaline is replaced by quartz .

Optical microscopic study shows that skeletal or incompletely formed crystals of tourmaline occur exclusively within euhedral and subhedral feldspar grains of leucogranite . It also occurs as anhedral interstitial grains. (red sentence must be checked by microscope) Based on this textural relationship, the development of disseminated tourmaline patches within the feldspar grains may be regarded as an indication of the B fluid metasomatism.

The tourmaline quartz veins, ranging in thickness from a few cm to more than one meter, cross-cut the granitic rocks. Mineralogy of quartz tourmaline veins is simple consisting of quartz, tourmaline and small amounts of opaque minerals. Microscopic study of the obtained samples shows the aggregates of tourmaline occurring in quartz veins do not exceed 15% by volume. Therefore the term tourmalinite veins cannot be used in the sense of Nicholson (1980) and Fortey and Cooper (1986). Most of the grains of tourmaline display a light blue-green core changes into a darker brownish green rim. Optically Irregular zoning occurs as patchy domains of blue green in brownish green regions. Some well-defined cores have outer zones showing an irregular distribution of coloring .Tourmaline grains may be unzoned, irregularly zoned or have two sharply defined zones. Color zonation is characterized by a light bluish green core and a deep green rim. Some crystals have several distinct zones .

The fourth type of tourmaline is very fine grained (<6 mm) and found in the metamorphic country rock at the contact of granite. Some of the grains of tourmaline display two optically distinct growth-zones (Figs. 2d), which are developed concentrically about the c axis and nearly parallel to the crystal faces. A greenish blue in the core gives way to a brownish green rim. Optically unzoned crystals are also common.

Subsequently, the rocks have been strongly affected by a younger retrograde metamorphic event under the greenschist facies (M3).

Textural differences among the tourmaline samples from the various types of rocks led to identification of four modes of occurrences an be established. The first one is a medium to very fine-grained (5 cm - <6 -m), prismatic tourmaline, that appears homogeneously distributed in the intragranitic pegmatites (1), in the quartz-andalusited ykes.

The modal concentration of tourmaline does not exceed 10% by volume, and its distribution in the veins is quite uniform. Fracturing of the needle-like crystals is commonly attributed to deformation accompanying metamorphism quartz heals the fractures .

Inclusions in tourmaline or quartz-tourmaline intergrowths are present but scarce. Traces of the feldspars and white mica occur sporadically in the quartz veins. Compositional zoning parallel to the (0001) growth direction is common in tourmaline.

Most of the grains of tourmaline display two optically distinct growth-zones, which are developed concentrically about the c axis and nearly parallel to the crystal faces. A light blue-green core gives way to a darker brownish green rim. Optically Homogeneous (i. e., unzoned) crystals are rare. Irregular zoning occurs as patchy domains of blue green in brownish green regions. Some well-defined cores have outer zones showing an irregular distribution of coloring .

Euhedral to subhedral and skeletal (incompletely formed) crystals and intergrowths with the Associated silicates also are present. In most cases, the development of these intergrowths did not significantly affect either the euhedral character (outer

Tourmaline grains from Thasos may be unzoned, irregularly zoned or have two sharply defined zones.

Color zonation is characterized by a light bluish green core and a deep green rim. Some crystals have several distinct zones .

The study tourmalines were found within the Broujerd granitoid, generally either in the form of veins which crosscut the granitoids as tiny veins, veinlets or networks of fracture fillings and in the country rock of contact zones surrounding both granite and pegmatite. Thus, the Broujerd granitoid is established as the host rock of the quartz-tourmaline rocks.

Tourmaline occurs in the pegmatites surrounding the boroujerd Granite, in the granite itself.

The first comprises medium- to fine-grained prismatic tourmaline (0.5 mm - 3.0 cm) in quartz-tourmaline veins, the width of the crystals attaining 2.0 mm. Widespread euhedral chlorapatite accompanies the tourmaline . This type of tourmaline typically shows concentric color-zonation, with a light bluish green core and a deep green to brown rim under crossed nicols . Reverse color-zonation has also been observed locally in some of the vein-hosted tourmaline. The second mode of occurrence is most common in tonalite porphyry. The tourmaline in this case is in general unzoned, but color zonation without major-element variation is present in some anhedral crystals Well-developed microscopic tourmaline suns are encountered in the matrix of the tonalite porphyry . In amphibole-bearing tonalite porphyry, tourmaline occurs as disseminated anhedral to subhedral grains and shows brown and bluish green pleochroism . Replacement of amphibole by tourmaline was observed in some cases Microscopic needles of tourmaline occur as fracture fillings in tonalite porphyry, with blue to colorless pleochroism .Secondary tourmaline also is present in tonalite porphyry in association with chlorite in the core of altered plagioclase. Tourmaline in this type of occurrence was developed at the expense of plagioclase. The compositions of tourmaline change slightly in terms of magnesium content toward the north side of the study area, where tourmaline-rich rock is encountered between the contact between the lower basic series and coarse granodiorite. In the third mode of occurrence, tourmaline forms small crystals and is associated with pyrite and magnetite. Late-stage tourmaline developed in fractured tonalite porphyry contains inclusions of subhedral to euhedral zircon and apatite

A series of NW-trending aplite and pegmatite dykes from a few meters to tens of meters in length and a few metres wide, occur in the study area, commonly in the granodiorite unit. Aplites are characterized by a fine grained equigranular assemblage of quartz, alkali-feldspar, some muscovite and opaque minerals. The petrology and geochemistry of the pegmatites have been described by Masoudi (1997). The pegmatites have a simple mineralogy with graphic texture and are characteristically composed of quartz, feldspar, muscovite and minor zircon and apatite, as well as local andalusite and garnet.

Thin tourmaline-rich layers are found along the boundary between granitoid and its contact aureole.

Tourmaline grains are typically zoned with black to blue-green cores, frequently with numerous quartz inclusions. The rims are yellow-brown in pyrrhotite-rich rocks or green-blue in pyrrhotite-poor rocks. The color change from the core to rim may be gradational or involve sharp optical discontinuities.

25 samples analyzed are mineralogically simple, consisting of quartz, muscovite, and tourmaline, which typically occurs in clusters of small (<1 mm), randomly oriented, prismatic crystals .

The tourmaline is strongly pleochroic, with bluish green .

Tourmalinite is a rock in which tourmaline and quartz are the dominant minerals. Minor amounts of muscovite are common. Accessory minerals include biotite, epidote, titanite, and garnet. Tourmaline and quartz are fine to very fine-grained (< 250 Am in length), and in thin sections cut normal to the lineation they display a granoblastic texture with interlobate to polygonal grain boundaries.

In thin section, tourmaline crystals display variable colors: pale to very dark green, bluish green, blue, orange and yellowish brown; but green colours predominate. Many tourmalines show distinct zones of dark green interiors and pale rims.

MATERIALS AND METHODS

For this study, we collected a total of 30 rock samples from different locations in the study area. Tourmaline analyses were obtained by wavelength-dispersive X-ray spectrometry on polished thin sections prepared from each rock sample for 12 elements using Cameca SX-100 electron microprobe using wavelength dispersive spectrometers at the Research Center for Minerals of Iran. Typical beam operating conditions were 15 kV and probe current 20 nA. Natural oxide and silicate mineral reference materials were used for calibration. Analytical errors on all analyses are 1% relative for major elements and 5% relative for minor elements.

Eight tourmaline samples were selected from a total of 30 samples, to represent the entire range of textural types present at the study area. In general a total of 65 point analyses were carried out on tourmalines from various rocks: three samples of leucogranite (23 points), one sample of pegmatite (10 points), three samples of quartz vein (25points), and one sample of hornfels (7 points). In general, a minimum of three analyses were taken per grain.

Structural formulae were calculated on the basis of 31 oxygens, assuming stoichiometric amounts of H₂O as (OH), i.e., OH + F = 4 apfu (atoms per formula unit). Since B and Li cannot be directly measured on the microprobe; B₂O₃ concentrations were calculated stoichiometrically to 3 B per formula unit. The amount of Li assigned to the Y site corresponds to the ideal sum of the cations occupying the T + Z + Y sites (15 apfu) minus the sum of the cations occupying these sites, i.e., [Li = 15 – (T + Z + Y)], assuming no vacancies in the octahedral sites (Henry and Dutrow, 1996). all Fe and Mn was assumed to be divalent, since crystal-structure studies have demonstrated that this is the most frequent valence state of Mn and Fe in tourmaline (Burns, 1994, Bloodaxe, 1999). The average composition of tourmaline grains from different rocks is presented in Table 1.

Table 1. Average chemical compositions of tourmaline from pegmatite, leucogranite, quartz veins and hornfels schist along with their structural formulae based on 31 (O, OH, F). The measured FeO is considered as Fe²⁺

Formula	F	Na ₂ O	K ₂ O	MgO	CaO	MnO	FeO	ZnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	TiO ₂	Total	O=F	Total	X	Y	Z
1/1.	0.12	1.6	0.03	5.1	0.59	0	7.51	1.11	33.95	0.3	33.37	1.77	85.45	0.05	85.45	11756	-32385	460
3/1.	0.21	1.73	0.04	5.55	0.73	0	6.97	2.1	34.49	0.05	33.54	2.55	87.96	0.09	87.96	11600	-32385	460
4/1.	0.07	1.76	0.03	5.57	0.66	0	6.33	1.88	35.15	0.09	33.71	2.1	87.35	0.03	87.35	11569	-32285	460
6/1.	0.26	1.67	0.06	4.32	0.81	0	8.49	2.63	34.25	0.05	32.12	3.12	87.78	0.11	87.78	12888	-18818	460
7/1.	0.25	1.7	0.06	4.18	0.9	0	8.96	1.2	34.15	0.23	33.78	1.18	86.59	0.1	86.59	12833	-18930	460
8/1.	0.33	1.68	0.07	4.17	0.87	0	9.01	0.9	34.1	0.16	33.82	1.68	86.79	0.14	86.79	12736	-18943	460
10/1.	0.09	1.81	0.02	5.5	0.6	0	7.32	3.08	32.93	0.06	32.68	3.7	87.79	0.04	87.79	2530	-19498	460
11/1.	0.11	1.54	0.01	5.25	0.63	0	7.7	2.25	32.79	0.16	32.62	3.95	87.01	0.05	87.01	2528	-19725	460
13/1.	0.44	2.04	0.08	5.18	0.76	0	9.4	0.76	32.29	0.5	35.13	1.2	87.78	0.18	87.78	-7538	-19375	279
14/1.	0.41	1.07	0.07	4.98	0.64	0	9.68	1	33.09	0.43	35.06	1.09	87.52	0.17	87.52	-7512	-19367	279
15/1.	0.41	2.05	0.06	5.24	0.61	0	8.77	1.06	33.76	0.4	35.2	0.76	88.32	0.17	88.32	-6781	-24856	279
16/1.	0.55	2.11	0.07	4.92	0.61	0	9.46	1.15	33.11	0.41	35.04	0	87.43	0.23	87.43	-6784	-24870	279
17/1.	0.42	2.04	0.07	4.94	0.61	0	9.3	0.38	32.65	0.47	35.66	0.93	87.47	0.18	87.47	-7021	-24823	279
19/1.	0.34	2.09	0.07	5.38	0.42	0	8.74	1.62	33	0.28	33.69	0.82	86.45	0.14	86.45	-3405	-31682	279
22/1.	0.43	2.07	0.1	4.56	0.45	0	10.75	0.84	32.72	0.27	33.46	0.74	86.39	0.18	86.39	-3418	-31695	279

8-1
8-2
8-3
22-4
22-5
22-6

Formula	F	Na ₂ O	K ₂ O	MgO	CaO	MnO	FeO	ZnO	Al ₂ O ₃	Cr ₂ O ₃	SiO ₂	TiO ₂	Total	O=F	Total	X	Y	Z
1/1.	0.08	1.71	0.03	4.22	0.68	0	9.39	1.07	32.96	0.09	34.48	1.32	86.03	0.03	86.03	-13054	28937	444
2/1.	0.15	1.9	0.06	4.62	0.3	0	8.69	1.25	33.35	0.04	34.59	2.12	87.07	0.06	87.07	-13329	29056	444
4/1.	0.37	1.71	0.06	4.43	0.27	0.17	9.63	1.03	32.93	0.05	33.78	2.03	86.46	0.16	86.46	-13453	28497	444
5/1.	0.28	1.91	0.05	4.98	0.67	0	8.76	1.35	32.66	0.02	34.63	0.69	86	0.12	86	-13007	29173	444
6/1.	0.17	1.83	0.05	4.52	0.39	0	9.33	1.21	32.86	0	33.94	0.99	85.29	0.07	85.29	-13173	23803	444
8/1.	0.21	1.88	0.03	4.18	0.36	0	9.44	1.51	33.07	0	33.72	0.79	85.19	0.09	85.19	-12940	23778	444
9/1.	0.08	1.79	0.07	4.32	0.3	0.22	9.51	1.71	33.06	0	34.15	1.05	86.26	0.03	86.26	-12695	23749	444
10/1.	0.14	1.89	0.04	3.6	0.19	0.27	10.06	1.55	33.03	0	33.71	1.65	86.13	0.06	86.13	-6250	20384	444
11/1.	0.15	2.08	0.11	4.8	0.31	0	8.94	2.28	32.26	0	33.83	1.65	86.41	0.06	86.41	-5992	20370	444
12/1.	0.27	1.84	0.03	4.81	0.23	0	9.82	2.67	32.6	0	32.67	2.26	87.2	0.11	87.2	-6651	20556	444
13/1.	0.24	1.01	0.02	4.58	0.08	0	9.93	0.89	33.42	0.01	33.79	1.21	85.18	0.1	85.18	12494	24543	444

14/1.	0.16	0.96	0.02	4.35	0.07	0	8.99	1.78	33.64	0	34.08	0.97	85.02	0.07	85.02	12489	24425	444
17/1.	0.24	1.89	0.06	4.73	0.36	0.07	8.85	1.29	33.37	0.01	35.09	1.38	87.34	0.1	87.34	13339	30610	235
18/1.	0.26	1.95	0.07	4.48	0.39	0.02	9.2	1.35	32.71	0	34.97	1.3	86.7	0.11	86.7	13339	30682	235
21/1.	0.14	1.92	0.04	4.36	0.37	0.06	9.57	1.17	33.09	0.02	35.56	1.2	87.5	0.06	87.5	13326	30630	235
22/1.	0.27	2.04	0.04	4.5	0.41	0.52	9.62	2.04	32.03	0	35.6	0.65	87.72	0.11	87.72	13522	30485	235
24/1.	0.25	1.65	0.04	4.28	0.22	0	8.89	1.52	34.48	0	35.35	0.34	87.02	0.1	87.02	8213	34066	235
25/1.	0.16	1.77	0.04	4.24	0.36	0	9.2	1.47	33.45	0.02	34.55	0.74	86	0.07	86	8021	33509	235

1-1
1-2
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20-4
20-5
20-6

Table 2. Trace element concentrations (ppm) of Mastroun tourmaline determined by ICP-MS

Formula	F	Na2O	K2O	MgO	CaO	MnO	FeO	ZnO	Al2O3	Cr2O3	SiO2	TiO2	Total	O=F	Total	X	Y	Z
1/1.	0.53	1.93	0.07	4.8	0.58	0.01	8.99	0.27	32.9	0.05	35.66	0.63	86.42	0.22	86.42	3786	-28644	402
2/1.	0.6	1.9	0.04	4.75	0.68	0	9.24	0.09	32.71	0.01	35.48	0.96	86.46	0.25	86.46	3669	-28651	402
4/1.	0.54	1.9	0.05	4.96	0.62	0.09	8.99	0	33.2	0.03	35.68	1.33	87.39	0.23	87.39	3445	-28791	402
5/1.	0.41	1.99	0.04	4.87	0.61	0.01	8.76	0.24	32.9	0.01	35.8	1.11	86.75	0.17	86.75	3480	-29024	402
6/1.	0.55	1.86	0.07	4.79	0.57	0	9.12	0	32.95	0.01	35.35	0.75	86.02	0.23	86.02	4171	-29056	402
14/1.	0.21	1.67	0.02	0.41	0.11	0.07	14.48	0.36	34.25	0	35.05	0.35	86.98	0.09	86.98	-5015	-29627	320
15/1.	0.37	1.82	0.05	0.49	0.13	0.25	14.48	0.14	34.19	0.03	34.97	1.03	87.95	0.16	87.95	-5047	-29627	320
16/1.	0.5	1.9	0.08	0.6	0.33	0	14.34	0.1	34.11	0	34.77	0.44	87.17	0.21	87.17	-5089	-29627	320
17/1.	0.62	1.72	0.03	0.57	0.17	0	14.45	0.18	34.34	0	34.8	0.67	87.55	0.26	87.55	-5168	-29653	320
18/1.	0.48	1.8	0.05	0.52	0.09	0.19	13.97	0	35.01	0.03	35.69	0.13	87.96	0.2	87.96	-5205	-29653	320
20/1.	0.48	1.67	0.05	1.13	0.12	0.05	13.32	0	33.91	0	34.67	0.64	86.04	0.2	86.04	-5707	-18890	292
21/1.	0.34	1.64	0.03	1.13	0.12	0.05	13.4	0.07	33.37	0.05	34.15	2.86	87.21	0.14	87.21	-5579	-18898	292
22/1.	0.4	1.7	0.04	1.18	0.14	0.12	13.47	0.19	33.59	0.03	34.47	0.86	86.19	0.17	86.19	-5514	-18891	292
23/1.	0.43	1.63	0.04	1.18	0.12	0.15	13.45	0.55	33.3	0.02	34.81	1.38	87.06	0.18	87.06	-5308	-18891	292
24/1.	0.34	1.7	0.05	0.94	0.08	0.12	13.43	0.24	33.68	0	34.75	0.84	86.17	0.14	86.17	-5006	-18961	292

3/1.
17/2.
17/3.

Formula	F	Na2O	K2O	MgO	CaO	MnO	FeO	ZnO	Al2O3	Cr2O3	SiO2	TiO2	Total	O=F	Total	X	Y	Z
1/1.	0.13	1.69	0.04	5.91	1.05	0	6.9	0	34.9	0.08	35.32	0.75	86.77	0.05	86.77	-3067	20871	399
2/1.	0.19	1.77	0.05	5.61	0.78	0	6.8	0	34.41	0.08	36.43	0.38	86.5	0.08	86.5	-3079	20868	399
3/1.	0.13	1.67	0.03	5.5	0.83	0	6.84	0	33.91	0.15	36.04	0.2	85.3	0.06	85.3	-3097	20868	399
4/1.	0.05	1.57	0.04	5.52	0.73	0	6.87	1.54	34.33	0.08	36.18	0	86.91	0.02	86.91	-3108	20859	399
5/1.	0.14	1.66	0.02	5.51	0.86	0.04	6.54	1.29	34.18	0.07	36.04	0.26	86.61	0.06	86.61	-3251	21117	399
6/1.	0.12	1.82	0.02	5.81	0.75	0.1	6.91	1	34.13	0.15	35.2	1.17	87.18	0.05	87.18	-3209	21494	399
7/1.	0.29	1.74	0.06	4.62	1.05	0	8.14	1.15	34.53	0.03	35.01	1.18	87.8	0.12	87.8	-5413	26741	399
8/1.	0.36	1.68	0.04	4.44	0.92	0	8.67	0	34.52	0	35.17	1.38	87.18	0.15	87.18	-5478	26741	399
9/1.	0.13	1.51	0.02	5.32	0.74	0	7.05	0	34.17	0.35	35.58	2.07	86.94	0.06	86.94	-5598	26741	399
10/1.	0.35	1.79	0.06	4.75	0.99	0	8.05	0	34.73	0.03	34.8	0.93	86.48	0.15	86.48	-5481	26629	399

26/3.
26/4.

Formula	F	Na2O	K2O	MgO	CaO	MnO	FeO	ZnO	Al2O3	Cr2O3	SiO2	TiO2	Total	O=F	Total	X	Y	Z
2/1.	0.17	1.79	0.05	6.12	0.89	0.3	6.47	1.34	34.48	0.02	35.32	0.9	87.85	0.07	87.85	8650	32228	259
4/1.	0.19	1.53	0.01	5.55	0.51	0	6.73	1.39	34.4	0.02	35.72	1.05	87.1	0.08	87.1	8692	32195	259
5/1.	0.19	1.53	0.01	5.52	0.7	0.1	7.21	0.64	33.98	0.04	35.91	0.74	86.57	0.08	86.57	8695	32190	259
8/1.	0.22	1.37	0	5.37	0.52	0	7.41	0.24	35.11	0	35.78	1.24	87.26	0.09	87.26	8663	32194	259
10/1.	0.23	1.67	0.03	5.67	0.62	0	7.41	0.48	33.42	0.01	35.67	1.09	86.3	0.1	86.3	7466	31898	259
12/1.	0.19	1.8	0.01	6.64	0.76	0	5.26	1	33.8	0.03	35.81	1.12	86.42	0.08	86.42	7213	32007	259
14/1.	0.15	1.64	0.02	5.84	0.86	0	6.87	1.58	32.89	0.04	35.64	0.81	86.34	0.06	86.34	7429	31883	259

28/1. تمامی مقادیر بر حسب درصد می باشد
28/2.

Tourmaline separates were prepared for 4 samples, using a combination of hand picking, magnetic separation, and heavy liquid separation. The separates were examined with a binocular microscope to remove contaminated grains.

They were ground by hand in an agate mortar and analyzed. The separates were also used for lithium and trace-element determinations by atomic absorption spectrometry. (1977). Data for 28, minor, and trace elements were obtained by ICP-AES using a high efficiency.

RESULTS AND DISCUSSION

Mineral Chemistry

The chemical composition of the study tourmalines determined by electron microprobe along with their structural formulae calculated based on general formula of tourmaline $XY_3Z_6T_6O_{18}(BO_3)_3(F,OH)_4$, (London and Maning, 1995), where X = Ca, Na, K, (vacancy); Y = Li⁺, Fe²⁺, Mg²⁺, Mn²⁺, Zn²⁺, Al³⁺, Cr³⁺, V³⁺, Fe³⁺, Ti⁴⁺, (vacancy); Z = Mg²⁺, Al³⁺, Fe³⁺, V³⁺, Cr³⁺; T = Si, Al, (B); B = B, (vacancy); V=OH, O; W= OH, F, O are presented in Table (1).

Table 1 provides chemical compositions of tourmaline from the various rocks studied. Calculations of site occupancies show that in almost all samples of our tourmaline, Si is insufficient to completely fill the tetrahedral sites; therefore, some Al is required to complete the T sites (Table 1). The six octahedral Z sites are fully occupied by Al and the three octahedral Y sites, slightly larger and more distorted, are occupied by different cations including Al, Ti, V, Mg, Mn, Fe²⁺, Zn and Li. In fact, the main compositional variable of tourmaline is the occupancy of the Y site. The sum of T + Z + Y cations is 15 indicating no vacancies in the T, Z, and Y sites and consistent with ideal formula of tourmaline. The occupancy of the X site by Ca, Na and K ranges from 0.33 to 0.76 apfu compared to the ideal value of 1.0 apfu for tourmalines of the schorl-dravite solid solution. This implies the presence of vacancies in the X-site ranging from 0.67 to 0.24. The X-site vacancy is smallest in hornfels tourmalines and largest in pegmatite ones (Table 1).

All the samples have Na dominant over Ca and K at the X site. The Ca contents are low with the range from 0.01 to 0.19 apfu.

The amount of B₂O₃ necessary to produce three B cations in the structural formula was calculated from stoichiometry. The triangular B site is occupied exclusively by B.

There is major variation in Fe content (1.01-1.96 apfu), but Al varies slightly between 6.50 and 6.76 apfu. In all cases, FeO contents are greater than MgO (Table 1).

Minor elements detected in the study tourmalines include K, Mn, Ca, Cr, and Zn. Among these, Zn displays the highest values, reaching on average 0.18, 1.19, 1.03 and 0.97 wt% in pegmatite, leucogranite, quartz veins and hornfels schist, respectively.

The classification and compositional details are best revealed by plotting the results of electron microprobe analyses on a series of compositional diagrams (Figs. 1-5). On the ternary (Ca, X-site vacancy, Na + K) diagram of Hawthorne and Henry (1999), except a few samples, the majority of samples plot in the alkali group field with minor X-site vacancies and Ca substitution for Na (Fig. 1).

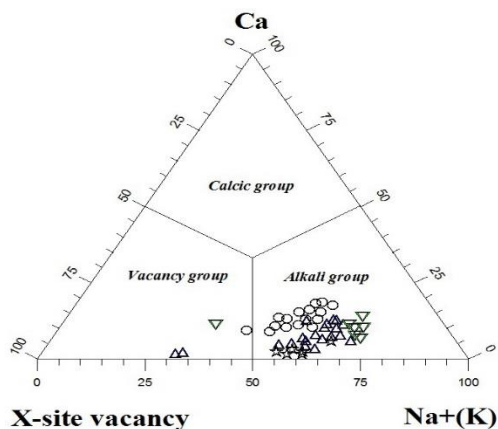


Figure 1. Geological map of the study area (adapted from 1/100,000 Varche geological quadrangle, Geological Survey of Iran)

The tourmalines are aluminous with the calculated Al in the structural formulae greater than 6 and up to 6.61 apfu. Al³⁺ occupancy is significant in the Y site of tourmalines from various rocks: in leucogranite 0.06 to 0.50 a.p.f.u. on average of 0.25, it is relatively high in pegmatite 0.38 to 0.67 a.p.f.u. on average 0.54, in quartz veins 0.01 to 0.51 a.p.f.u. on average 0.29, and relatively less in hornfels 0.05 to 0.27 a.p.f.u. on averages 0.17.

As all of the analyzed tourmaline specimens are aluminous (Al > 6 apfu), the best diagram for classification of the tourmaline species is established by Hawthorne and Henry (1999) in which X-vacancy/(X-vacancy + Na) is plotted versus Mg/(Mg + Fe). On this diagram, most of the tourmaline specimens fall within the schorl and dravite except a small number of them in foitite fields (Fig. 3). As it can be seen from (Fig. 2), tourmaline crystals from pegmatite have higher concentrations of Fe and lower concentrations of Mg than those found in the granite, quartz veins and country rock (Fig. 4).

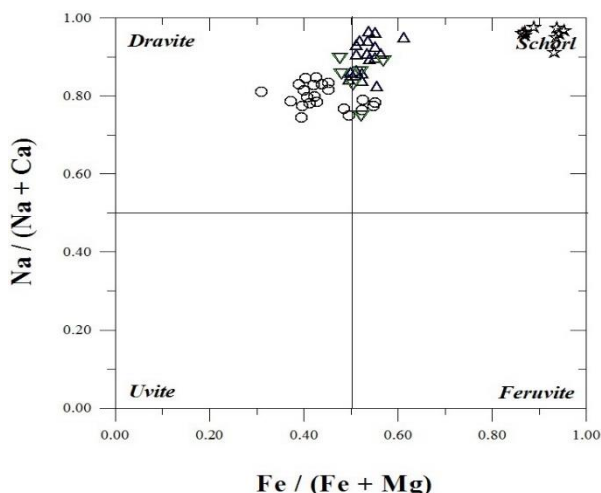


Figure 2. A view of the tourmaline outcrop

The tourmalines from quartz veins are slightly dravitic with respect to the rest which are intermediate in composition between dravite and schorl, with a slight tendency toward the schorl end-member (Fig.3).

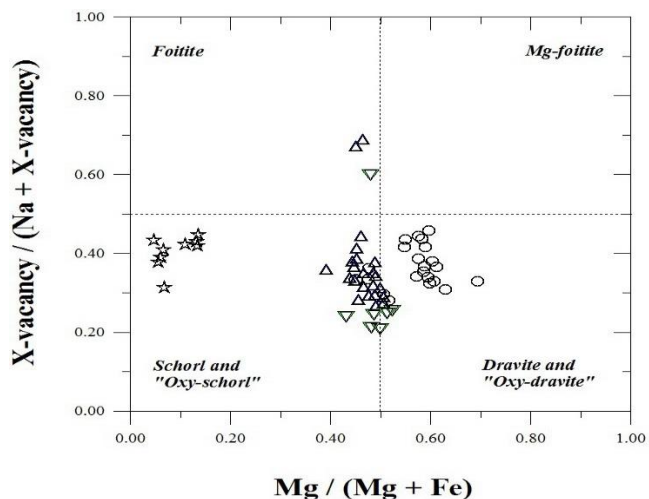


Fig. 3 A close up view of the tourmaline outcrop associated with quartz veins shown in Figure 2.

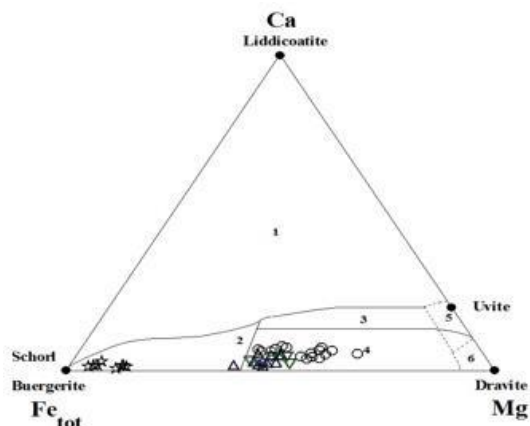


Figure 4. Radiating aggregates of tourmaline in the pegmatites of the study area

On the Mg versus Fe diagram of London and Manning (1995), tourmaline defines a compositional trend that corresponds closely to the dravite–schorl exchange vector $Mg^{2+} \leftrightarrow Fe^{2+}$ (Burt 1989). There is, however, a systematic departure toward alkali-deficient tourmaline and oxy-tourmaline, which is due to the occurrence of additional elements, such as Al, at the Y site.

The Fe/(Fe + Mg) ratio increases with Al in the Y-site (Fig. 5), and the values plot along the line $\Sigma(Fe+Mg) < 3$ are due to Al substitution in the Y-site.

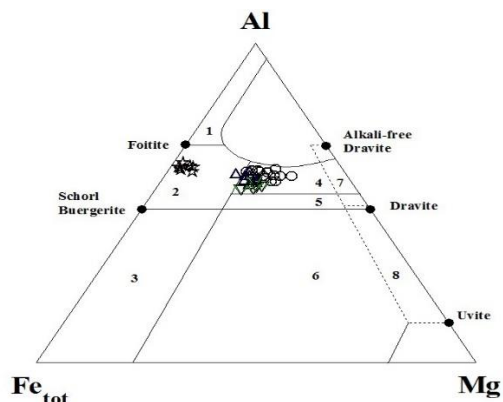


Figure 5 Plot of tourmaline from study area in Fe/(Fe+Mg) vs. Na/(Na+Ca) diagram

London and Manning (1995) have shown that substitution of Al^{3+} for divalent cations such as Mg^{2+} and Fe^{2+} in Y site is charge-compensated by deficit of alkalis and proton in other structural sites of tourmaline.

On the diagram of London and Manning (1995), the schorl-dravite composition plots at $Z=6$ and $X+Y=4$. Comparing with schorl-dravite, our compositional data which are plotted in terms of the cation groups, i.e., R3 versus $R1 + R2$ where $R1 = (Na+Ca)$, $R2 = (Fe+Mg+Mn)$, $R3 = (Al+1.33Ti)$. R1, R2 and R3 correspond to X, Y and Z cations of the tourmaline formula, respectively. All of the tourmaline compositions fall on or close to the proton deficient exchange vector implying alkali deficient substitution has been less effective than the proton deficient one on the composition of the study tourmalines. This suggests that the crystallization of tourmaline was mainly buffered by alkalis instead of H_2O . In fact H_2O -rich systems are favoring alkali-defect substitution (Gallagher 1988).

It should be noted that pleochroic color does not always correspond to the chemical composition. In other words, optical zonation which is originated possibly from the variation of Fe^{2+}/Fe^{3+} , does not correlate always with considerable chemical contrast. Conversely, some optically unzoned grains are zoned chemically. Anyway, it is possible to link the pleochroic color and zonation of tourmaline to its mode of formation, i.e. igneous or hydrothermal. Since the changes in pleochroic hue, intensity or zonation are not compatible clearly always with composition, backscattered electron images were applied to show compositional differences such as relative variations in Fe/(Fe+Mg) and approve if optical zonation correlates with chemical contrast.

The study tourmalines have some insignificant degree of uvite component with mean value of $Ca < 0.05$ apfu.

Figure (Mn+Fe+Mg versus Al+Li) shows that chemical variation in these tourmalines has been somehow controlled by elbaite substitution (LiAlFe_2), an indicator of fractionation and internal evolution of pegmatites and of compositional evolution of tourmalines in pegmatites (Keller, 1999; Roda-Robles, 2004).

On the Al-Fe-Mg and Ca-Fe-Mg diagrams of Henry and Guidotti (1985) which show the relationship between tourmaline composition and the host rock type, tourmaline compositions from pegmatite exclusively plot in field 2, which corresponds to tourmaline from Li-poor granitic rocks and associated pegmatites and aplites, and those from leucogranite, quartz veins and hornfels schist plot in field 4, corresponding to Ca-poor metapelites, metapsammites and quartz-tourmaline rocks. What seems inconsistent here is that tourmaline from leucogranite does not display compositions typical of Li-poor granitoids and their associated pegmatites and aplites, i.e., its composition is similar to tourmaline of Ca-poor metapelites and metapsammites and quartz-tourmaline rocks. It is known that the metapsammites are metamorphosed feldspathic sandstones which can be approximately similar to the mineral contents of the study leucogranite, and then it may imply that the compositions of tourmaline are fully consistent with field and petrography observations.

All studied tourmalines show some elbaite component, as they lie below the line of $R_2^* = 3$ a.p.f.u.

Tourmaline taken from the pegmatite has the highest Fe/Mg value, whereas, tourmalines from the leucogranite, quartz veins and country rock show the lowest Fe/Mg value.

Aluminum-rich tourmaline generally contains enough Al to fill completely the Z site; excess Al is located in the Y site according to the $\text{AlOMg}_1(\text{OH})_1$ and AlNa_1Mg_1 substitutions (Henry and Dutrow 1990).

In lithium-poor aluminous tourmaline, calcium incorporation in the structure can be controlled by the dominant $\text{CaMgO}_{-1}\text{Al}_1(\text{OH})_1$ substitution and, to a lesser extent, CaMgNaMg_1 and $\text{AlOMg}_r(\text{OH})_1$. Henry & Dutrow (1990) pointed out that in cases of $\text{CaMgOMn-rAl-r}(\text{OH})_r$ as the dominant mechanism of substitution in aluminous tourmaline, there should be a general inverse correlation between Ca and X-site vacancies, and a poor correlation between Ca and Na. This substitution develops only in tourmaline in relatively aluminous bulk compositions, and is associated with significant X-site vacancies (Henry & Dutrow 1990). In all 65 analyses, the T site of tourmaline is almost fully occupied by Si (5.87 -5.98 atoms per formula unit [apfu]). The tourmaline is aluminous, with total Al ranging from 6.09 to 7.02 apfu. In terms of Fe and Mg contents, our samples have a broad range of Fe/(Fe + Mg) ranging from 0.38 to 0.85. Note as it can be seen from Table (1) Fe is reported as Fe^{2+} in the electron microprobe analyses.

Aluminum-rich tourmaline generally contains enough Al to fill completely the Z site; excess Al is located in the Y site according to the $\text{AlOMg}_r(\text{OH})_1$ and $\text{nAlNa}_1\text{Mg}_r$ substitutions (Henry and Dutrow 1990).

Higher values of Al in Y-site (Table 1) may suggest AlOMg_1 and AlNa_1Mg_1 substitutions (Harras and El-Sharkawy 2001).

On the diagram of London and Manning (1995) in which Al in R_2 ($R_2 = \text{Al} + 1.33\text{Ti} + \text{Si} - 12$) is plotted versus R_2^* ($R_2^* = \text{Fe} + \text{Mg} + \text{Mn} + \text{Al}$), some elbaite substitutions can be revealed in our samples (Fig. 9d). The scattered data on the Na versus Ca plot indicate other substitutions like AlNa_1Mg_1 may have occurred displaying vacancies in X-site (Pesquera et al. 1999). Similarly, uvite substitution is insignificant in our tourmaline data as inferred from the plot of $\text{Ca} + \text{Mg}^*$ versus $\text{Na}^* + \text{Al}^*$ of Henry and Dutrow (1990) in which their parameters are defined as $\text{Mg}^* = \text{Mg} + \text{Fe} + \text{Mn} + 2\text{Li} - \text{Ti}$, $\text{Na}^* = \text{Na} + \text{K}$, and $\text{Al}^* = \text{Al} + \text{Fe}^{3+} + 2\text{Ti} - \text{Li}$.

As it can be seen from Figure 11 tourmalines plot in field 4 are above the schorl–dravite line with $(\text{Fe} + \text{Mg}) < 3$ suggesting yet again insignificant uvite component in these minerals.

Discussion

Based on geologic, petrographic and geochemical data, the infiltration of large volumes of B-rich fluid may have been focused along lithological boundaries and shear zones around the pluton. B-rich fluids must have been derived from external system. Boron-rich hydrothermal fluids exsolved from a magmatic source and expelled into the surrounding rocks is a likely source.

Comparison of our data with compositional fields of tourmalines with known origins (from Henry and Guidotti 1985) indicates that Psammopelitic metasediments are most likely the protholith. Since psammopelitic metasediments contain enough Al, Mg, Fe, Ca, and Na to form tourmaline through reaction of boron-rich fluids with feldspar, phyllosilicates and other minerals (Morgan and London, 1989; Fuchs and Lagache, 1994). Therefore, tourmaline-rich rocks formed as a result of the metasomatic replacement of psammopelitic rocks by boron-rich hydrothermal fluids that were derived from adjacent felsic magma.

The origin of the quartz veins could be related to hydrothermal fluids connected to local magmatic activity, to a process of metamorphic remobilization, or to separate epigenetic processes. Field relations show that the tourmaline-quartz veins may be related to nearby felsic plutonic intrusions.

The abundance of tourmaline in the quartz veins suggests high concentrations of boron in the hydrous silica-bearing fluids or long-term supply or abrupt change in P-T-X conditions. Boron could be released into circulating

fluids from sedimentary precursor rocks by increasing temperature or complexing with other phases. Possible sources of these fluids include the host sedimentary precursor-rocks of the tourmaline-bearing veins, complex through-going hydrothermal solutions, or magmatic or postmagmatic fluids. In any case, we infer that the B-enriched fluids reacted with the host rocks along zones of structural weakness or narrow fractures and through inter- or intragranular pore-space. The reaction involving the B-enriched fluids mixed with permeating meteoric waters and the country rocks resulted in the breakdown of early phyllosilicates and stabilized a tourmaline-bearing assemblage.

According to London and Manning (1995), quartz-tourmaline veins within granitic bodies reflect a hydrothermal origin rather than a magmatic origin.

The origin or source of the boron will be left unanswered in this study and its isotopic determinations are planned for the future study.

Nodular tourmaline from Astaneh granite and tourmaline from aplite and pegmatite show similar chemical composition.

The composition of tourmaline from different types of GG and the hydrothermal quartz veins is intermediate between end members schorl-dravite (Fig. 6.1, 6.4 and 6.5). Foit and Rosenberg (1977) reported both alkali-defect and dehydroxylation substitutions can produce the intermediate composition between schorl-dravite end-member. The tourmaline from the study area shows optical zoning of different shades of blue and green, which could be related to another common substitution called dehydroxylation substitution involving $(\text{Fe}^{2+} \text{OH}^-) = (\text{Fe}^{3+}, \text{O}^{2-})$. The dehydroxylation and alkali-defect substitution are common between schorl-dravite series. The substitution between Fe^{2+} and Fe^{3+} is also one of the factors responsible for the colour zoning in tourmaline (Dietrich, 1985).

Tourmaline is a relatively common phase in leucocratic peraluminous granites and starts to crystallize when the aluminum saturation index (ASI) of magma reaches a value between 1.3 and 1.4, B_2O_3 is concentrated to a value of ~2 wt%, and sufficient Fe and Mg are available in the melt (London & Manning 1995, London, 1996, Wolf & London 1997). Tourmaline is unstable in peralkaline, metaluminous and slightly peraluminous melts with an ASI less than 1.2 (Wolf & London 1997).

As the study leucogranite composed of feldspar and quartz without any Al-rich or Fe-Mg bearing minerals (e.g., muscovite and biotite), it seems that none of the above conditions exist in the study rocks to meet the situation for direct crystallization of tourmaline.

The isolated, relatively homogeneous prisms or interstitial grains disseminated as a minor or accessory phase in pegmatite. In this case, this type of tourmaline crystallized directly from the magma, and is here referred to as primary tourmaline.

Tourmaline occurs in hydrothermal veins and breccias in the marginal parts of intrusions and in their country rocks. This type of tourmaline may form massive tourmalinites, quartz-tourmaline veins, or may be related to ore deposits in skarn or greisen. Its chemical composition generally represents a mixture of boron derived from a magmatic intrusion and major (Fe, Mg) and minor components derived mostly from the country rocks.

Several previous investigators have documented the chemical evolution of tourmaline with magmatic differentiation or have compared primary magmatic to late-stage hydrothermal tourmaline (Trumbull & Chaussidon 1999, Trumbull, 2007, Buriánek & Novák 2007, Jiang, 2008). However, most studies have focused on a particular stage of granite evolution, and few studies have documented a complete sequence of tourmaline generations from primary magmatic to the pegmatitic and miarolitic stages to the hydrothermal impregnation of the country rocks (e.g., London & Manning 1995). Furthermore, most studies are based on incomplete chemical analyses, lacking elements such as Li, H and the halogens, and thus providing an incomplete picture of the chemical evolution of tourmaline.

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