Major and trace element geochemistry of tourmaline in feldspathic schist & tourmalinite from Pathargora & Surda, Singhbhum shear zone, eastern India

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Certified that the dissertation entitled "***Major and trace element geochemistry of tourmaline in feldspathic schist and tourmalinite from Pathargora and Surda, Singhbhum Shear Zone, eastern India***" submitted by **Ayan Sasmal** for the partial fulfilment of the M.Sc. Final Year, Final Semester Examination in Applied Geology, 2019, Jadavpur University embodies the results of studies carried out by him under my supervision and guidance. This work has not been submitted elsewhere for the award of any other degree.

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ABSTRACT:

Tourmaline super group of minerals are often found as accessory minerals in the rocks of the earth crust. Tourmaline composition is used as petrogenetic indicator. Because of its sensitivity to secondary processes and negligible diffusion, it can infer the physic-chemical ambience of the host environment. Tourmaline from Pathargora area is mainly associated with feldspathic schist and tourmaline from Surda area is mainly associated with tourmaline bearing quartzite. Both the regions are located in eastern part of Singhbhum shear zone (SSZ) and suffered alteration. Singhbhum Shear Zone is one of the most important mineralized area of India and it hosts uranium, copper and sulphide mineralization. Tourmaline samples are classified into two broad category – altered and unaltered sample from both the region. Field observations, Petrographic study and microprobe data document a multi-stage formational history of tourmaline samples. In most of the cases brown or yellowish brown tourmaline is replaced by blue tourmaline along grain boundary or micro fracture. Pathargora altered tourmaline is characterized by large variation of Ti content whereas the unaltered tourmaline from Pathargora and both the altered and unaltered tourmaline from Surda contain a constant amount of Ti. Blue tourmaline grains are rich in Mg and poor in Al whereas brown tourmaline is rich in Fe, Al. Alteration pattern indicates the ingress of hydrothermal fluid. Tourmaline grains with brown core and blue rim and replacement texture shows that blue tourmalines formed through a late hydrothermal event. The compositional variations can be explained by a combination of coupled substitutions represented by $Fe^{2+} \leftrightarrow Mg^{2+}$, $^{X}R^{1+} + R^{3+} \leftrightarrow {}^{X}Ca + R^{2+}$ and $^{X}R^{1+} + R^{2+} \leftrightarrow {}^{X}\square + R^{3+}$ and $Ti + R^{2+} \leftrightarrow 2\ R^{3+}$. The $^{X}R^{1+} + R^{3+} \leftrightarrow {}^{X}Ca + R^{2+}$, $Ti + R^{2+} \leftrightarrow 2\ R^{3+}$ and $^{X}R^{1+} + R^{2+} \leftrightarrow {}^{X}\square + R^{3+}$ substitution occurred in both this two region. Trace element data of tourmaline shows a strong positive Eu anomaly. This study incorporates field study, petrographic study and major and trace element composition which can potentially identify different generations of tourmaline.

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CHAPTER 1

INTRODUCTION:

1.1 ORIGIN OF THE PROBLEM

The project titled ‘Major and trace element geochemistry of tourmaline in feldspathic schist & tourmalinite from Pathargora & Surda, Singhbhum shear zone, eastern India. Present study aims to characterize tourmaline texturally and compositionally from two different host rocks, i.e; feldspathic schist and tourmalinite. This study also aims to propose a substitution scheme to explain the geochemical variation. Because of its structure, tourmaline has the capability to incorporate various kinds of ion. It is a common accessory mineral found in very low P, low T diagenetic condition to granulite facies of metamorphism (Morgan & London1989, Marschall1 & Jiang 2011**).** This mineral can be associated with each of the major three types of rocks, i.e; igneous, metamorphic, sedimentary. Most importantly it can record primary information which can be used as a proxy with the physical and chemical ambience at that time. So they can be used as a petrogenetic indicator. This study area i.e. Pathargora and Surda belongs to Singbhum Shear Zone which is one of the most important proterozoic poly-metallic belts in India. It hosts several Uranium (U), Copper (Cu), apatite and magnetite deposits. Nickel (Ni), cobalt (Co), gold (Au), silver (Ag), tellurium (Te) and molybdenum (Mo) also have been recovered as by-product of Uranium-Copper mining. Most of the previous literature characterize tourmaline with the aid of major element concentration only. This study incorporates trace element concentration as well as major element concentration. So detailed study will add a valuable insight in understanding the nature of mineralisation in the eastern part of Singhbhum shear zone. To understand a ore deposit it requires a detailed study of ore mineral as well as gangue mineral and their association in space and time. From magmatic ore deposit point of view it is easy to find a genetic link between the mineral and the magma but in case of hydrothermal ore deposit it is quite difficult. So by studying the mode of occurrence and compositional differences in tourmaline samples from the eastern part of the Singhbhum Shear Zone may give a proper understanding of the ore genesis model.

1.2 GENERAL INFORMATION ABOUT OUR AREA OF STUDY:

Present study was carried out in two different location in the eastern part of Singhbhum shear zone namely Pathargora (22º 32’ 27.9” N 86º 27’ 0.10” E) & Surda (22º 32’52.90”N 86º 26’ 15.70” E). Both these two areas are geologically located in the eastern segment of Singhbhum Shear Zone (Eastern India).

CLIMATE:

Our study area in and around Pathargora and Surda features a tropical wet and dry climate according to the climate classification system made by climatologist Wladimir koppen (natural vegetation is the best expression of climate).Summers start in mid-March and can be extremely hot in May and June. The temperature variation during summer is from 35 to 49 °C (95 to 120 °F).The climate of this area is marked by south-west monsoon and gets heavy rainfall from July to September and receives about 1,200 mm (47 in) of rainfall annually.

WATER RESOURCES:

Subarnarekha is the most important river that flows towards east leaving the Chotonagpur Plateau behind to reach West Bengal and finally in Bay of Bengal. So it is the prime source of water which is located in the area under observation.

1.3 OBJECTIVE OF THE STUDY

In the previous section it is mentioned that this study incorporates trace element geochemistry as well as major element geochemistry to understand ore forming process. So our study aims on-

1. Identification of different host rocks of tourmaline and their field occurrence and study of host rock mineralogy.

2. Petrographic observations of tourmaline and their mode of occurrence with other minerals and therefore characterize the different texture

3. Study the compositional variations in tourmaline and geochemical characterization of samples geochemical tools.

4. Propose an efficient substitution scheme which reflects the way of substitution occur

1.4 METHODOLOGY

The methodology incorporated for doing this project can be subdivided into two groups-

1. Field Studies 2.Laboratory methods.

1. 4.1 Field Studies

Field studies were done during the time interval of 24th February to 28th February, 2018 which include detailed identification and sampling of rocks and observe & understand their field of occurrence. Samples were collected from different location and lithology.

1.4.2 Laboratory studies

Laboratory work mainly includes of detailed mineralogical and petrographical observations. For mineralogical and petrographical analysis thin sections are prepared. Microscopic studies were carried out using a Nikon H600L microscope. EPMA (Electron Probe Micro-Analysis) were done on the slides to get the oxide percentage. Major elements (major oxide) can be measured through EPMA analysis. LA-ICPMS (Laser-Ablation-Inductively Coupled Mass Spectrometry) were done on the slides to get the concentration of different elements.

1.5 SCOPE OF THE PRESENT WORK

Present study aims to inspect the geochemical characterisation of different tourmaline samples from Pathargora and Surda areas of the eastern part of the Singhbhum Shear zone during the present course of this thesis work. However one of the most important attributes of this project is to understand the possible mechanism for the geochemical variations.

CHAPTER 2

GEOLOGICAL BACKGROUND

The chosen area for our field work is located in and around Pathargora and Surda .This area belongs to the eastern part of the Singhbhum Shear Zone (SSZ) of Eastern Indian Shield (EIS). In this chapter we are going to discuss the regional and the local geology of the study area.

2.1 REGIONAL GEOLOGY:

The ~200 km long and ~1–5 km wide Singhbhum shear zone separates the Proterozoic North Singhbhum Fold Belt on the north and the Archaean Singhbhum cratonic nucleus on the south (Pal et al, 2010). The arc-shaped belt of the Singhbhum Shear Zone (SSZ), with extensive occurrences of mylonites and phyllonites, is developed close to the contact between the fold belt and the Archaean nucleus (Sarkar and Saha 1977, Sengupta et al 2005). The Precambrian belt of Singhbhum has an Archean nucleus containing granite, granite gneiss, and supracrustal rocks ranging in age from 3 to 3.4 Ga (Sharma et al. 1994, Sengupta et al, 2005).The Singhbhum craton is a granite-greenstone terrain comprising (i) Singhbhum granite (Phase A& Phase B) and (ii) The iron ore group consisting Iron ore basin (with Iron Ore Group greenstone sequence; ~3.3–3.5 Ga; Mukhopadhyay et al., 2008) occupy the north western part of the cratonic nucleus (Pal et al,2010). Available geochronological data (Moorbath et al. 1986; Saha et al. 1988; Saha 1994; Sharma et al. 1994; Mishra et al. 1999) indicate that the craton formed between the period ∼3.5 and ∼3.1 Ga. The Dhanjori Group is represented by vesicular basalts (locally pillowed), and komatiite with intercalated arkose, feldspathic arenite–litharenite/lithic wacke, and pelitic meta-sediments (Mazumder and Sarkar, 2004; Pal et al 2010). The North Singhbhum Proterozoic fold belt contains thick volcanic and inter-bedded meta-sediments, metamorphosed in greenschist to amphibolite facies. It abuts against the

Chotonagpur Gneiss in the north, and its southern boundary is demarcated by a deep-seated fracture, described as the Singhbhum Shear Zone. The SMB consists of two geologically distinct parts namely the Dalma Range and the Singhbhum Shear Zone (SSZ). The Singhbhum Group (Siliciclastic rocks) is inferred to have been deposited in a shallow to deep marine environment with later transition to mostly terrestrial (fluvial-aeolian) or shallow marine environment (Mazumder, 2005). The rocks in the Singhbhum Shear Zone are kyanite-quartzite, kyanite- muscovite -schist, apatite-magnetite rock, biotite-muscovite-schist, quartz-chlorite-schist, quartz-sericite -schist, quartz-biotite-schist, quartzite, meta-conglomerate, tourmalinite, soda granite/feldspathic schist. “Soda granite” is bit controversial to many authors and they thought them to be product of Na-metasomatism of meta-basic/metasedimentary rocks (Banerji and Talapatra 1966; Sarkar 1984) containing fine-grained variable proportions of quartz, potash-feldspar and albite. The Singhbhum brittle–ductile shear zone (SSZ) cuts across rocks of Iron Ore Group Dhanjori Group and the Singhbhum Group (Pal et al, 2010).

The SSZ rocks show a well-developed mylonitic foliation with conspicuous down-dip stretching lineation (Sengupta et al, 2010). The Singhbhum Shear Zone represents a deep-seated tectonic boundary (Sarkar and Saha 1962; Naha 1965; Banerji 1981), where the rocks of the northern fold belt were thrusted southward onto the Archean cratonic nucleus (Ghosh and Sengupta 1987, 1990; Mukhopadhyay and Deb 1995). Compression and progressive ductile shearing associated with this southward crustal movement resulted in south-vergent isoclinal folds (F1) with SE–NW/E–W fold axes, development of pervasive mylonitic foliation that dips steeply to the NE/N, and formation of down-dip mineral lineation (Ghosh and Sengupta 1987, 1990). That the mylonitic foliation is parallel with the axial planar cleavage in the northern fold belt and folding of mylonitic foliation indicates that ductile shearing initiated early in the evolution of the SSZ. A second generation open, sub-horizontal asymmetric folds

(F2), parallel to the SSZ, with shorter southern and longer northern limbs mark the waning stage of this southward crustal movement (Ghosh and Sengupta 1987). The third generation of less intense, locally developed gentle upright folds (F3), transverse to the shear-zone trend, occur either as fine crenulations or warps. Several generations of quartz veins formed during this kinematic evolution of the SSZ, which were thoroughly, or incipiently mylonitized (Sengupta and Ghosh 1997). The prograde metamorphic event (M1) grades into epidote-amphibolite transition facies and had a pressure, temperature regime 6.4+-0.4 kbar, 480+_40^{0}C (Sengupta et al,2005).The retrogression event (M2) was exemplified by hydration of the M1 assemblages which was outlasted the shear deformation. . Finally, multiple stages of brittle deformation followed the ductile shearing stage (Srivastava and Pradhan, 1995).

2.2 LOCAL GEOLOGY:

The present study was carried out in and around two different areas namely Pathargora 22º 32’ 27.9” N 86º 27’ 0.10” E) and Surda area (22º 32’52.90”N 86º 26’ 15.70” E).In Surda there is a small exposure (hillock type) of tourmalinite .Other than this there present quartzite hillock . In pathargora area several kinds of rocks are there. Feldspathic schist, chlorite--biotite schist, apatite-magnetite pocket which are hosted by biotite-Schist. In general, however, the rocks in and around Pathargora and Surda are represented mainly by Singhbhum group of meta-sedimentary rocks. The litho-types belonging to Chaibasa Formation of Singhbhum Group of meta-sediments are represented mainly by polymictic conglomerate, quartzite, quartz-sericite schist, quartz-chlorite/chlorite-quartz schist, quartz-chlorite-sericite schist, Quartz - tourmaline-rock (tourmalinite), pyrophyllite-rich sericite-quartz schist and feldspathic schist/gneiss. The meta- sedimentary rocks overlie the Singhbhum Granite exposed on the south-west of Pathargora.

Singhbhum granite

Singhbhum granite composed of predominantly of quartz, feldspar .The rock is coarse-grained and nearly massive in nature, with weakly developed foliation at places but interlocking texture can still be identified and the foliation display a general attitude of 262°/68° towards northwest.

Conglomerate

Conglomerate with large clasts (up to about 30 cm in long direction) are present outside the study area. A continuous body of conglomerate are found at SW of Bhatin mine which is underlain by a country rock of chlorite-biotite schist (22º 39’53.2” 'N/86º 19’29.1”E).The conglomerate is clast supported polymictic conglomerate. Composition of clast is mainly quartz (rounded), feldspar and disseminated grains of magnetite. Magnetite is also present in the matrix. There are black veins cutting across many of the clasts. The clasts are highly elongated in both X and Y-direction of strain ellipsoid attaining the shape of ellipsoid to lenticular. This veins have magnetite, apatite and tourmaline. Previous study shows that veins containing magnetite have Cr-rich core. The largest clast’s length and width are 50cm and 16cm respectively. The magnetite-rich conglomerates are commonly strongly radioactive, with about 15-20 times higher radioactivity than the background.

Quartzite

Quartzite exposed in both (Pathargora & Surda) the study area is mineralogically and texturally diverse. In both the areas quartzite occurs as small hillock. Near pathargora quartzite shows slickenslide surface where mineral lineation has developed. It is occurring close to the feldspathic Schist . Quartzite belonging to Chaibasa formation are laterally not persistent. Some of these quartzite are nearly massive in character, while some are distinctly banded with alternating quartz-rich and magnetite-rich bands. In Surda area quartzite also appeared as a hillock. In both the areas conjugate fracture have been seen. Schistosities are prominent in micaceous-quartzite, containing sericite.

Feldspathic schist

The rock is mainly schistose in nature but weakly developed alternative bands of dark coloured and light coloured minerals are present. Light coloured band is defined by mainly quartz and kaolinite, albite, sericite (secondary alteration of muscovite) and minor apatite. Dark coloured band is defined by mainly biotite (80%), magnetite and fine grained tourmaline (not in everywhere). Chlorite is also present within the dark band but abundance is very low. Biotite is defining the schistosity. Some lumpy hard black coloured and rounded minerals (resistive to weathering process) are present on the schistose plane with an extremely high abundance (near about 35%). These are tourmaline minerals. Tourmalines are present on the alternative unites of schistose rock. Foliation wraps around these cluster. In some places biotite and magnetite pockets are found and general schistosity wraps the pockets.

In southern part there is a mafic unit below this upper protolith which is almost devoid of felsic part. Malachite is present in very low abundance).In the northern part quartz grains are found to be extremely fined grained. Quartz grains associated with apatite magnetite are coarser in nature.

Chlorite-quartz schist

Chlorite-quartz schist or quartz-chlorite schist is melano-cratic, fine- to medium-grained schistose rock comprising variable proportions of quartz, chlorite, magnetite, apatite and sericite. Volume proportion of quartz and chlorite varies at different exposures of the rock. Thus may be termed as quartz-chlorite schist or chlorite-quartz schist depending on the most dominant mineral. The volume proportion of chlorite is ≤ 50 vol. percent of the rock. The prominent schistosity plane in the rock is defined by chlorite grains. Prominent zones of silicification exemplified by foliation-parallel quartz veins are common. Additionally, quartz-tourmaline veins and quartz-chlorite veins are also noted.

Quartz-tourmaline rock/ Tourmalinite

Quartz-tourmaline rich rock or tourmalinite (>15%) present as discontinuous small hillock. Sedimentary structure in the form of cross-lamination are there, although this structure is not persistent throughout the rock. Alternate dark and light colour bands are there .These are compositional band, one is tourmaline –rich and the other is tourmaline poor. At places, within the exposure, extremely dark coloured, fragmented /brecciated clast of tourmalinite are there. Around the tourmalinite clast a light coloured thin film of less darker tourmaline are present. Besides this two types of occurrence of tourmalinite there present a massive variety of tourmaline. The tourmalinite in Surda area is fine-grained black coloured, comprising mainly of quartz and tourmaline, the modal proportion of the later locally exceeds 50-60 vol. %. Tourmaline in the Pathargora area is coarser-grained compared to that in Surda area and the volume proportion of tourmaline is much less compared to that in Surda area. Quartz dominates over tourmaline in this rock and the rock appears more to be tourmaline-bearing quartzite.

Somewhere massive very fine grained tourmaline rich bands are present within the quartz-tourmaline rock quartzite which may not be of same generation of original quartz-tourmaline country rock. In some cases these layers are associated with some quartz veins which cut across the original quartz-tourmaline fabric. Secondary copper minerals i.e; malachite are present as patches at some places. The rock body strikes 235-250° and dips 35-50° towards northwest. Mineral lineation is measured on the rock body as 44° towards 35-42°.

Biotite-chlorite Schist

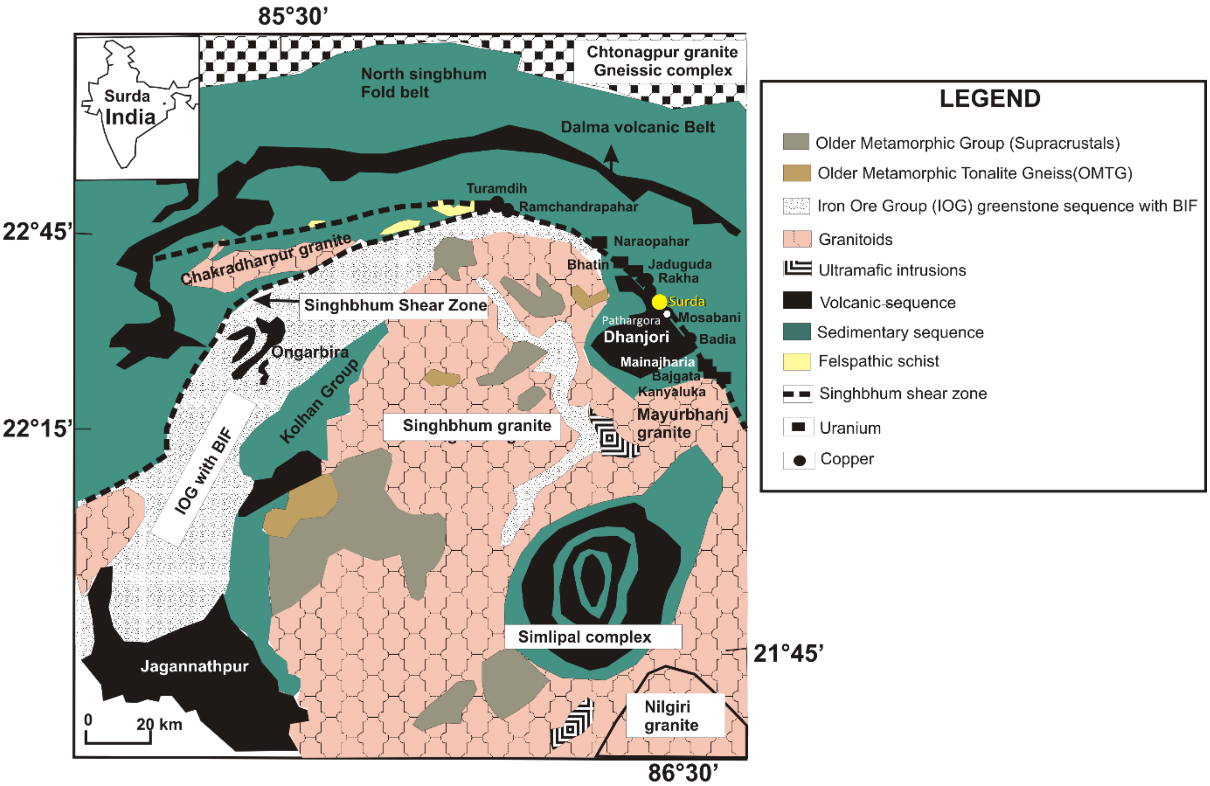
The host rock comprises predominantly biotite and chlorite, fine-grained quartz .The rock is showing extensive foliation. There are veins of apatite-magnetite-quartz. These veins are showing asymmetric to sheath fold perpendicular to foliation plane. A massive pocket of magnetite in the southern part of shear zone is found which is completely devoid of apatite. This body cuts the foliation plane at high angle and has a lenticular shape.

Chlorite-quartz-sericite schist

Chlorite-quartz-sericite schist appears to be one of the most extensive rock types in the area. However, due to the low preservation potential they are mostly soil covered and reasonably large exposures are present only when this rock is silicified, exemplified in the form of quartz veins, which we frequently confront during our fieldwork. The less-deformed and metamorphosed variety of this rock locally preserves the original sedimentary structures e.g. convolute laminations, cross-bedding etc.

Dolerite

Several dolerite dykes are present in the study area. The rock is medium-grained melanocratic in nature comprising mainly pyroxene, amphibole and feldspar. The rock is showing interlocking texture and exposes at the surface as a linear body. Volume proportion of mafic to felsic minerals is almost 60:40 (from the weathered surface). These dykes do not show any deformation fabric and perhaps indicate their emplacement postdating the main deformation event or at the closing stage of deformation.



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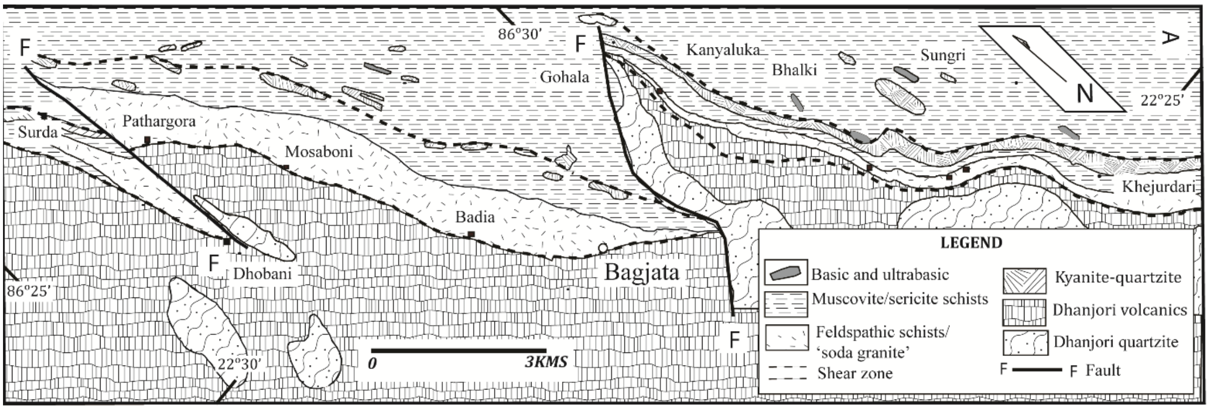

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Fig 2.1 A) Simplified geological map of eastern Indian shield (redrawn from Pal et al, 2010)

B) geological map in an around Pathargora and Surda (Pal et al, 2011)

Chapter 3

DESCRIPTION OF HOST ROCKS AND MODE OF OCCURRENCES OF TOURMALINE

For the present investigation on mode of occurrence and geochemistry of tourmaline, samples were collected from two different rock types namely feldspathic schist and tourmalinite/ tourmaline-bearing quartzite. The feldspathic schist and tourmalinite occur at Pathargora and Surda areas respectively in the Singhbhum Shear Zone. All these rocks contain tourmaline mainly as clusters or as disseminated grains. In the following sections, firstly the rocks that contain tourmaline are described followed by the different modes of occurrences of tourmaline.

3.1 Description of host rocks of tourmaline:

Feldspathic schist:

The rock under study is strongly deformed and schistose, with intense mylonitic foliation It is composed predominantly of quartz and albite with varying proportions of tourmaline, sericite, biotite and chlorite. Minor ilmenite and magnetite are also present. In general the rock is leucocratic and fine-grained in hand specimen (Fig 3.1 C) However, locally high abundance of biotite imparts dark color to the rock. The specific gravity of the feldspathic schist is generally low but when it contains tourmaline, the Sp. gravity of the rock becomes moderate. Nodular aggregates of tourmaline stand out on the surface as weathering resistant material imparting blistery look to the rock. (Fig 3.1C). Tourmaline occurs as nodular aggregate as well as isolated grains in the quartzo-feldspathic matrix. At places small rounded apatite grains are also present. Although albite is the dominant feldspar, minor K-feldspar is also present, the latter is commonly altered to kaoline.

The rock is strongly foliated foliated (Fig 3.1A and 3.1B), the foliation being defined by sericite, chlorite and biotite and stretched quartz grains.

The foliation warps around nodular aggregate of tourmaline, large porphyroclastic tourmaline and albite augens, the latter is defined by albite aggregate. Very fine-grained ultra-mylonitic albite bands also warp around tourmaline.

Tourmalinite /Tourmaline –bearing rock:

The quartz-tourmaline rich rock or tourmalinite in Surda area occurs as mount like exposure in quart-chlorite schist country rock is hard and compact and either banded or massive. At places sedimentary structures such as cross-lamination [Fig 3.1 E] are seen. The rock is composed .composed predominantly of quartz and tourmaline [Fig 3.1 D and 3.1 F]. At places it also contains abundant apatite and magnetite, the former often occurs as veins and also disseminated grains. The banded variety is characterized by alternate tourmaline- rich and tourmaline-poor bands. The volume proportions of the constituent minerals vary spatially. Locally the tourmaline volume percentage exceeds 80-90% of this rock. Numerous quartz veins cut both the massive and banded variety. Schistosity is poorly developed in this rock. A thick (~70-80 cm) folded layer comprising angular clasts of dark tourmalinite embedded in quartz-tourmaline matrix is noted. Malachite (a copper-carbonate mineral) stains are primarily concentrated in the clast-bearing unit.

3.2 MODE OF OCCURRENCES OF TOURMALINE:

In the previous section the host rocks of tourmaline samples from Pathargora and Surda have been described. In surda area the tourmaline samples are mainly hosted by quartzite where the primary sedimentary structure is still retained. In pathargora the tourmaline samples are mainly hosted by feldspathic schist/soda granite. In this section the mode of occurrences and micro-textures of tourmaline and the associated minerals are described. This description is based on hand-specimen studies and petrographic study using optical microscope and scanning electron microscope (SEM). The tourmaline grains commonly show internal colour variations under optical microscope suggesting compositional zoning. However, as the grains are commonly dark in colour, it is difficult to decipher the nature of contact between different zones. Therefore, back scattered electron images (BSE) were generated using SEM and electron probe micro analyser (EPMA) to identify possible internal compositional zoning. In general tourmaline occurs mainly in two different modes, disseminated grains in the host rock and as clusters of different mineralogical compositions.

3.2.1 TOURMALINE ASSOCIATED WITH FELDSPATHIC SCHIST:

Tourmaline occurs in the feldspathic schist mainly as cluster with some other mineral, patches or as independent grain.

Cluster of tourmaline:

The rock comprises predominantly of fine-grained quartz and albite with varying proportions of k-feldsper, biotite and chlorite. Additionally there are magnetite, muscovite and apatite. The schistosity is defined by oriented flakes of biotite and chlorite and stretched and elongated quartz. Tourmaline occurs as clusters and the foliation warps around augen-shaped tourmaline cluster (Fig

3.2 A). The tourmaline clusters are either nearly monomineralic comprising predominantly of tourmaline or polymineralic comprising tourmaline, and variable proportions albite, quartz, biotite, apatite and magnetite (Fig 3.2 J, K). Similar to tourmaline-rich clusters there are clusters devoid of tourmaline and comprising quartz, K-feldspar, biotite and albite (showing lamellar twining). Albite, at places, is altered. This albite contains lots of inclusion quartz. Biotite which represents the schistosity warps around these clusters. Unlike foliation defining biotite, biotite in the albite-rich clusters do not show any orientation. In addition to these two different biotite types, massive biotite-rich bands are also present. At places rootless folds defined by albite-rich clusters are common. Muscovite occurs at high angle with the schistosity. Primary rhythmic zoning of tourmaline, defined by different gray shades in BSE images is common (Fig 3.2 B). Tourmaline grains are often extensively fractured and the fractures are filled with quartz. The walls of tourmaline in contact with the fractures are altered. Brown tourmaline is present both inside and outside the cluster but finer tourmaline grains outside the cluster and within the foliation are consistently blue in color Commonly brown tourmaline is altered to blue tourmaline along grain boundary and fractures (Fig-3.2 E-I). Magnetite occurs as inclusion within the tourmaline grain as well.

Patchy tourmaline:

Patch like occurrences of tourmaline in the host feldspathic schist. In this patch tourmaline grains are quiet large and anhedral in shape. Quartz-inclusion is present within tourmaline. Ample evidence of alteration is present where brownish yellow tourmaline is replaced by blue tourmaline (Fig 3.2 C). Tourmaline grains are highly pleochroic (brownish yellow to blue). Small prismatic blue tourmaline is present as a disseminated grain. Interestingly this prismatic blue tourmaline is present also at the boundary of brown tourmaline and also at the core of tourmaline grain where quartz is present as an inclusion (3.2 D).

3.2.2 TOURMALINE ASSOCIATED WITH TOURMALINITE:

Tourmaline in quartz- tourmaline rock/tourmalinite mainly occurs in four different variety. These four –type occurrences of tourmaline are described below.

Tourmaline in banded tourmalinite:

This variety is characterized by alternating light and dark color band. (Fig 3.3 A, F). The thickness of the bands varies from <1 mm to up to 2 cm. Bands are mineralogically different. Lighter band comprises predominantly of quartz and some minor proportions of tourmaline. Darker band contains abundant tourmaline and some minor proportions of quartz and magnetite. The content of tourmaline in the tourmaline-rich bands also vary significantly, comprising almost 80-90 % tourmaline to 50-60 % tourmaline. Magnetite and apatite contents also varies. Apatite primarily occurs as millimeter thick discontinuous veins whereas magnetite is disseminated in the rock and also occurs as inclusions in tourmaline (Fig 3.3 F). Tourmaline, quartz and magnetite all are anhedral in shape. Biotite, magnetite and greenish blue tourmaline are often intimately associated (Fig 3.3 G). The tourmaline is optically zoned with a greenish yellow core (brighter gray shade in BSE image; compositionally schrol; (chapter 4) and greenish blue rim (darker in shade in BSE; compositionally dravite; (chapter 4). They also occur as fracture filling and also in the core part of the grain (Fig 3.3 D). Inclusion of quartz is present within the tourmaline. Triple junction of tourmaline is present (Fig 3.3 E).

Tourmaline in tourmalinite clasts in quartz-tourmaline matrix:

The quartz-tourmaline rock in which the tourmalinite clasts are embedded comprises predominantly of quartz and tourmaline with subordinate apatite and magnetite (Fig 3.3 C). The rock does not show any banding However, the constituent minerals are orientated (Fig 3.3 I).There are two types of tourmalinite fragment. One type is composed of only green colored tourmaline and the another type is composed of yellow and blue tourmaline (Fig 3.3 H). The grain size of tourmaline in the fragments is relatively less than the tourmaline which are present in the ground mass. Apatite vein locally has intruded the tourmalinite fragments. Tourmaline in the fragment adjacent to this apatite vein is primarily blue in color. Straight boundary of quartz and triple junction formed by tourmaline are noted.

Tourmaline in massive tourmalinite:

The sample comprises of quartz, tourmaline, apatite and an unidentified brown (under optical microscope) phase. Tourmaline is homogeneously distributed without any specific orientation (Fig 3.3 J). Apatite is heterogeneously distributed, locally with high abundances (Fig 3.3 L). Tourmaline grains are variable in size and are anhedral in nature. Greenish blue tourmaline replaces greenish yellow tourmaline both along micro-cracks and the boundary.

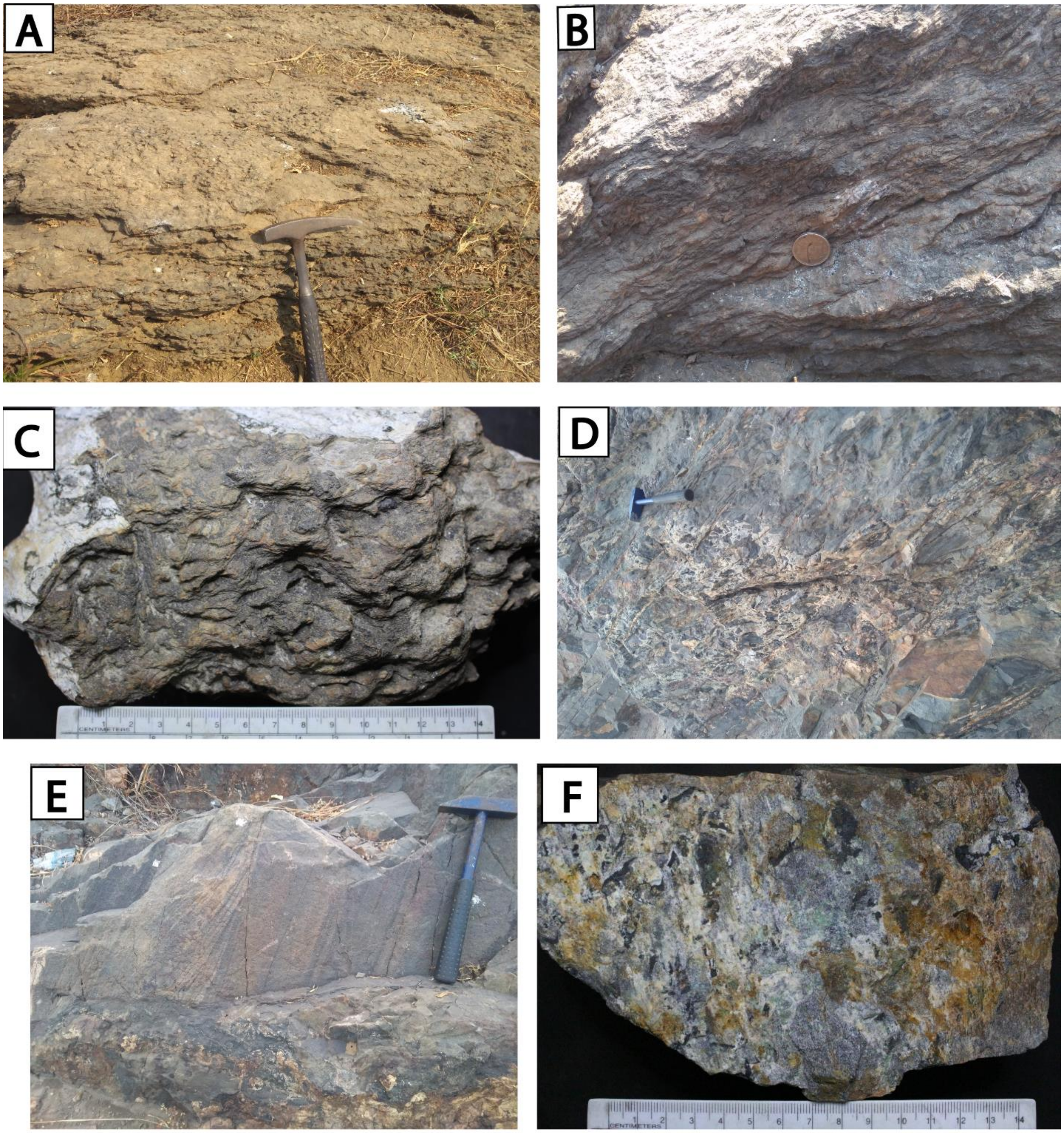

Fig 3.1 A) and B) is showing field occurrence of feldspathic schist C) handspecimen of feldspathic schist D) field photograph of quartz-tourmaline rock /tourmalinite E) large scale cross-stratification F) handspecimen of tourmalinite rock .

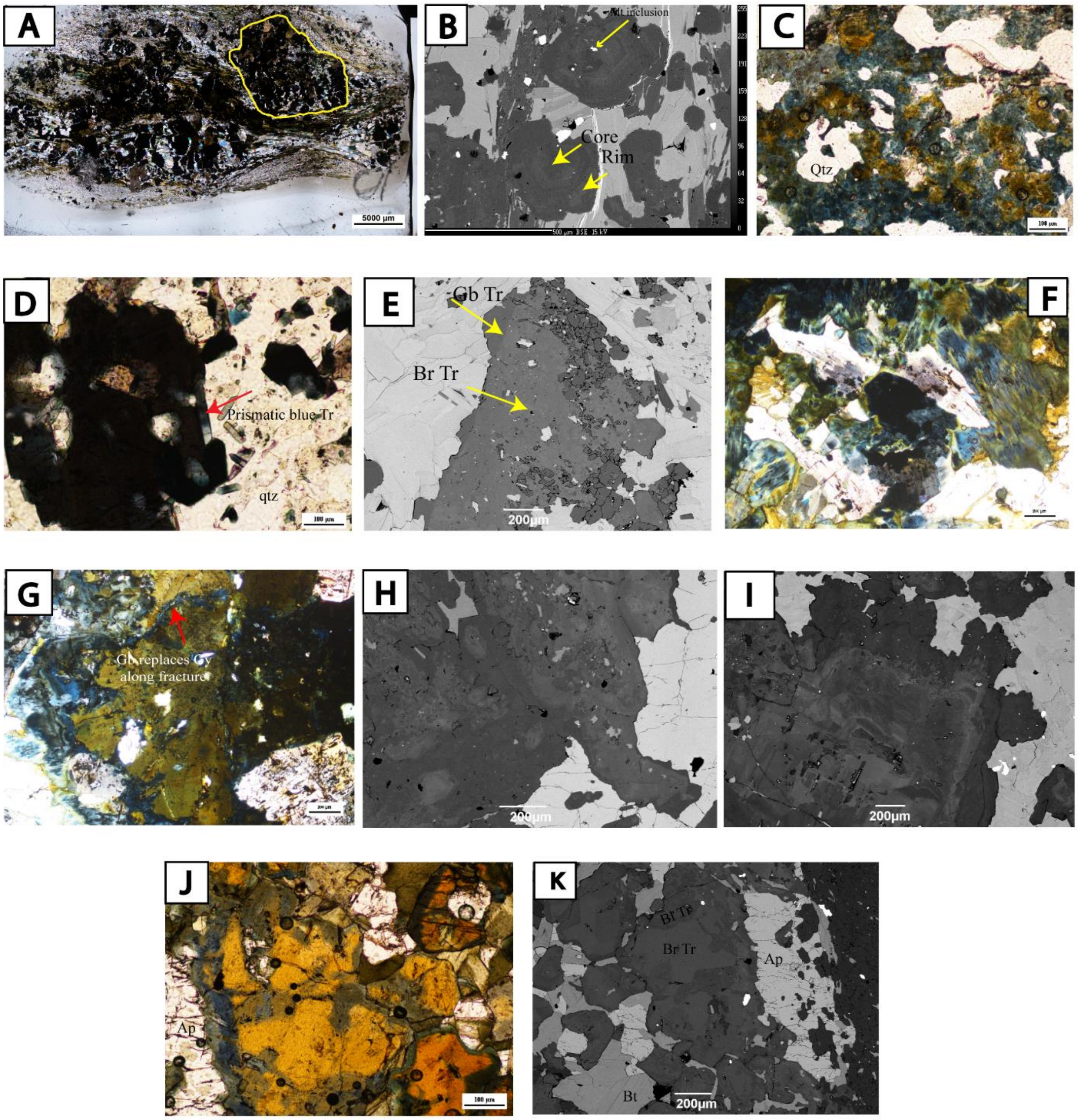

Fig 3.2.Photomicrographs is showing A) whole slide of image of feldspathic schist ,schistosity warps around tourmaline cluster. B) BSE image of primary zoned tourmaline. C) Alteration of greenish yellow tourmaline by geenish blue tourmaline. D) Small prismatic blue tourmaline present in the matrix and inclusion of quartz in tourmaline. E) and J) and K) Image showing alterartion of tourmaline around the boundary. F) and G) Alteration along cracks and fracture. H) and I) BSE image of different pattern of alteration

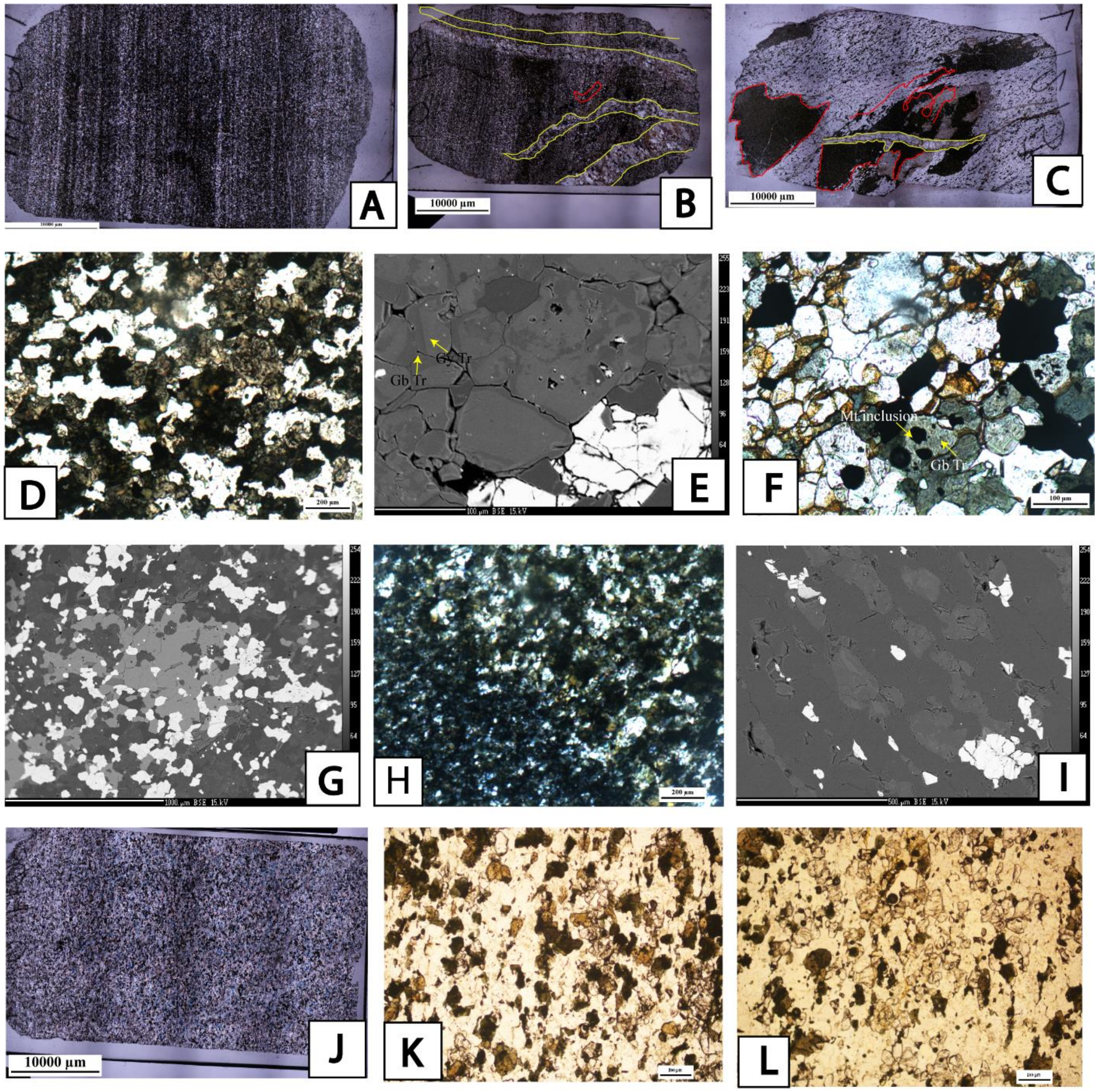

Fig 3.3 Microscopic & BSE image A) Banded type tourmalinite B) Banded type tourmalinite where compositional banding are cut by quartz vein (represented by yellow lines). Wormy appearence of apatite (red lines) C) Fragmented tourmalinite(represented by red lines) in quartz-tourmaline rock. Apatite vein (represented by yellow lines) intrdes within tourmalinite fragment. D) and E) Different patterns of alteration, Gb Tr replaces Gy Tr.[Banded type tourmalinite,ref A].F) Magnetite inclusion in Gb Tr.[Banded type tourmalinite,ref. B]. G) Biotite, magnetite and greenish blue tourmaline are intimately associated.[Banded type tourmalinite,ref.B]. H) Blue and yellow Tr association [Fragmented type tourmalinite,ref.C]. I) A crude orientation of Tr [Fragmented type tourmalinite,ref.C] J) Massive tourmalinite K) and L) Apatite poor and apatite rich zone respectively.

Abbreviation: Gb-greenish blue; Gy-greenish yellow; Tr-Tourmaline ; Mt-Magnetite; ref.-Reference.

CHAPTER 4

TOURMALINE MINERAL CHEMISTRY: COMPOSITIONAL VARIATION AND ELEMENT SUBSTITUTION

4.1 TOURMALINE-STRUCTURE, CHEMISTRY & STABILITY

Minerals of tourmaline super group is one of the most common accessory minerals and the most common Borosilicate in the earth’s crust. Tourmaline is a cyclo-silicate mineral, and the Si:O ratio for tourmaline is 6:18. The generalized chemical formula of tourmaline given by Hawthorne and Henry (1999) is like this –

$X\ Y_3\ Z_6\ T_6\ O_{18}\ (BO_3)_3\ V\ {}_3W$

$X=Na, K^{+}, Ca^{+2}$ & vacancy

$Y=Fe^{+2}, Mg^{+2}, Mn^{+2}, Al^{+3}, Cr^{+3}, Fe^{+3}, V^{+3}, Ti^{+4}, Li^{*}$

$Z= Al^{+3}, Cr^{+3}, Fe^{+3}, V^{+3}, Fe^{+2}, Mg^{+2}$

$T=Si^{+4}, Al^{+3}$

$W=F^{-}, OH^{-}$

$V=B^{+}$

In terms of a classification scheme, most of the compositional variability occurs at the X, Y, Z, W and, to a lesser extent, at the V sites. The T site is typically dominated by Si, and the B site exclusively contains B, such that the cationic occupancies at these sites do not serve as primary parameters for classification, except in some unusual tourmaline species. Tourmaline is a uniaxial (-) mineral. Tourmaline has a rhombohedral unit cell with a=15.8-16.0 and c=7.10-7.25 Å. Tourmaline belongs to the space group R3M. However, there are some reports of tourmalines, or sectors within tourmaline crystals, having orthorhombic, monoclinic, or triclinic symmetry (e.g. Akizuki et al. 2001; Shtukenberg et al. 2007)

Chapter 4: Tourmaline Mineral Chemistry

Tourmaline was once considered to be no more than a collectable mineral, a semiprecious gemstone, or a curious accessory mineral in select rock types. But recent advances in the understanding of tourmaline’s chemical and crystallographic complexities and isotope systematics have led to new applications of tourmaline in deciphering and interpreting geologic processes (Dutrow and Henry 2011). As a sensitive indicator of fluid composition, tourmaline and its isotopic composition are used to better understand the chemistry of ore-forming fluids (Slack and Trumbull 2011) and subduction zone processes (Marschall and Jiang 2011).

The complex and variable chemistry, coupled with low diffusivities, makes tourmaline an ideal indicator of its host environment—from salt domes to pegmatites to ultrahigh-pressure (>2.5 GPa) metamorphic rocks (van Hinsberg et al. 2011). This is further enhanced by negligible diffusion up to high temperatures and a strong refractory character during subsequent host rock alteration and weathering as well as mechanical transport of grains (Hinsberg et al. 2011). Tourmaline is not known to form at the Earth’s surface conditions (25 ºC, 0.0001 GPa), but it can develop during diagenesis and in relatively low-*T*–*P* hydrothermal environments. It is likely that tourmaline can form below 150 ºC and 0.06 GPa, although its development would depend on the kinetics of nucleation and growth ((Dutrow and Henry 2011). Experiments show that tourmaline undergoes melting between 725 and 950 ºC, depending on pressure and composition (van Hinsberg et al. 2011). Dravite stability, established in experiments, extends to temperatures of at least 950 ºC (Werding and Schreyer 1996). The composition of the fluid phase can significantly influence the stability of tourmaline, even within its overall T–P stability range. In aqueous fluids tourmaline is stable in highly acidic to neutral solutions (e.g. Henry and Dutrow1996).

From the cation distribution over the different sites of tourmaline (X, Y, Z, W) it can be easily seen that a large no. of ionic substitution is possible in tourmaline structure. So tourmaline geochemistry is a very tool for understanding different physicochemical conditions in geological environment in which it grows.

4.2 ANALYTICAL METHODS

The geochemical analysis of tourmaline and associated phases are done in three stages. Back scattered electron imaging (BSE) and mineral phases are initially identified by a JEOL JSM 6490 Scanning Electron Microscope (SEM)-Energy Dispersive Spectrometry (EDS).

For obtaining precise major element geochemistry Electron Microprobe Analyzer (EPMA) is used. Tourmaline composition were determined on polished carbon coated thin section by a Cameca SX-100 EPMA equipped with four wavelength dispersive spectrometers (WDS). This was operated at acceleration voltage of 15 kV, beam current of 20nA and beam size of 5µm.

All of the analysis were performed at the Department of Geology and Geophysics, Indian Institute of Technology (IIT), Kharagpur.

4.3 CLASSIFICATION SCHEMES AND CLASSIFICATIONS OF TOURMALINES

Compositions of natural tourmaline are extremely variable mainly due to several possible elemental substitution at different sites. Tourmaline thus can be classified in different groups using site occupancy as the key parameter. Several classification and nomenclature schemes have been proposed (Novak et al. 2009; Henry et al., 2011). Most common classification scheme involves the X-site occupancy.

Tourmaline can be classified into 3 primary groups based on the dominant occupancy of X-site (Hawthorne and Henry, 1999)-

1. Calcic group of Tourmaline
2. Alkali group of Tourmaline
3. Vacant group of Tourmaline

Tourmaline usually contains dominant amount of Na^+, Ca^{+2}, $\square^X$ and rarely K^+. The K-rich tourmalines is relatively rare in occurrences, So it would be most feasible to combine K^+ cation with like charges, Na^{+1} and K^{1+} into an alkali group. This results in the formation of 3 primary groups namely alkali, calcic and X-site vacant- tourmaline groups.

Tourmaline, with a general formula of $XY_3Z_6T_6O_{18}(BO_3)_3V_3W$, is not a single mineral, but a super group currently consisting of 18 species approved by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification (Henry et al. 2011; Hawthorne and Dirlam 2011). Structural and chemical complexities of tourmalines are evaluated thoroughly to develop the IMA-accepted tourmaline minerals and their end-member composition.

Another common classification scheme (Henry and Guidotti, 1985) involves the dominant cations at the Y-site (Al, Mg, Fe). In this classification, based on the compositions of natural tourmaline, several compositional zones are marked for different rock types.

Most of the studied tourmaline samples from Surda & Pathargora plot in the alkali group in the ternary classification diagram of Hawthorne & Henry (1999) which is based on the X-site occupancy (Fig 4.1.a). Only one sample plot near the boundary of alkali group and the vacant group (Fig 4.1a) and one sample plot in calcic group. To get a insight into the classification of studied samples based on Y-site major cations, the compositions of different tourmaline have been plotted in the Al-Fe-Mg ternary diagram after Henry and Guidotti (1985) (Fig 4.1.b). The figure shows that all the studied tourmaline straddle around the schorl-dravite join. The two different cluster of altered and unaltered grains in Surda area can be attributed to the process and thus provide important geological information.

In the binary classification diagram of Na/(Ca+Na) vs Fe/(Mg+Fe) it is observed that all the tourmaline straddle the boundary between schorl and dravite (Fig 4.2 A).

Thus in general most of the tourmaline can be classified as alkali-group tourmaline belonging to schorl-dravite sub-group composition. Overall Na/Ca+Na values range in between 0.490 to 0.950 and Fe/Mg+Fe values range in between 0.263 to 0.688. Tourmaline in Surda area hosted with tourmalinite are showing two distinct zonation (Schrol and Dravite) in Na/(Ca+Na) versus Fe/(Fe+Mg) diagram where tourmaline from pathargora area hosted with feldspathic schist mainly falls in the Dravite field with some being plotted in the Schrol field. So our studied samples mostly fall in Schrol and Dravite

4.4 MAJOR ELEMENT COMPOSTION OF TOURMALINE AND THEIR VARIATION FROM SURDA AND PATHARGORA

A close look in the different classification diagram and binary correlation plots, shows that although most tourmaline belong to schorl-dravite sub-group, there are recognizable differences and patterns in the compositions of tourmaline from Surda tourmalinite and Pathargora feldspathic schist. Tourmaline samples from different rock types generally show overlapping concentration to a certain extent, but different clusters can be identified. As discussed in the previous chapter, tourmaline occurs in tourmalinite and tourmaline occurs in feldspathic schist. An attempt is therefore made to check the compositional variations of tourmaline in the different host rocks.

It is evident that tourmaline from Surda tourmalinite fall into more alkali enriched field. Where tourmaline from feldspathic schist fall also into alkali group but they do contain more x-site vacancy and they are more calcic compared to tourmaline from tourmalinite in the ternary classification diagram. In Al-Mg diagram altered tourmaline from Surda are more Mg-rich and poor in Al, where unaltered tourmaline are more Al-rich and Mg-poor (Fig 4.2 C). In pathargora area both the altered and unaltered tourmaline show similar composition as with the altered tourmaline from Surda. Tourmaline from Surda show a positive trend where tourmaline from Pathargora do not show a general trend in binary Fe-Al diagram (Fig 4.2 B). Although altered sample from Pathargora show a negative trend but this relations is not hold for individual sample level when samples are plotted in binary Fe-Al diagram (Fig 4.2 B). In Mg-Al diagram (Fig 4.2 C) Tourmaline from Surda show a strong negative trend where tourmaline from Pathargora show a gentle negative trend. Tourmaline from Surda show a prominent negative trend where tourmaline from Pathargora also show a negative trend but weaker in Fe-Mg diagram (Fig 4.2 D)**.** In R^{2+} (Fe+Mg+Mn) versus Ti diagram, it is observed that the tourmaline from Surda area contain a specific concentration of Ti and tourmaline from pathargora area show a large range of Ti concentration (Fig 4.2E). The altered samples from Surda show higher concentration of (Fe+Mg+Mn) than unaltered sample from Surda. The tourmaline from Surda, (Fe+Mg+Mn) enrichment is independent of their Ti concentration. The tourmaline from Pathargora, (Fe+Mg+Mn) enrichment is showing haphazard trend. The tourmaline from Pathargora (Al+Cr) enrichment is showing negative trend when they are plotted in $R^{3+(}$Al+Cr) versus Ti diagram where the tourmaline from Surda (Al+Cr) enrichment is independent of their Ti concentration**.** Altered samples from surda have lower concentration of (Al+Cr) than unaltered sample from surda (Fig 4.2 F). In R^{2+} (Fe+Mg+Mn) versus Ca diagram. Altered samples from surda have higher concentration of Ca and unaltered samples have lower concentration of Ca. Samples from pathargora do not show this kind of cluster. A strong positive correlation is found for both the tourmaline from Surda & Pathargora. The same cluster is observed for the tourmaline from Surda when they are plotted in R^{1+} (Na+K) versus Ca diagram. Tourmaline from Surda shows a negative correlation and tourmaline from Pathargora also does same .Only an altered sample from Pathargora is showing a positive correlation.

4.5 ELEMENT SUBSTITUTION IN TOURMALINE:

Several substitution schemes are reported to occur in tourmaline. Amongst these, substitution of bivalent Fe by Mg is a very common substitution mechanism in the Y site, particularly in tourmaline belonging to schorl-dravite group. The Fe Vs Mg (apfu) plot shows a general negative correlation suggesting substitution of one by the other ($MgFe^{-1}$ vector). However, the significant scatter in this plot, particularly involving data from the Pathargora, also indicates that other substitution mechanism might have occurred besides a simple $Fe^{+2} \leftrightarrow Mg$ substitution. Such scatter might be generated due to part substitution of Fe^{+3} by Al^{+3} in the Y site. The Al vs Fe_{Total} plot does not show any important correlation. This indicates that the studied tourmaline did not contain much of Fe^{3+} and thus substitution of Fe by Al did not play much role in controlling the compositions of tourmaline. In contrast, the Al vs Mg plot shows a better negative correlation. Such substitution of Al $\leftrightarrow$ Mg would require involvement of some other cations to maintain charge balance. Some of the common coupled substitution involving monovalent, bivalent and trivalent cations that occur in tourmaline are $(NaAl)(MgFe)^{-1}$, $(NaAl)(CaMg)^{-1}$, $(NaAl)(CaFe)^{-1}$, $(NaMg)(\square Al)^{-1}$, $(NaFe)(\square Al)^{-1}$. These substitution schemes can be simplified to ${}^{X}R^{1+} + R^{2+} \leftrightarrow {}^{X}\square + R^{3+}$, ${}^{X}R^{1+} + R^{3+} \leftrightarrow {}^{X}Ca + R^{2+}$ where $R^{1+} = Na^{1+} + K^{1+}$, $R^{2+} = Mg^{2+} + Fe^{2+} + Mn^{2+}$ and $R^{3+} = Al^{3+} + Cr^{3+}$. To examine, which of these substitution schemes actually operated in controlling the compositions of tourmaline several correlation diagrams are produced. All tourmaline compositions show a very strong negative 1:1 correlation in R^{2+} vs R^{3+} plot (Fig 4.3A), implying that the one or combination of two general substitution schemes mentioned above played very significant role. To examine whether the alkali-defect substitution or the uvite-type substitution or both played important role, the R^{3+} cations are plotted against X-site vaccancy(Fig 4.3B) . The plot shows a positive correlation from both the region. An opposite relation is observed in the R^{2+} vs X-site vacancy plot (Fig 4.3 C). This likely suggests, ${}^{X}R^{1+} + R^{2+} \leftrightarrow {}^{X}\square + R^{3+}$ substitution have occurred both in the Pathargora and Surda area. It may be mentioned in Surda area altered samples are poor in Ca but unaltered samples are richer in Ca. In Pathargora area this clustering with respect to Ca is not found. A weak negative correlation between R^{1+} and $^{X}\square$ of the tourmaline samples paralleling the $(^{X}R^{1+} + R^{2+})(\,^{X}\square + R^{3+})_{-1}$ vector further supports the above substitution mechanism (Fig 4.3 D). $^{X}R^{1+} + R^{3+} \leftrightarrow {}^{X}Ca + R^{2+}$ might have played some role. By plotting Ca vs R^{3+} plot a strong negative correlation is found (Fig 4.3 E) and by plotting Ca vs R^{2+} a strong positive correlation is found (Fig 4.3 F). So this substitution $(^{X}R^{1+} + R^{3+})(^{X}Ca + R^{2})_{-1}$ scheme is also took place. The Ti concentration is almost constant in Surda area for both the altered and unaltered samples. But in Pathargora area Ti concentration is showing a negative trend with R^{3+} in R^{3+} vs Ti diagram (Fig 4.4 A). The foregoing discussion suggests that several substitution scheme played important role in controlling the compositional variations of tourmaline both in Surda and Pathargora. A combination of $Fe^{2+} \leftrightarrow Mg^{2+}$, $^{X}R^{1+} + R^{3+} \leftrightarrow {}^{X}Ca + R^{2+}$ and $^{X}R^{1+} + R^{2+} \leftrightarrow {}^{X}\square + R^{3+}$ and $Ti + R^{2+} \leftrightarrow 2\ R^{3+}$ have played variable roles in element substitution in tourmaline. However, the $Ti + R^{2+} \leftrightarrow 2\ R^{3+}$ Probably only occur in Pathargora area.

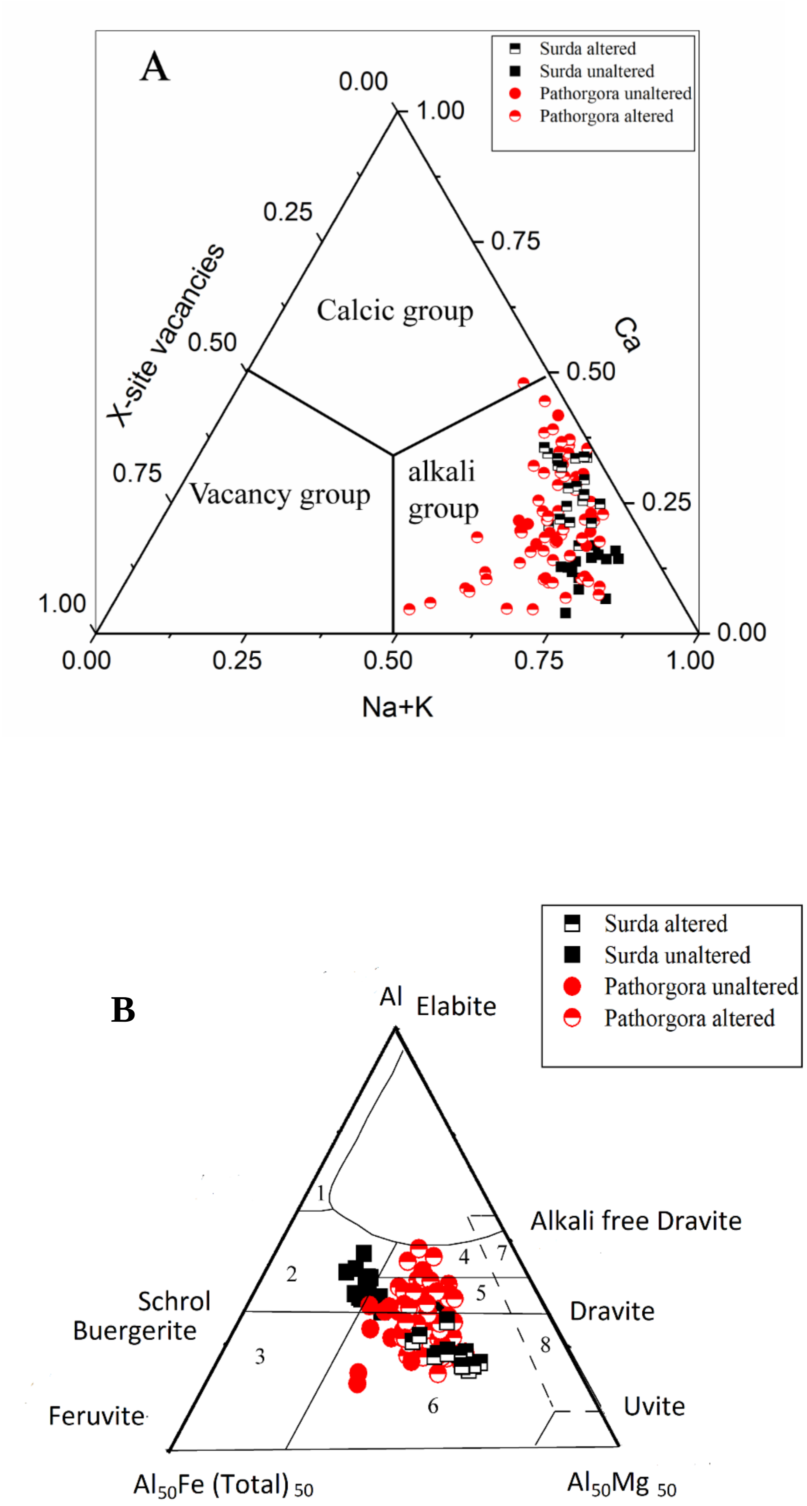

Fig 4.1 A) Ternary classification of the tourmalines from Surda -Pathargora area after Hawthorne & Henry (1999) based on the X-site principal constituents at the X-site. B) Al-Fe-Mg ternary diagram after Henry and Guidotti (1985) with the compositions of tourmalines under analysis. The labelled fields are-1)Li-rich granitoid pegmatite and aplite, 2)Li-poor granitoids, pegmatites and aplites,3)Fe3+ rich quartztourmaline rocks(altered granitoids),4) metapelites and metapsammites lacking Alsaturating phase,6)Fe3+ rich quartz-tourmaline rocks,calc-silicate rocks and metapelites,7) low-Ca ultramaphic rocks and Cr-V-rich metasediments and 8) metacarbonates and meta-pyroxenites.

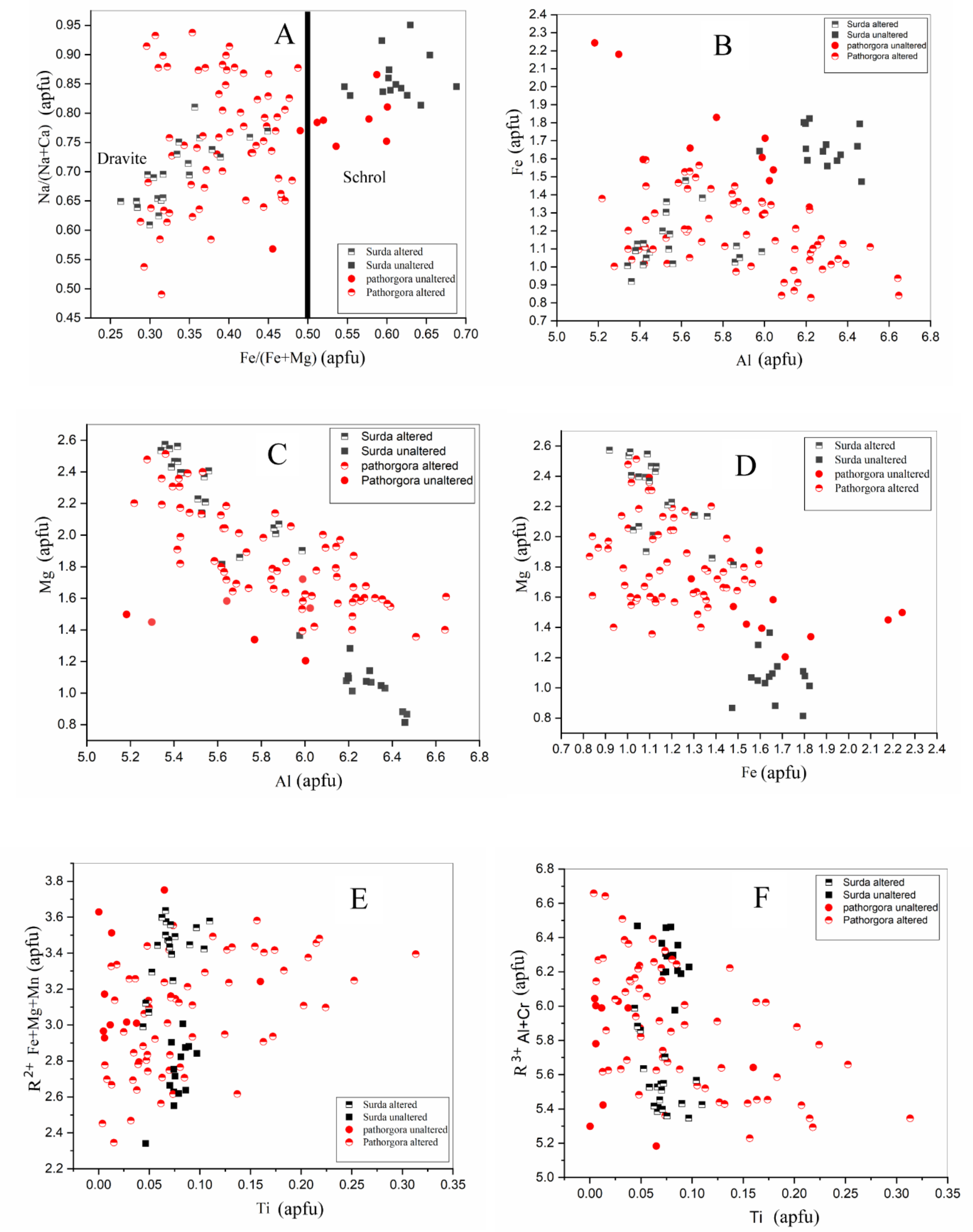

Fig 4.2 A) Classification scheme for tourmaline ,Na/(Na +Ca) vs Fe/(Fe+Mg) ; Correlation plots involving different cations in terms of atoms per formula unit (a.p.f.u.) (from B-F) B) Fe (apfu) vs Al(apfu) C) Mg (apfu) vs Al (apfu) D) Mg (apfu) vs Fe (apfu) E) R^{2+}(Fe+Mg+Mn) (apfu) vs Ti (apfu) F) R^{3+}(Al+Cr) (apfu) vs Ti (apfu)

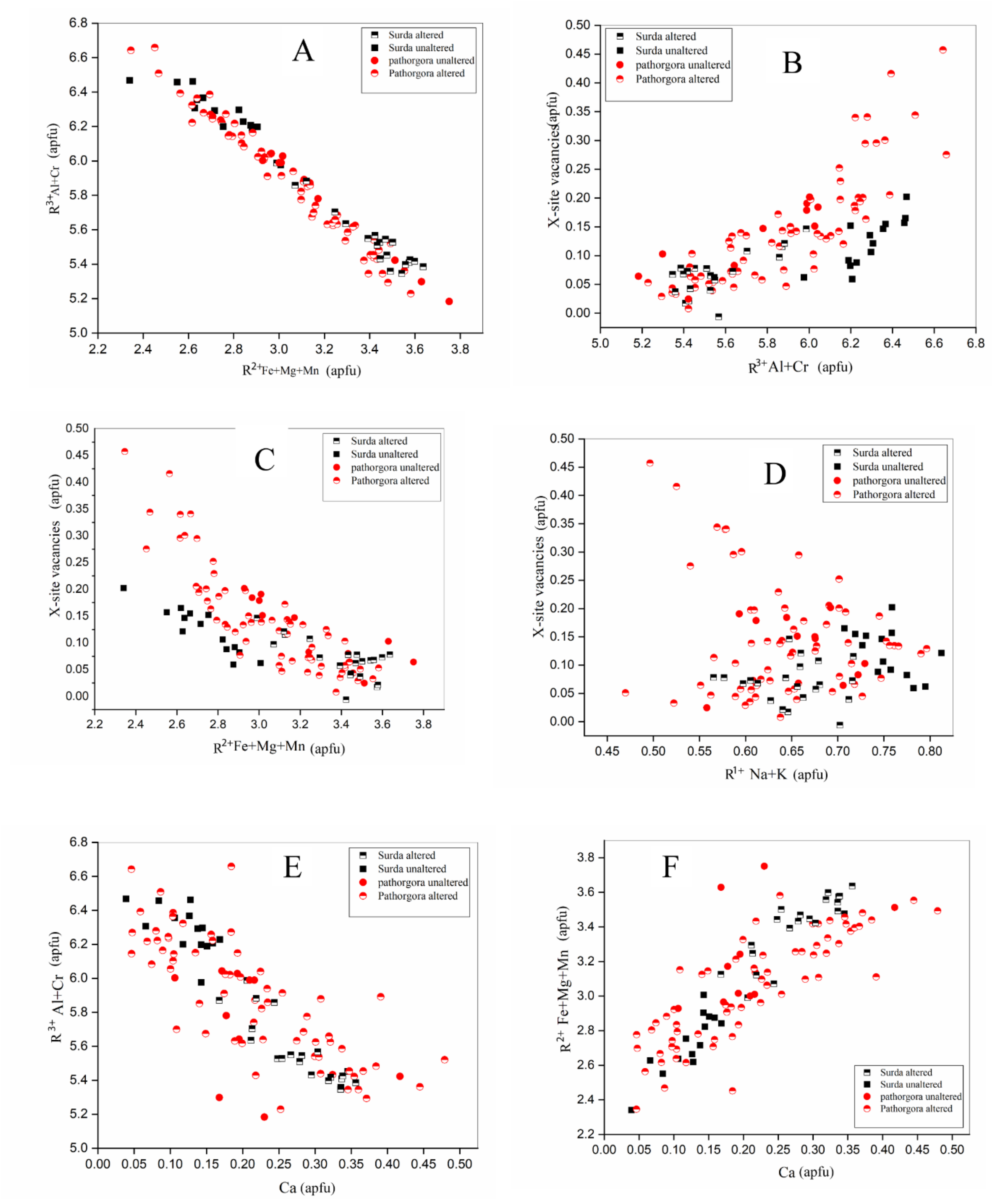

Fig 4.3 Correlation plots involving different cations in terms of atoms per formula unit (a.p.f.u.) A) R^{3+} (Al+Cr) vs R^{2+}(Fe+Mg+Mn) B) R^{3+}(Al+Cr) vs X-site vacancy C) R^{2+}(Fe+Mg+Mn) vs X-site Vacancy D) R^{1+} (Na+K) vs X-site Vacancy E) R^{3+}(Al+Cr) vs Ca F) R^{2+}(Fe+Mg+Mn) vs Ca

CHAPTER 5

TRACE ELEMENT GEOCHEMISTRY OF TOURMALINE

5.1 Analytical Procedure:

The trace elements concentrations in minerals were measured using a Thermo Fisher Scientific iCap-Q Quadrupole Inductively Coupled Plasma Mass Spectrometer (Q–ICPMS) coupled with a New Wave Research 193nm Ar–F excimer laser ablation system at the Department of Geology and Geophysics, Indian Institute of Technology (IIT), Kharagpur. The laser was operated at 5 Hz repetition rate and ca. 5 J/cm 2 beam energy density, spots size were 45–50 µm for sample and bracketing standards. The instrument was optimized for maximum sensitivity in low medium and high mass range using the NIST SRM 612 reference glass. The raw counts for each isotope were measured in the time resolve mode with 30 second of gas blank without laser firing and 45 second during ablation. The external standardization was done by bracketing the group of ten unknowns with two measurement of the NIST SRM 610 glass. The data was reduced off line using the GLITTER © data reduction software. The data quality was monitored by analyzing the reference glass NIST SRM 612 as unknown interspersed with the measurements of the samples.

5.2 Trace Element Results:

Lithophile elements:

Average Li concentration in tourmaline from both the Surda and Pathargora area mostly ranges between 2 to 20 ppm with some having higher values. In Surda area highest Li content is 49.9 ppm whereas in Pathargora area it is 41.7 ppm. No distinct variation in Li- concentration is found in altered and unaltered sample. Average Be content in tourmaline from Surda-tourmalinite is <1 ppm whereas in Pathargora it is 2-5 ppm. Scandium content in tourmaline is significantly higher in core part, average value ranges 120-150 ppm, than the rim, average, value ranges 30-60 ppm, part in Pathargora. Overall Sc content in Surda is lower than in

Pathargora tourmaline. In Surda altered tourmaline samples have higher Sc content than unaltered samples. Tourmaline from both the area contains higher vanadium in core part than in the rim part Chromium content in tourmaline is somewhat different from these two areas. In Pathargora area altered tourmaline grains are poorer in Cr, values range from 50 to 350 ppm, whereas unaltered tourmaline grains are richer in Cr values range from 400-800 ppm. But in Surda area completely opposite trend is showing. The Rb contents in most of the case are less than 1ppm but some high value (563ppm) is also present. Strontium value is significantly higher in core than in rim part from Pathargora tourmaline samples. In Surda area, altered tourmaline samples have higher Sr value ranges from70 -100 ppm than the unaltered average values range 30-70 ppm, version of it. Core part & unaltered part of tourmaline samples are richer in Ti, Nb and Ta and rim part & altered part are poor in those elements from Pathargora area. Hafnium concentration is <1 ppm in most of the tourmaline samples. Zirconium concentration is low in tourmaline from quartz-tourmaline rock, average value ranges from 1to 3 ppm, but in banded type of tourmaline contains a higher concentration of Zr, average value ranges from 48 to 50 ppm.

Siderophile & Chalcophile elements:

Ni, Co concentration is higher in rim part, average value ranges from 320 to 450 ppm of tourmaline than in the core part average value ranges from 250 to 300 ppm in Pathargora area. Overall Ni content is higher in Surda, average value ranges from 800-1200 ppm than in Pathargora, average value 300-500 ppm. Manganese content is higher in the rim part than in the core part. In Surda area altered tourmaline grains are richer in Mn and unaltered part is poor in Mn. Copper concentrations are variable and no discernible pattern is observed in the concentration between core and rim and unaltered and altered tourmaline. From both the area Zn content in tourmaline for altered samples is lower than the unaltered samples. Ga content is higher in core than in rim.

Rare Earth Elements (REE):

All the tourmaline from different host rocks are enriched with LREE (Fig 5.1 A & B). Tourmaline from Pathargora area is showing that the unaltered tourmaline grains incorporate higher amount of LREE in its structure than the altered tourmaline samples. Overall it shows a enrichment with LREE and HREE shows a flat trend with a strong positive Eu anomaly. In Surda the REE pattern is similar with that of Pathargora. But here altered and unaltered samples show overlapping character. Similar to Pathargora, a strong positive Eu anomaly is present in Surda tourmaline.

5.3 Different Ratio plots:

Overall Ni/Co ratio is much higher in tourmaline from Surda area (>20-45) than Pathargora area (most of the sample has Ni/Co ratio < 20) (Fig 5.2 A). V/Sc ratio is slightly higher for altered tourmaline in Surda area (Fig 5.2 B). In Nb/Ta vs Sr/Rb plot a parallel line (parallel to Sr/Rb axis) is found which shows that Nb/Ta ratio (3-10) is independent to Sr/Rb and Sr/Rb ratio is quiet higher for Pathargora tourmaline (most of the samples show > 200) compared to those in Surda mostly (0-150) (Fig 5.2 D). In Zn vs Zn/Fe plot it is evident that the unaltered samples have higher Zn/Fe ratio (>0.0003) compared to altered tourmaline (0.0001-0.0002) (Fig 5.1 C& D). Another graph is plot Mg vs Zn/Fe which shows with enrichment of Mg, Zn/Fe ratio becomes lower. So it is evident that Zn is leached away during alteration.

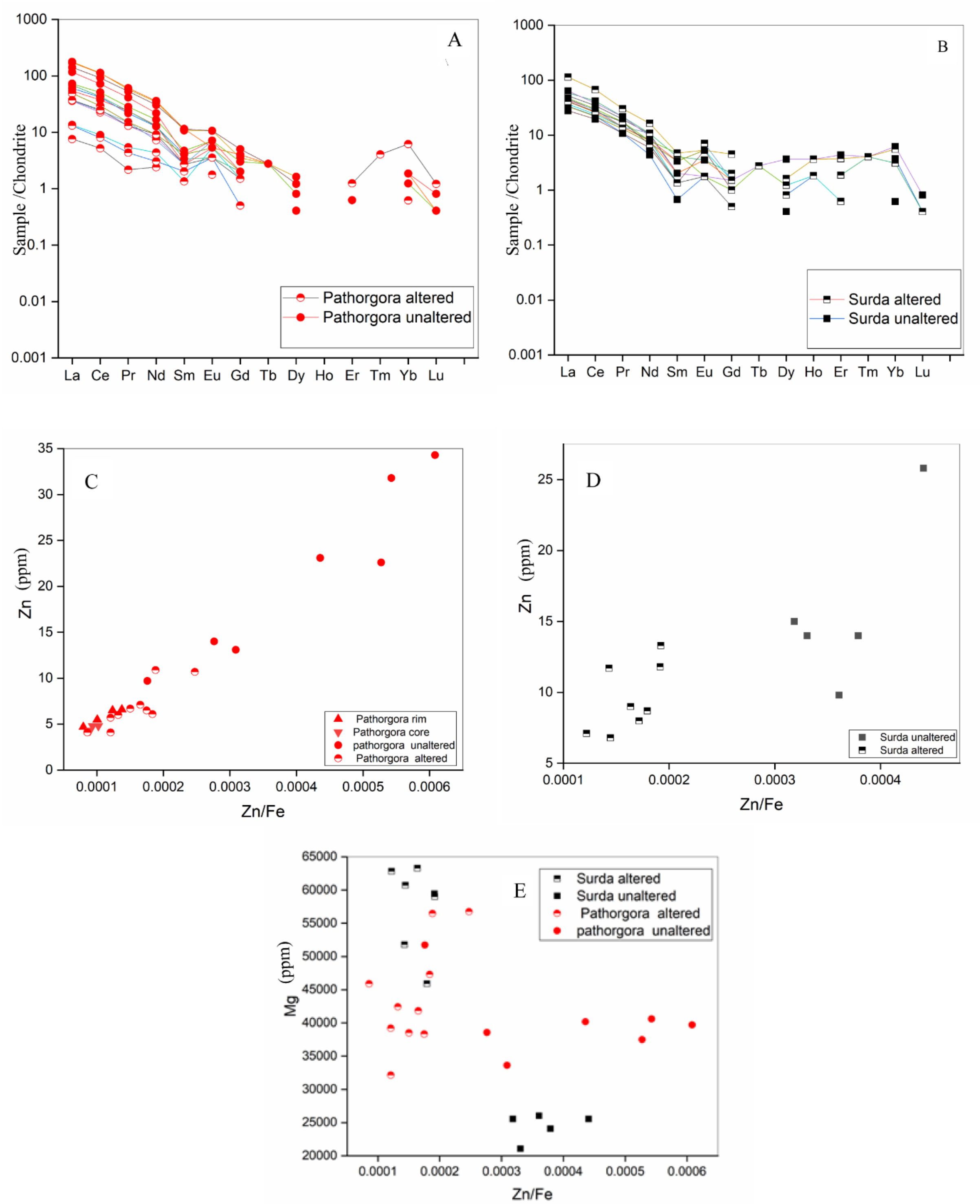

Fig 5.1 Chondrite normalized (McDonough and Sun1994) REE patterns for A) Tourmaline from Pathargora area B) Tourmaline from Surda area. Different Ratio plots (from C,D,E) ; C) & D) Zn vs Zn/Fe showing different cluster of altered and unaltered tourmaline from Pathargora and Surda area respectively. E) Mg vs Zn/Fe showing altered samples have low Zn/Fe ratio whereas unaltered samples have relatively higher Zn/Fe ratio.

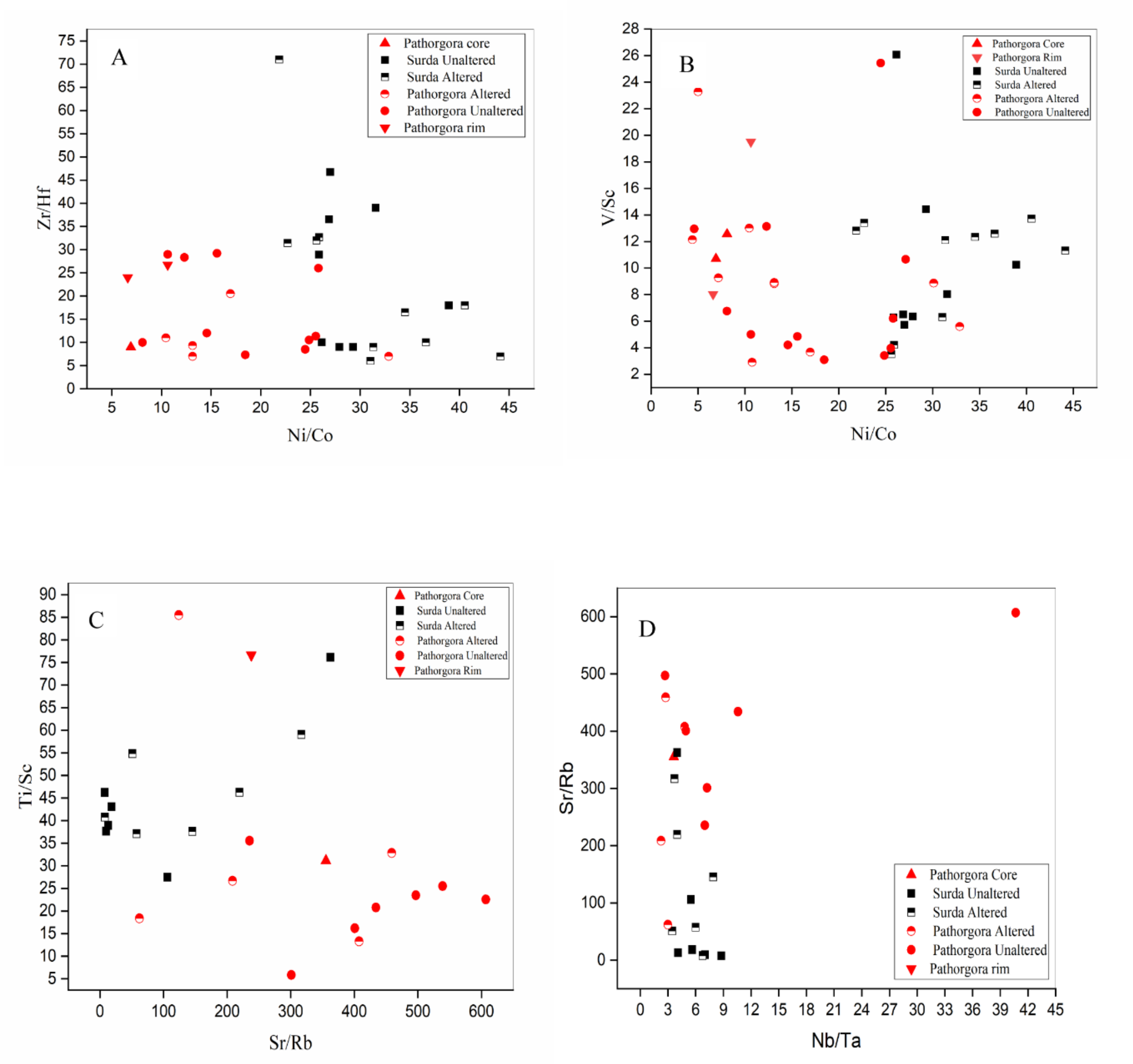

Fig 5.2 Different Ratio plots A) Zr/Hf vs Ni/Co showing overall Ni/Co ratio ia higher for Surda Tourmaline B) V/Sc vs Ni/Co C) Ti/Sc vs Sr/Rb D) Sr/Rb vs Nb/Ta Showing Nb/Ta ratio is independent to Sr/Rb ratio.

CHAPTER 6

DISCUSSION

Present study incorporates two different area namely Pathargora and Surda where tourmaline occurs in two different host rocks feldspathic schist and quartz-tourmaline rock /tourmalinite. In Pathargora tourmaline occurs in two modes a) as cluster which is made up of aggregates of tourmaline only or with other minerals and b) as patches. In Surda area tourmaline occurs in three modes a) banded tourmalinite where alternative tourmaline poor and tourmaline rich layer present b) Fragmented tourmalinite where tourmalinite clast (made up of volumetrically >80-90% tourmaline) is present within the host (made up of volumetrically 10-20% tourmaline) and c) massive tourmalinite. Tourmaline from this two different association show alteration. The effect of alteration in Pathargora is quite higher than Surda. That is likely controlled by the physical and mineralogical character of the host rock. Feldspathic schist is highly foliated and predominantly made up of albite, K-feldspar, quartz, and tourmaline. On the contrary, tourmalinite is hard and compact composed primarily of quartz and tourmaline. Albite makes the feldspathic schist very fragile, so when it suffered deformation, ingress of fluid is quite easy and hence effect of alteration is greater in Pathargora. Petrographic study shows brown tourmaline or brownish yellow tourmaline is replaced by blue tourmaline or greenish blue tourmaline along the grain boundary, micro-cracks or fracture. In advance cases they form prismatic blue tourmaline which are present along the grain boundary or at places sitting within the matrix. So, from the alteration pattern it is evident that this later generation tourmaline are the product of hydrothermal fluid activity. Major element geochemistry shows earlier brown tourmaline is rich in Fe, Al and altered tourmaline is rich in Mg and poor in Al. In Pathargora altered tourmaline is characterized by large variation in Ti content whereas the unaltered tourmaline from Pathargora and both the altered and unaltered tourmaline from Surda contain a constant amount of Ti. From field study it has been observed that in Pathargora apatite-magnetite veins are present. This magnetite contain lots of Ti in its structure. Now if the formation of this vein is contemporaneous with the formation of second generation of tourmaline, then the high Ti content in most of the altered tourmaline might be explained by incorporation through hydrothermal alteration by Ti-bearing fluid. Among trace elements, Ni, Co, and Mn are enriched in the rim tourmaline compared to the core suggesting that these elements were supplied by the interacting fluid. Tourmaline rim part is poor in Zn .Tourmaline shows a enrichment of LREE and positive Eu anomaly. That is because of tourmaline has a strong affinity for Eu^{2+} (Marks et al 2013) over $Eu^{3+.}$ Based on this study alone the different fluid source cannot be deciphered unequivocally. However, it is certain that the blue tourmaline formed due to alteration of existing tourmaline by later hydrothermal fluid or even new tourmaline formed during this hydrothermal event. Determination of source or character of such hydrothermal fluid is beyond the scope of this thesis work.

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Appendix

Major oxide data of tourmaline from EPMA

Mineral	Sample NO	Comment	Na_2O	F	MgO	Cl	P2O5	K_2O	CaO	TiO_2	Cr_2O_3	FeO	MnO	Al_2O_3	SiO_2	V_2O_3	Total
Tourmaline	L12	Rim	2.181	0	5.79	0	0.05	0.005	0.49	0.406	0.005	9.844	0	30.641	34.045	0	83.458
Tourmaline	L12	core	2.118	0	6.205	0.018	0.018	0.034	1.055	0.566	0	12.334	0	28.037	34.714	0.237	85.337
Tourmaline	L12	Rim	2.118	0	5.739	0	0.05	0.006	0.512	0.377	0.015	9.302	0.015	31.141	35.055	0.002	84.332
Tourmaline	L12	core	1.803	0	6.843	0.02	0	0.035	1.573	1.043	0	10.581	0	27.34	34.488	0.238	83.966
Tourmaline	L2C5	Altered	1.932	0	7.036	0.007	0	0.028	1.198	0.388	0	9.632	0.006	29.458	35.143	0.136	84.964
Tourmaline	L2C5	Unaltered	1.787	0	8.579	0.02	0.015	0.047	1.958	2.428	0	8.377	0.001	26.427	34.665	0.236	84.539
Tourmaline	L2C5	Unaltered	2.12	0.002	5.573	0	0.013	0.055	0.898	0.002	0	14.938	0	25.758	34.809	0.191	84.358
Tourmaline	L2C5	Altered	1.912	0	9.411	0.026	0	0.068	1.966	1.637	0	7.237	0	27.358	35.665	0.191	85.472
Tourmaline	L112	Unaltered	1.902	0.004	6.395	0.006	0.014	0.055	1.237	0.195	0.059	9.482	0.007	30.172	35.224	0.27	85.022
Tourmaline	L112	Altered	1.707	0.008	6.638	0.011	0	0.007	1.057	0.031	0.09	6.182	0	34.64	36.161	0.075	86.607
Tourmaline	L112	Unaltered	2.285	0	6.217	0.041	0	0.068	0.995	1.309	0.282	9.863	0.078	30.713	35.719	0.149	87.719
Tourmaline	L112	Altered	1.816	0	9.364	0.028	0	0.032	2.069	1.314	0.464	7.917	0.009	27.664	36.155	0.312	87.143
Tourmaline	L112	Unaltered	1.863	0	6.662	0.037	0.004	0.059	1.719	1.61	0.169	10.353	0	29.705	34.735	0.126	87.042
Tourmaline	L 10 1	Unaltered	2.096	0	6.237	0.006	0	0.027	0.576	0.268	0.067	8.003	0	32.11	34.932	0.106	84.428
Tourmaline	L 10 1	Altered	2.414	0	7.843	0	0	0.006	0.496	0.347	0.023	6.479	0	31.007	35.051	0.1	83.767
Tourmaline	L 10 1	unaltered	1.82	0	9.332	0.006	0.052	0.058	1.902	1.686	0.016	7.748	0	26.729	35.284	0.865	85.497
Tourmaline	L102	Altered	1.827	0	6.5	0	0.005	0.004	0.664	0.591	0.015	7.327	0	32.415	36.2	0.098	85.645
Tourmaline	L102	Unaltered	1.978	0.002	5.746	0.043	0.044	0.039	0.964	0.039	0	11.082	0.053	30.895	36.079	0.106	87.071
Tourmaline	L102	Altered	1.982	0	8.506	0.017	0	0.003	1.346	0.369	0.027	7.399	0.03	31.05	36.711	0.139	87.579
Tourmaline	L102	Unaltered	1.638	0	8.453	0.01	0.036	0.051	2.11	0.376	0.078	9.126	0	27.291	35.452	0.45	85.071
Tourmaline	L102	Altered	1.785	0.008	6.769	0.006	0	0.015	0.45	0.103	0	7.093	0.012	32.015	36.306	0.451	85.014
Tourmaline	L102	Unaltered	1.697	0	7.678	0.037	0.012	0.043	2.336	0.103	0.051	11.443	0.055	27.541	36.288	0.313	87.597
Tourmaline	L102	Altered	1.862	0.01	6.935	0.018	0.052	0.014	1.072	0.558	0.023	7.817	0	31.041	35.4	0.138	84.941
Tourmaline	L122	Altered	1.979	0	9.063	0	0	0.05	1.577	0.566	0	8.695	0.033	28.325	36.284	0.187	86.759
Tourmaline	L122	Altered	1.929	0	10.069	0	0	0.034	1.836	0.583	0.074	8.31	0	28.204	36.859	0.223	88.122
Tourmaline	L1211	Unaltered	2.441	0	4.237	0.024	0	0.056	0.365	0.583	0.025	11.03	0	31.617	35.433	0.034	85.844
Tourmaline	L1211	Altered	2.236	0	8.162	0.026	0.014	0.002	0.948	0.386	0.038	8.072	0	30.108	36.042	0.068	86.103
Tourmaline	L1211	Unaltered	2.289	0	3.494	0	0	0.035	0.465	0.585	0.067	11.791	0	32.318	34.971	0.021	86.037
Tourmaline	L1211	Altered	1.755	0	9.515	0	0.014	0.01	1.909	0.538	0.032	7.66	0	27.37	35.559	0.447	84.808
Tourmaline	L1210	Altered	2.073	0	9.854	0.011	0.005	0.031	1.687	0.733	0	7.693	0	28.227	36.965	0.304	87.583
Tourmaline	L1210	Unaltered	2.186	0.004	7.319	0	0	0.051	1.186	0.421	0.109	10.634	0	28.654	36.172	0.186	86.919
Tourmaline	L-12-5	Unaltered	1.848	0.004	9.882	0.004	0.013	0.025	1.794	0.498	0	8.072	0.02	27.447	35.367	0.197	85.171
Tourmaline	L-12-5	Altered	2.163	0	9.784	0.031	0	0.049	1.718	0.84	0.059	7.371	0	28.575	35.79	0.29	86.67
Tourmaline	L-12-5	Altered	2.074	0	8.589	0	0.033	0.046	1.423	0.527	0	9.758	0.041	28.121	35.404	0.19	86.206

Trace element data table of tourmaline

Mineral	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline
Sample NO	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora
Comment	Rim	core	Rim	core	Altered	Unaltered	Unaltered	Altered	unaltered	Altered	Unaltered	Altered
Li7	3.7	3.8	4.3	4.9	6.2	8.5	4.8	2	8.8	13.3	11.1	6.2
Be9	8.6	3.7	3.3	3.8	6.4	2.8	0.3	<0.48	0.8	2.2	<0.47	<0.72
B11	26586.7	27122.9	30869.7	28523.7	27657.2	32654.7	24278.9	31703.3	29302.6	31699.9	27232	35847.4
Mg24	34919.8	37422.7	34612.2	41270.5	42434.5	51740.4	33611	56758.2	38568.6	40034.1	37495	56474.7
P31	76.7	70.2	91	52.8	72.9	77.4	56.1	82.6	65.3	86.7	120	65.9
Fe57	47932.1	51266.5	52625.1	47995.7	45386.4	55094.8	42409.6	43241.8	50674.3	40313.1	42862.2	57867.1
K39	113.5	265.1	148.4	216.9	212.5	388.8	412.5	458	393.9	332.2	390	337.3
Sc45	37.1	147.8	24.2	124.3	139.1	371	251.9	239.5	164	82.7	83.3	425.8
V51	724.1	1582.3	194.6	1561	1233.8	1266.4	778.7	1341.4	690.5	304.1	404.3	1237.9
Cr52	233.4	205.1	27.9	166.8	56.5	432.6	335.1	88.3	754.8	797.2	861	484.7
Co59	46.3	32.8	50.4	32.6	28.6	31.7	26.8	36.3	40.8	37.5	39	51
Ni60	492.4	226.9	333	264	861.7	788.5	494.4	1193.8	594.8	635.9	608.3	549.7
Cu63	0.5	141.6	370.8	1.3	3.5	8.3	3.8	1.8	0.7	28.4	85.9	0.9
Zn66	6.6	4.8	6.5	4.3	6	9.7	13.1	10.7	14	15.1	22.6	10.9
Ga71	45.1	89	35.8	77.6	164.5	137.3	66.5	101.6	96.8	96.3	76.5	72.8
Ge73	<1.24	1.6	<1.37	<2.34	1.6	1.8	2.2	1.7	<1.76	<2.95	<2.62	<2.09
As75	<5.54	<5.52	<6.96	<5.51	<5.74	<7.21	<4.54	<6.04	<6.17	<7.63	<5.90	<6.90
Rb85	<0.054	0.2	0.1	<0.078	<0.082	<0.092	0.1	0.1	0.1	0.3	0.2	<0.102
Sr88	66.6	71.1	23.8	67.4	91.6	79.6	49.7	45.9	43.4	62.6	47.1	110.5
Y89	0.5	0.3	0.3	0.1	0.4	1.1	0.3	0.3	0.2	0.9	1.6	0.1
Zr90	10.7	1.8	2.4	0.2	1.2	2.1	2.2	2.1	1.2	4.1	14.6	<0.088
Nb93	0.4	6.9	0.1	2.5	0.4	4.6	2.7	1.1	5.3	0.9	2.8	0.5
Mo95	0.1	<0.169	0.1	<0.174	0.1	<0.206	<0.187	<0.194	0.2	0.5	1.2	0.1
Hf178	0.4	0.2	0.1	0	0	0.2	0.3	0.3	0.1	0.2	0.5	<0.093
Ta181	0.1	1.9	0	0.6	0.1	0.6	1	0.4	0.5	0.4	0.4	0.3

Ba137	0.2	0.4	0.1	0.1	0.6	1.3	2	3	1.3	1.7	1.3	0.3
Ti49	3011.6	4606.8	1854.6	5469.7	2216.5	5622.8	5912.8	7867.8	3410.1	2205	2963.5	6224.4
Mn55	29.5	17.8	50.6	20.2	13.9	28.5	30	22.7	46.8	40.8	56.8	26
Ag107	<0.147	<0.204	<0.230	<0.136	<0.183	<0.178	<0.140	0.2	<0.235	<0.29	<0.222	<0.253
Cd111	<0.40	<0.00	0.3	<0.29	0.3	0.1	<0.31	<0.45	0.4	<0.63	0.1	<0.33
Sn118	10.1	37.1	3.2	23.8	37.1	43.1	10.2	13	21.4	8.4	8.1	6.5
Sb121	<0.216	<0.158	<0.242	<0.28	0.2	0.3	<0.215	<0.196	<0.26	<0.38	0.3	<0.205
Cs133	0	0	0	<0.0193	<0.029	0	<0.0147	0	<0.0222	<0.037	0	0
La139	2.1	29.8	1.2	14.8	1.8	12.9	14.3	19.7	16.3	14	11.9	8.5
Ce140	3.5	50.8	2	25.5	3.2	23	25.7	33.6	26.6	23.8	22	13.8
Pr141	0.3	4.6	0.1	2.2	0.2	2.2	2	2.7	2.2	2	1.8	1.2
Nd146	0.8	13.2	0.5	5.8	1.1	6	5.8	6.9	5.9	5.7	6.2	3.7
Sm147	0.2	1.5	0.1	0.6	<0.00	0.4	0.6	0.6	0.5	0.7	0.9	0.4
Eu153	0.1	0.3	0.2	0.3	0.1	0.3	0.3	0.2	0.2	0.1	0.2	0.4
Gd157	0.1	0.6	0.1	0.2	0	0.4	0.3	0.5	0.4	0.4	0.5	<0.131
Tb159	0	0.1	0	0	0	0	0	0	0	0	0.1	0
Dy163	0.1	0.2	0	0.1	0.1	0.3	0.1	<0.076	0.1	0.1	0.5	<0.00
Ho165	0	0	0	0	0	0	0	0	<0.0203	0	0.1	0
Er166	0	0.1	<0.00	0	0	0.2	0	<0.056	0.1	0.2	0.2	<0.00
Tm169	0	0	<0.0200	0	0	0	<0.0121	0	0	<0.018	0	<0.00
Yb172	0.1	0.1	0	<0.00	0	0.3	0	<0.00	0.1	<0.116	0.3	0.1
Lu175	0	0.1	<0.00	0	0	0.1	0	0	0	0.1	0.1	<0.020
Au197	<0.63	<0.55	<0.78	<0.58	<0.68	0.7	<0.45	<0.66	<0.65	<0.72	<0.58	<0.67
Pb208	0.2	0.5	0.4	0.2	0.2	0.3	0.7	1.1	0.9	2	1.3	0.3
Bi209	<0.034	<0.033	0	<0.050	<0.036	<0.031	<0.033	<0.045	<0.039	<0.060	0.1	<0.053
Th232	0	0.1	0.1	0	0	0.1	0.1	0	0	0.8	5.1	0
U238	0.1	0.3	0.6	0	0.1	0.1	0.1	0	0	2.9	21.6	<0.00

Mineral	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline
Sample NO	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Pathargora	Surda
Comment	Unaltered	Unaltered	Altered	unaltered	Altered	Unaltered	Altered	Unaltered	Altered	Unaltered	Altered	Altered
Li7	8	14.8	5.6	1.8	3.5	6.4	3.3	2.5	3.8	4	8.3	4.2
Be9	0.7	1.7	1.5	0.4	1.6	2.2	1.1	0.5	1.6	0.9	20.1	<0.50
B11	28525.8	29141.8	29430.3	29702.9	22309.5	27182.2	29140.5	30475.9	27374.6	32286.8	28354.7	30947.2
Mg24	40178.9	37615.6	47301.5	56281.7	39201.8	34654.4	51300.1	50980.5	40824.2	46306.4	41825.3	54659.4
P31	54	63	62.9	114.1	66.1	72.2	75.6	128.5	88.2	73.4	78	119.5
Fe57	53009.9	35283.6	33207.2	39905.8	33933.4	42298.4	47238.8	45836.7	44578.3	57963.2	42972.1	46628.9
K39	480	192.3	102.4	400.9	242.6	249.9	273.9	408.7	198.4	310	249.2	470.5
Sc45	201.8	59.4	26	187.1	127.3	239.5	169.6	142.8	116.4	219.2	123.1	84.4
V51	800	769.2	605.3	4759.9	1123.8	1199.2	2205.8	1874.4	1037	1482.8	1140.5	955.2
Cr52	378.9	169.4	163.4	233.8	110.8	20.7	204.3	2436.5	91.1	50.2	273.7	837.8
Co59	44.3	35.8	36.8	14.7	18.8	31.6	28.2	24.2	31.9	36.9	37.3	17
Ni60	1131.8	165	184.7	359.9	247.1	336.1	295	298	419	298.9	268.1	750.4
Cu63	1.2	<0.37	2.9	0.9	0.7	28.4	<0.51	24.7	52	1.4	<0.54	4.6
Zn66	23.1	8.2	6.1	4.9	4.1	4.4	5.7	9.5	6.7	5.9	7.1	8
Ga71	68.6	73.8	34.5	137.7	52	82.5	82	84.7	95.1	102.8	66.3	102.3
Ge73	2.4	<2.36	1.5	<2.65	2.5	2.8	1.1	1.1	2.8	3.1	1.7	3.6
As75	<5.42	<4.41	<4.30	<4.67	<3.83	5.5	<5.20	<5.79	<5.69	<5.84	<6.09	<6.43
Rb85	<0.073	0.1	0.2	<0.082	<0.063	0.2	0.2	0.2	<0.082	<0.126	1.1	<0.152
Sr88	63.5	53.9	24.8	106.2	59	60.2	81.5	80.2	68.6	84.9	68.3	64.6
Y89	0.9	0.2	0	0.3	0.2	0.8	0.3	0.7	0.8	0.3	0.1	0.2
Zr90	3.4	<0.064	0.3	3.4	2.8	2.9	1.1	8.5	0.7	2	<0.080	3.5
Nb93	2.3	0.2	<0.032	29	6.7	15.9	4.8	7.4	4.6	13.8	0.6	3.9
Mo95	<0.231	<0.21	0.2	<0.263	<0.181	0.1	<0.168	0.4	<0.167	<0.26	<0.269	<0.31
Hf178	0.3	<0.00	<0.00	0.4	0.3	0.1	0.1	0.3	0.1	0.2	0	0.5

Ta181	1.1	0	0	9.1	2.8	2.2	1	1.5	0.1	1.5	0.2	0.7
Ba137	1.2	1.1	0.1	1.6	0.9	0.5	2	2.6	0.5	1	1.3	1.8
Ti49	8359.1	1514.5	2222.2	9313.4	4546.7	1397.7	2253.8	2314.3	765.8	1047.5	2262.1	3446.6
Mn55	74.7	25.3	48.4	16.2	14.3	16.8	26.7	27.8	23.5	24.3	21.1	19
Ag107	<0.194	<0.246	<0.237	<0.201	<0.144	<0.141	<0.142	<0.156	<0.183	<0.236	0.1	<0.242
Cd111	<0.268	<0.231	<0.22	<0.244	0.1	0.1	0.1	<0.30	0.1	0.1	<0.31	0.1
Sn118	6.8	8.7	2.3	60.5	34.1	33.1	27.8	38.3	60.2	46.9	9.7	37
Sb121	<0.177	<0.28	<0.182	<0.32	<0.196	<0.201	<0.185	0.3	<0.27	<0.251	<0.28	<0.29
Cs133	<0.0182	<0.00	<0.0155	0	<0.00	<0.0174	0	0	0	0	<0.021	<0.034
La139	41.9	1.4	0.9	33.6	11.6	40.8	8.7	17.2	8.8	27.7	3.1	12.4
Ce140	69.6	2.6	1.6	56.7	18.1	68.3	14.8	31.3	15.3	44.2	4.9	21.2
Pr141	5.3	0.2	0.1	4.9	1.4	5.6	1.4	2.6	1.2	3.8	0.4	1.8
Nd146	15.9	0.6	0.3	14	4.2	16.4	3.3	7.7	4.2	10	1.4	4.8
Sm147	1.6	0.1	0.1	1.7	0.6	1.7	0.4	0.7	0.4	0.6	0.3	0.3
Eu153	0.6	0.2	0.1	0.6	0.3	0.3	0.4	0.4	0.2	0.4	0.2	0.2
Gd157	0.7	0.1	<0.00	1	0.4	0.8	<0.107	0.6	0.3	0.4	0.1	0.3
Tb159	0.1	<0.00	<0.00	0.1	0	0.1	0	0.1	0	0	0	0
Dy163	0.4	0.1	<0.00	0.3	0.1	0.2	0.1	0.2	0.1	0.1	0	0.1
Ho165	0	<0.0152	<0.0206	0	0	0	0	0	0	0	<0.00	0
Er166	0.1	0.1	<0.00	0.1	0	0.1	0	0.1	0.2	0	0	0
Tm169	0	0	<0.00	<0.0142	0	0	<0.0153	0	0.1	0	<0.00	0
Yb172	0.1	0.1	<0.150	0	0	0.3	0.1	0.2	1	0.3	<0.081	0
Lu175	0	0	<0.00	0	0	0.1	0	0.1	0.3	0.2	0	<0.0205
Au197	<0.50	<0.78	<0.69	<0.55	<0.40	<0.52	<0.52	<0.61	<0.53	<0.55	<0.54	<0.66
Pb208	0.7	1.5	0.4	0.3	0.1	0.7	2.3	2.6	0.8	0.9	2	0.5
Bi209	<0.035	<0.062	<0.059	<0.051	<0.030	<0.024	<0.039	0.1	<0.039	<0.048	<0.033	<0.033
Th232	0.1	0	<0.00	0	0	0.4	0.1	6	0.2	0.2	0	0.6
U238	0.1	0	0	0	0	0.4	0	1.5	0.7	0.1	<0.00	<0.00

Mineral	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline	Tourmaline
Sample NO	Surda	Surda	Surda	Surda	Surda	Surda	Surda	Surda	Surda
Comment	Unaltered	Altered	Unaltered	Altered	Altered	Unaltered	Unaltered	Altered	Altered
Li7	20.5	23.8	16.4	49.9	4.3	3.3	6.7	5.4	9.3
Be9	0.2	0.4	0.5	<2.62	0.4	0.4	<0.73	<0.00	1.6
B11	27831.2	39504.3	20811.7	67109.9	36874.5	29618.7	36727.7	39423.7	41734.9
Mg24	25553.6	49225.4	21072.5	57385.4	59430	44141.2	59598.8	59007.8	51800.7
P31	69	133	<66.19	300.7	97.9	85.5	<57.35	<184.45	<192.17
Fe57	58545.4	73289.2	42355.5	140878.3	61612.6	52135.3	65467.7	69247.5	81786.1
K39	386.2	619	488.2	942	485.2	497.1	485	557.7	630.1
Sc45	59.1	88.9	65.9	201.8	130.7	97.3	109.7	86.9	89.8
V51	249.4	1191.4	428.9	709.6	1614	997.4	1582.2	1192.9	1087.2
Cr52	18.3	1206.3	434.4	588.5	65.9	20.8	88.6	103.6	105.6
Co59	65.5	79.3	42.5	162	30.4	22.4	36.4	30.4	59.9
Ni60	1695.7	1800.8	1141.4	4150.4	1050	871.9	1066.2	1232.7	1877.3
Cu63	2.5	34.2	11.7	18.3	7.5	1.2	33.6	9.3	7.3
Zn66	25.8	26.7	14	45.3	11.8	6.7	9.3	13.3	11.7
Ga71	94.2	128.8	70.8	263.5	136	102.8	138.2	139	141.5
Ge73	2.2	<2.41	<2.57	<6.29	<2.32	<1.62	3.2	3.5	5.5
As75	<5.12	<5.60	<7.17	<22.71	<8.83	<7.88	<7.32	<22.19	<24.03
Rb85	0.1	1.8	2	0.7	<0.204	0.5	<0.095	<0.36	0.3
Sr88	31.7	92.2	36.8	101.7	72.9	53	92	76.5	65.9
Y89	1.1	1.4	5.8	3.1	1	0.2	0.7	1.1	0.3
Zr90	81.7	78.6	21.9	38.4	3.3	1.8	1.8	1.8	1.8
Nb93	2.6	3.8	4.5	7.1	1.2	1.1	2.1	1.3	1.6
Mo95	<0.234	<0.21	<0.27	<1.94	<0.41	<0.263	0.2	<0.81	<1.62
Hf178	2.5	2.5	0.6	1.2	0.2	0.1	0.2	0.1	0.2
Ta181	0.7	1.1	0.8	0.9	0.2	0.2	0.3	0.2	0.4

Ba137	0.5	1.9	1.8	2.5	1.7	1.9	1.2	2	0.6
Ti49	3491.1	4873	2839.2	7592.2	3551.7	2673.2	4002.5	3651.7	4154.5
Mn55	60.5	67.8	45	127.2	27.3	21.6	30.8	28.7	57.7
Ag107	<0.143	<0.235	<0.34	<1.16	<0.37	<0.27	<0.27	<0.66	<0.90
Cd111	<0.274	<0.49	<0.64	<1.31	<0.85	<0.88	<0.00	0.4	<1.37
Sn118	3.3	9.5	5.7	11.2	26.9	20.8	26	26.6	22.1
Sb121	<0.208	<0.30	<0.32	<1.05	<0.33	<0.28	<0.202	<0.87	<0.77
Cs133	0	0	<0.043	<0.00	<0.0322	0	<0.033	<0.126	<0.089
La139	8	14	15.1	27.1	8.7	6.6	9.7	11.2	9.8
Ce140	13.7	25.6	23.3	41.5	14.8	12	16	18.4	16.5
Pr141	1	2	2	2.8	1.3	1	1.3	1.6	1.6
Nd146	2	4.9	4.4	7.5	3.7	2.7	3.6	3.6	3.1
Sm147	0.1	0.6	0.3	0.7	0.2	0.2	0.3	0.7	0.2
Eu153	0.1	0.2	0.1	0.3	0.3	0.3	0.2	0.1	0.1
Gd157	<0.147	0.4	0.3	0.9	0.3	0.2	0.3	0.2	0.1
Tb159	<0.0161	0	0.1	<0.077	0	0	0	0.1	<0.00
Dy163	0.2	0.2	0.9	0.4	0.3	0.1	0.1	0.3	<0.00
Ho165	0.1	0	0.2	0.2	0.1	<0.037	0	<0.08	0
Er166	0.1	0.3	0.7	0.6	0.1	0	<0.083	<0.221	0
Tm169	0	0.1	0.1	0.1	0	<0.00	0	0.1	0
Yb172	0.6	0.5	1	0.9	0.1	<0.109	0.1	<0.33	<0.00
Lu175	0.1	0.1	0.2	<0.074	<0.027	<0.024	0	0	0
Au197	<0.51	<0.51	<1.51	<3.20	<0.89	<0.77	<0.66	<2.21	<2.20
Pb208	0.2	0.7	0.2	<0.44	0.3	0.2	0.2	0.4	<0.28
Bi209	<0.021	<0.057	<0.080	<0.221	0.1	<0.047	<0.047	<0.124	<0.144
Th232	0.1	0.6	0.3	0.1	0.5	0.1	0.3	0.4	0.2
U238	2.6	2.7	1.2	2.1	0.5	0	0.4	0.1	0.1