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Full Length Research Paper

Geochemical Study of Tourmalines from Some Parts of Southwestern Nigeria

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ABSTRACT

Tourmaline is a common gem mineral found in association with beryl, topaz, garnet and kunzite alongside other rock-forming minerals like quartz, feldspar and muscovite in pegmatite across southwestern Nigeria. This study undertook a geochemical study of tourmalines from southwestern Nigeria with a view of ascertaining their origin and petrologic significance. Twenty-two (22) differently coloured tourmaline samples from different locations in southwestern Nigeria were prepared and analyzed using inductively coupled plasma - mass spectrometry (ICP-MS) to determine elemental constituents. The tourmalines are enriched in SiO_2, with wide compositional variability in CaO, Al_2O_3, and FeO, with low contents of P_2O_5, TiO_2, MgO and the alkalis. This wide variation in chemical compositions is believed to be a reflection of the systematic changes associated with the heterogeneity in compositions of their host rocks and mineralizing fluids brought about by the diversity in their geologic settings. The strong negative correlations observed between CaO and the oxides Al_2O_3, Na_2O, K_2O and SiO_2 in the mineral samples clearly revealed features of magmatic deposits for the tourmalines, with their chemistry reflecting control by host mafic rocks and/or granitic-pegmatitic fluid. The tourmaline samples are extremely depleted in Heavy Rare Earth Elements (HREE) relative to Light Rare Earth Elements (LREE) suggesting that the crystallizing fluids are sourced from the upper continental crust rather than the mantle. The intensity of colouration in tourmaline is linked to the presence or otherwise of iron concentration.

Keywords: Southwestern Nigeria, Tourmaline, Pegmatite, host rock, magmatic deposits

INTRODUCTION

Tourmaline, a group of boron aluminum cyclosilicate with a typical complex chemical formula $(Na,Ca)(Mg,Li,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$ is a very common accessory mineral occurring in some mineralized pegmatites across southwestern Nigeria. It is usually associated with other gem minerals such as beryl, kunzite, garnet and topaz, alongside rock-forming minerals like quartz, feldspar and mica. Prominent locations with significant occurrences of tourmaline in southwestern Nigeria include Komu and Ofiki in Oyo state, Ijero in Ekiti state and Oro in Kwara state, where characteristic occurrences of euhedral gem tourmaline crystals are contained in granitoids intrusive rocks and their associated pegmatites and aplites. Sometimes tourmaline may be found as detrital grains in alluvial deposits where they have been deposited after being released and transported from their parent pegmatites. Mining of tourmaline and other gem minerals in pegmatites from these locations and some other areas in southwestern Nigeria has started many years ago and it is still continuing till date.

Tourmaline varies greatly in composition and consequently the colour varies with the chemical composition of the crystals. It has a wide range in chemical composition with major and trace elements substituting for one another in the crystal structure. This ability of tourmaline to accommodate major and trace elements of widely varying ionic charge and radius in its crystal structure makes it an excellent monitor of the major and trace element make-up of its local environment of growth. Tourmaline complex composition also reflects changes in its chemical and physical environment and therefore makes it well-suited to explore the conditions under which it formed, the varied mineral compositions allowing for conditions to be pinpointed more precisely (Henry and Dutrow 1996; Henry and Guidotti, 1985). The large stability range, in both pressure and temperature of tourmaline, facilitates its widespread occurrences in different geologic settings, and this coupled with its resistance to alteration and weathering, all make tourmaline an excellent indicator-mineral. Studies on the chemical composition of tourmaline have not being extensively undertaken in this part of the world, especially its use in the petrogenetic study of its parent pegmatite. This study was aimed at investigating the geochemical characteristics of tourmalines from some parts of southwestern Nigeria with a view to using the information obtained therefrom in elucidating the petrogenetic provenances of their parent pegmatite and host rocks. The study also attempted to establish a link between the tourmaline chemistry to exhibited color.

SAMPLING AND ANALYTICAL METHODS

Twenty two (22) flawless crystals of differently coloured tourmaline ranging from schorl, indicolite, elbaite and rubellite (Fig. 1) collected from various mining sites within southwestern Nigeria (Fig. 2) were analyzed and studied. A geological mapping of the two areas (Komu in Oyo state and Ijero-Ekiti in Ekiti state) from where majority of the tourmaline samples were obtained was undertaken. Each of these crystals was carefully selected to avoid colour zoning and then crushed by wrapping carefully in a paper and striking it with a hammer. This was necessary to avoid any iron contamination which might in any way develop. The selected particles were then ground in a thoroughly cleaned new agate mortar. The crushing process was continued until the tourmaline was reduced to fine grained powder to promote rapid and complete dissolution. The pulverized samples were sent to ACME laboratory, Vancouver, Canada for their major and trace element compositions analysis, using the lithium metaborate/tetraborate fusion and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) analytical method.

The pulverized samples were leached with hot HCl and HNO_3 to remove possible sulfides and carbonates. An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to be analyzed to ions which are then separated and detected by the mass spectrometer. The sample is typically introduced into the ICP plasma as an aerosol, either by aspirating a liquid or dissolved solid sample into a nebulizer or using a laser to directly convert solid samples into an aerosol. Once the sample aerosol is introduced into the ICP torch, it is completely dissolved and the elements in the aerosol are converted first into gaseous atoms and then ionized towards the end of the plasma. Once the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones. The interface region in the ICP-MS transmits the ions traveling in the argon sample stream at atmospheric pressure into the low pressure region of the mass spectrometer. Once the ions enter the mass spectrometer, they are separated by their mass-to-charge ratio. They must then be detected or counted by a suitable detector which fundamental purpose is to translate the number of ions striking the detector into an electrical signal that can be measured and related to the number of atoms of that element in the sample via the use of calibration standards. The results of the analysis were presented as data to document correlations between tourmaline samples and to provide the basis for interpreting the significance of tourmaline in the deposits.

Geologic setting

The area under study is located in southwestern part of Nigeria, underlain by crystalline rocks, collectively referred to as the Southwestern Nigerian Basement Complex. The Basement Complex rocks occupies about half the landmass of the country, and it is a polycyclic terrain which suffered deformation and mobilization during the Pan-African age (600±150 Ma) (Fig. 3). It is a part of the Pan-African mobile belt lying between the West African and Congo Cratons (Black, 1980) and has a complex geologic history as a result of the different episodes of rock formation spanning Archean to Lower Proterozoic. The Pre-Cambrian rocks consist predominantly of folded gneisses, schist and quartzite into which have been emplaced granitic and to a lesser extent, more basic rocks. Within the Basement Complex of Nigeria, four major petro-lithological units are distinguishable (Obaje, 2009), namely;

1. The Migmatite – Gneiss Complex (MGC),
2. The Schist Belts (Metasedimentary and Metavolcanic rocks)
3. The Older Granites (Pan African granitoids)
4. Undeformed Acid and Basic Dykes

The migmatite – gneiss – quartzite complex represents the oldest recognizable rocks (Grant, 1969) and it is considered to be banded, but migmatised to a variable extent. It has a heterogeneous assemblage comprising migmatites, orthogneises, paragneisses and a series of basic and ultrabasic metamorphosed rocks. Gneisses vary in mineralogical composition and character, with two types recognizable in the Basement Complex; the biotite gneiss and the hornblende biotite gneiss. The migmatite gneiss complex bears imprints of the Liberian (ca.

Figure 1. Study tourmaline samples

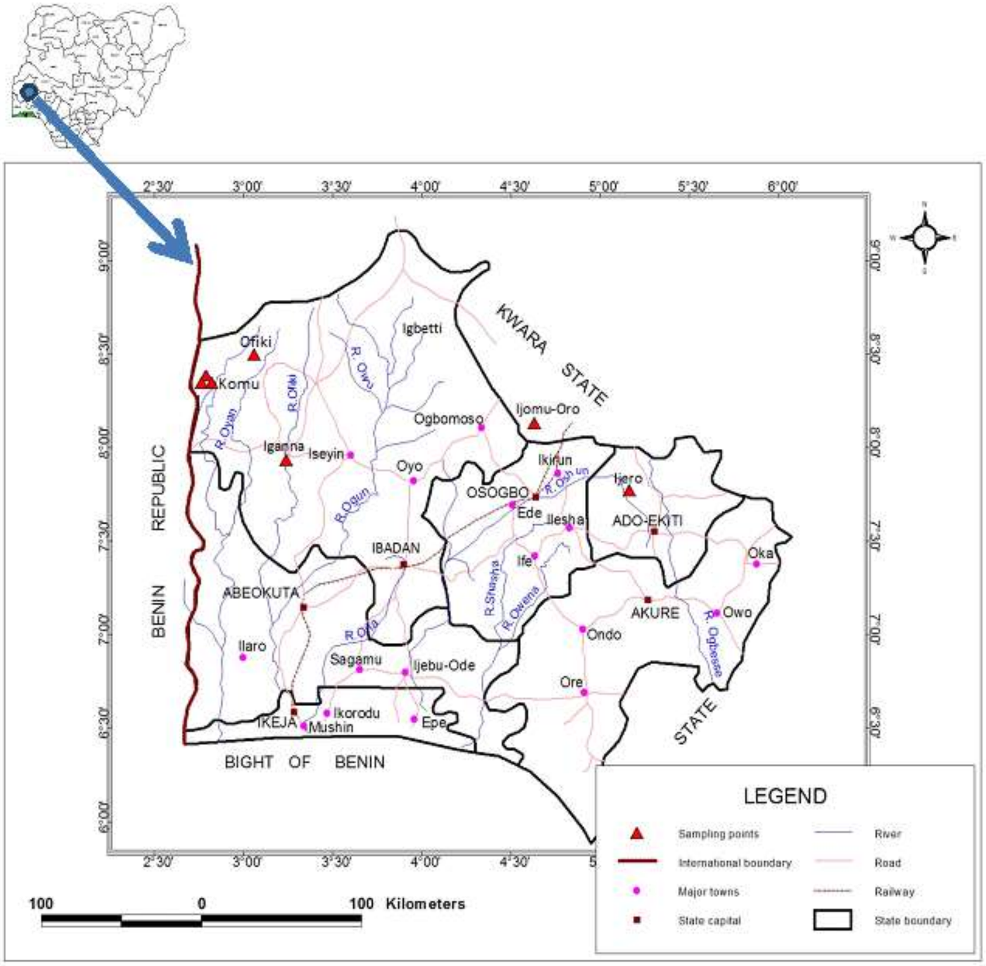

Figure 2. Map of southwestern Nigeria showing the sample locations (The authors, 2011)

2700Ma), Eburnean (ca 2000Ma) and Pan African (ca. 600±150Ma) tectonic events (Oversby, 1975; Turner, 1983). An obtained U-Pb zircon age of 709+27/-19Ma, representing the oldest Pan African magmatism has been reported in Southwestern Nigeria (Adetunji et al, 2016). The imprint of the Pan-African event did not only structurally overprint and re-set many geochronological clocks in the older rocks, but also gave rise to granite gneisses and migmatites.

The Schist belts, which are mainly N–S to NNE–SSW trending are considered to be Upper Proterozoic supracrustal assemblages of low to medium grade meta-sedimentary (and minor volcanic) rocks which have been in-folded into the presumably older migmatite-gneiss complex (Turner,1983). This belt consists of quartzites, amphibolites, pelitic and mica-schist, calc-silicate rocks, marbles, phyllites, metaconglomerate iron formations and subordinate meta-igneous rocks (Elueze, 1992).

The Older Granites occur intricately associated with the Migmatite-Gneiss Complex and the Schist Belts into which they generally intruded and are believed to have been emplaced during the Pan-African orogeny (Harper *et al,* 1973). The Pan-African intrusive suite comprises mainly granites and granodiorite, with subordinate pegmatite and aplites. Associated rocks include charnockites, syenites, tonalites, adamellites, quartz monzonites and gabbro plus extrusive and hypabyssal bodies, notably dolerite dykes believed to belong to the terminal stage of the Pan-African orogenic event in Nigeria (Olarewaju, 1999).

The undeformed acid and basic dykes are late to post-tectonic Pan African, cross-cutting the Migmatite-Gneiss Complex, the Schist Belts and the Older Granites. They include:

- Felsic dykes that are associated with Pan African granitoids on the terrane such as the muscovite, tourmaline and beryl - bearing pegmatites, micro-granites and aplites dykes (Dada, 2006).
- Basic dykes that are generally regarded as the youngest units in the Nigerian basement such as dolerite and the less common basaltic and lamprophyric dykes.

Geology of Komu study area

The Komu study area lies between latitudes 8° 16' 12'' N and 8° 17' 29'' N and longitudes 2° 59' 18'' E and 3° 01' 07'' E. This area is mainly underlain by amphibole and pelitic schists being the oldest rocks, and pegmatites which have mostly intruded semi-discordantly the older rock (Fig. 4). Field evidence showed observable lateral compositional and textural variations of the schist in the area. There is an increase in the quartzo-feldspathic content of the rock towards the west, hence more of the outcrops are preserved in this axis while in the eastern part, and the area is devoid of any appreciable rock exposures due to intense weathering of the amphibole schist. Rocks are rarely exposed in the central portion, except in mining excavations and along stream channels. The Komu amphibole schist is part of the Schist Belt, a member of the Precambrian Basement Complex of Nigeria comprising low grade meta-sediments-dominated belts trending N-S which are best developed in the western half of Nigeria (Annor et al., 1996). These belts are considered to be Upper Proterozoic supracrustal rocks which have been in-folded into the presumably older migmatite-gneiss-quartzite complex during the Pan African Orogeny (McCurry, 1976; Grant, 1978). The Komu schists have a general N-S strike direction and dips moderately to steeply (60^0- 80^0).

In Komu, sporadic occurrences of pegmatites are widespread, intruding the older amphibole schist. In some instances, they occur as intrusive bodies making visible contacts with the older rock bodies, while in many others they are found as veins, either cross-cutting themselves or with quartz veins within the older rocks. Thus two lithologically and chronologically different groups of Precambrian pegmatites are distinguishable in the area. The barren massive quartz-microcline pegmatites with minor muscovite and accessory tourmalines, usually occurring as isolated intrusive bodies in the area and the NNE-SSW trending, tourmaline-bearing pegmatite generally revealed to have intruded discordantly the amphibole schist as dykes and veins of various width and mainly observable in all mining excavations in the study area. This tourmaline-bearing pegmatite has been described by Dada (2006) as a member of the felsic dykes that are associated with Pan African granitoids on the terrane. They therefore belong to the undeformed acid and basic dykes believed to be late to post-tectonic Pan African, cross-cutting the Migmatite-Gneiss Complex, the Schist Belts and the Older Granites. This pegmatite field is believed to be part of the late Pan African rare metals granitic pegmatites (Jacobson and Webb, 1946; Wright, 1970). They are therefore believed to be younger than the simple massive quartz – microcline pegmatites which are believed to be associated and part of the Older Granite. This pegmatite field is believed to be part of the late Pan African rare metals granitic pegmatites (Jacobson and Webb, 1946; Wright, 1970). They are therefore believed to be younger than the massive quartz – microcline pegmatites which are believed to be associated with and therefore part of the Older Granite. Geochronological data from previous works (Rb-Sr whole-rock and U-Pb zircon) of Pan-African granitoids intruding the reactivated Archean to Lower Proterozoic crust of central and southwestern Nigeria showed that intrusive magmatic activity in these areas lasted from at least 630 to 530 Ma (van Breemen et a*l*., 1977; Rahaman *et al*., 1983; Dada *et al*., 1987; Matheis and Caen-Vachette, 1983; Umeji and Caen-Vachette, 1984; Akande and Reynolds, 1990). Results of the rock ages also showed that these pegmatities' emplacement in southwestern Nigeria occurred after the peak of the

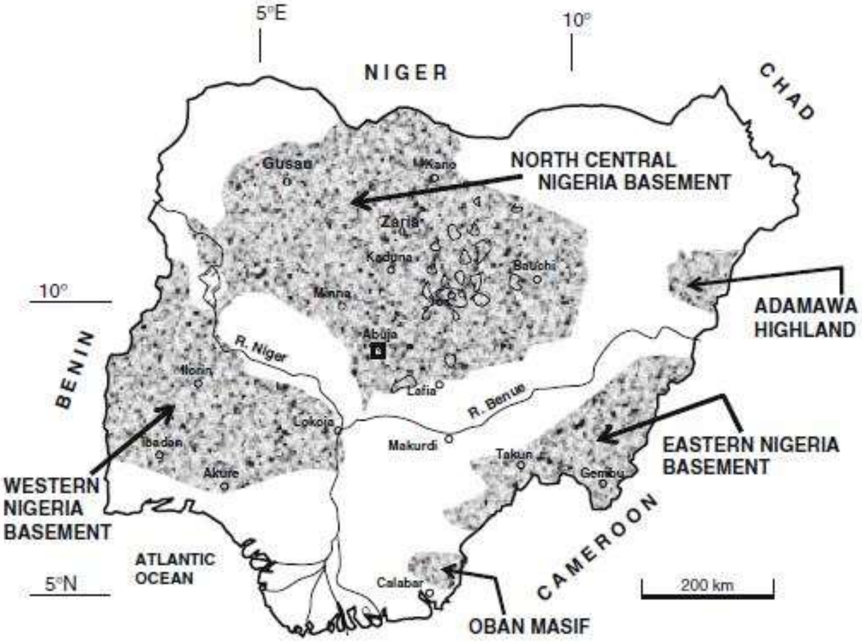

Figure 3. Geological map of Nigeria, showing the Basement Complex (after Obaje, 2009)

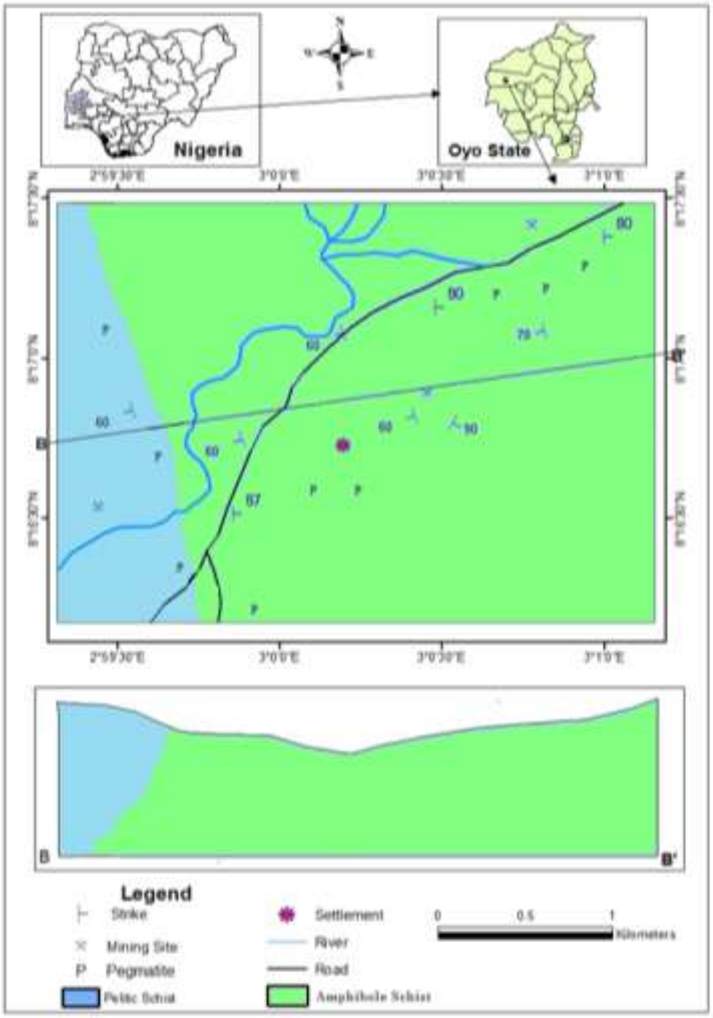

Figure 4. Geological map of Komu study area

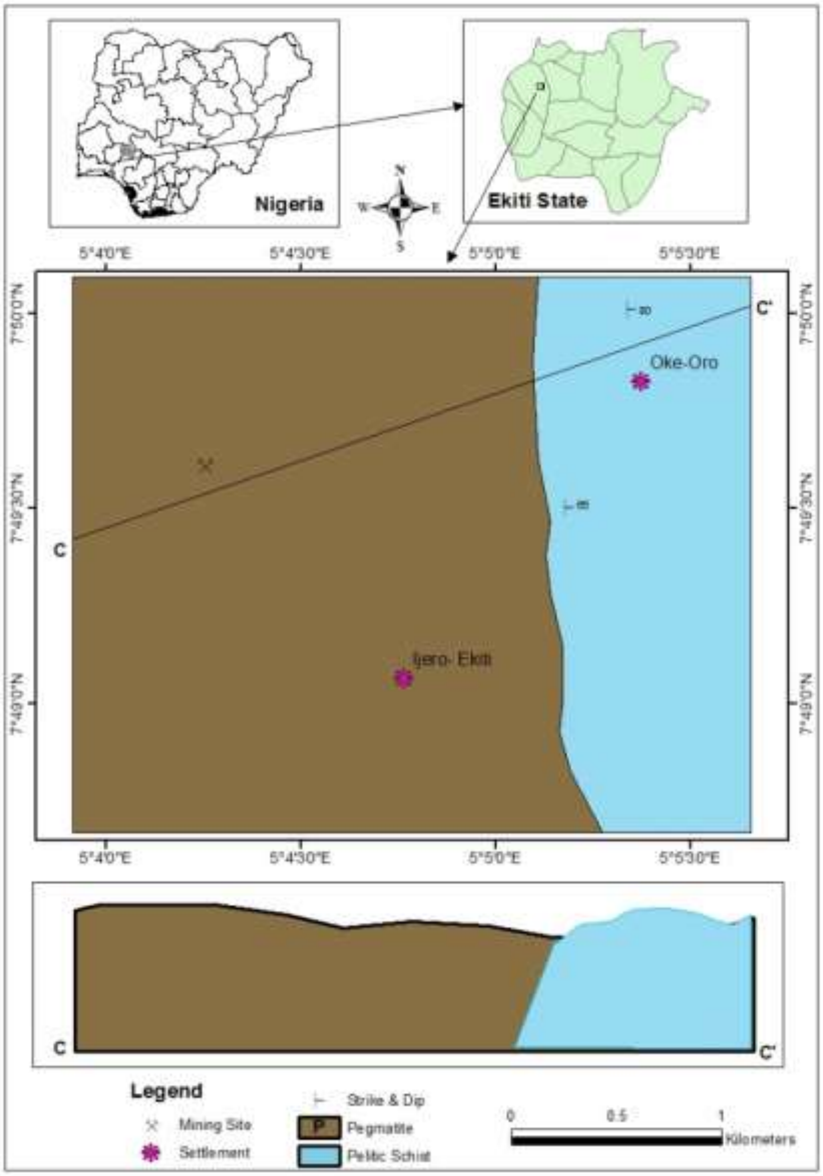

Figure 5. Geological map of Ijero-Ekiti study area

Pan-African orogenic event. The end of the Pan-African tectonic event is marked by a conjugate fracture system of the strike-slip faults (Ball, 1980). Gold and rare-metal pegmatities' mineralization is closely associated with the fractures in the Pan-African belt (Kuster, 1990; Ekueme and Matheis, 1995; Garba, 1992, 2003).

Geology of Ijero-Ekiti study area

The Ijero study area lies within latitudes 7^0 48' 36'' to 7^0 50' 06'' and longitudes 5^0 03' 54'' to 5^0 05' 42''. The lithology of the area is characterized by pegmatites and meta-sedimentary rocks, consisting of dark coloured amphibole and quartz-feldspathic pelitic schist, intercalated with amphibolite and some quartzites. The amphibole schists, observed in the central and western portions are highly weathered and therefore rarely exposed, with only a few bands of the strongly foliated weathered dark green rock feebly observed along stream channels and road side cuttings. The amphibole schist and amphibolite observed mainly in the western and central portions of the area have been heavily intruded by the tourmaline rich Precambrian pegmatites, making the older rocks sparsely seen, falsely revealing the pegmatite as the dominant rock type in the areas. The pelitic schist is however well exposed at the eastern part of the study area (Fig. 5), sometimes forming into high hills and valleys, thereby resulting into the rugged topography typical of the area. The Ijero pegmatites which cover more than two-thirds of the total landmass are most times tabular and expansive in nature. The Ijero pegmatite is believed to be part of the mineralized 400km NE-SW trending Nigeria pegmatites which belong to the terminal stage of Pan-African magmatism (Rahaman *et al.,* 1988). The schists have foliations striking in the north-south direction and dipping moderately to steeply (60^0-70^0) westwards and the mineral alignments seem conformable with the foliation planes of the adjacent schistose rocks.

RESULTS AND DISCUSSIONS

Major oxides geochemistry

The major oxides measured in the tourmaline samples analyzed include SiO_2, Al_2O_3, FeO, Na_2O, K_2O, CaO, P_2O_5, TiO_2 and MgO (Table 1). Measured SiO_2 concentrations ranged from 44.14% (M004) to 93.28% (M013) with a mean value of 86.36%. CaO concentration ranged from 0.01% (M005) to 54.99% (M004) with a mean value of 4.13%; Al_2O_3 ranged from 0.57% to 12.69% with a mean value of 7.8%, while FeO ranged from 0.01% to 2.10% with a mean value of 0.76% (Table 2). Most of the compositional variability observed in the tourmaline samples involved SiO_2, CaO, Al_2O_3, and FeO, with lesser involvements of P_2O_5, TiO_2, MgO and the alkalis. This variability reflected the changing nature of the mineralizing fluid as it interacts with the host rock, becoming increasingly oxidized, Fe-rich and calcareous in nature. The extremely contrasting values of CaO in samples M005 (0.01%) and M004 (54.99%) can essentially be due to huge contrast in geological backgrounds of the sources of the respective tourmaline samples, most probably brought about by the diversity and heterogeneity in their host rocks' chemistry. The tourmaline chemistry reflects the diverse compositions of host rock and hydrothermal fluids, as well as differences in temperature and pressure of formation (Demirel, 2004; Henry and Guidotti, 1985; Slack, 1996).

Variations in SiO_2, CaO and Al_2O_3 do not seem to be responsible for any difference in the physical properties of tourmalines, particularly the colour, but they are individually observed to adversely influence the distribution of other major oxides and trace elements. An inverse relationship exists between SiO_2 and CaO as can be observed in samples M004 and M012. This is an indication that the fluids from which the two samples were crystallized are enriched in Ca but deficient in Si. Since tourmaline compositions reflect both the host rock and fluid source characteristics and are strongly controlled by the mineral assemblage, the high CaO concentrations in these two tourmaline samples might have resulted either from possible high Ca content of the pegmatite housing the tourmaline minerals or could be due to contaminations from the mafic country rock rich in minerals such as amphibole. Adequate concentration of Al is necessary and required for tourmaline crystallization, as Grew (1996) has proved that in highly alkaline and/or silica- or aluminum-undersaturated conditions, tourmaline growth is inhibited and other borosilicates form instead. The activity of Al_2O_3 or equivalent aqueous species contributes to tourmaline stability and formation, which are favoured in acidic fluids with high availability of Al species. However, since Al transport is facilitated by alkali borate species such as $Na_2B_4O_7$, a mixture of acidic and alkaline boron compounds is essential to provide the necessary Al for tourmaline-forming reactions (Morgan and London, 1989). It therefore follows that maximum concentrations of the oxides SiO_2 and Al_2O_3 are required for tourmaline crystallization in an environment.

Na_2O, K_2O, MgO and TiO_2 were found to remain fairly constant in all the samples analyzed. The alkalis, Na_2O and K_2O even though exist in low concentrations, are evenly distributed in all the analyzed tourmaline samples. Low concentrations of alkalis are actually the requirements for tourmaline mineralization in an environment. Minerals containing relatively large amounts of alkalis that react with water to produce alkaline solutions inhibit tourmaline growth, as tourmaline formation is favoured in strongly to weakly acidic fluids (Frondel and Collette, 1957; Morgan and London, 1989). The low concentrations of MgO and TiO_2, both averaging 0.02% indicate pegmatitic origin for the tourmaline samples. Dunn (1977) also reported that MgO would not cause colour change in tourmalines, but would have influence on the presence or otherwise and amount of other oxides/elements. TiO_2 is found to be present in all the analyzed samples, and it is believed to be a substitute for iron and silicon (Hawthorne and Henry, 1999). P_2O_5 values were observed to be low in all the analyzed samples except in samples M008 and M013 which have relatively high values of 1.33% and 0.51% respectively. These samples were however obtained from Ofiki, thus confirming a possibly different environment of deposition from the other samples.

The mean FeO content of the tourmaline samples is 0.76% and it ranged from 0.01% (M001 and M002, both rubellites from Komu) to 2.1% (M019, a dark blue tourmaline from Oro). It was observed that while samples which appear dark have higher values of FeO, the values are low in samples that are pale in colour. It therefore confirms the earlier concept that the variations in FeO concentrations of the samples have tremendous effects on type and intensity of colouration in tourmalines. Whereas FeO was found to be of low concentrations in samples M001(0.01%) and M002 (0.01%) which are pink and pinkish-red tourmaline respectively, it was significantly present in samples M003 (0.87%), M007 (1.89%), M009 (0.72%), M011 (0.99%), M014 (1.26%), M016 (1.11%), M017 (0.89%), M019 (2.10%), M020 (1.99%), M021 (2.02%) which are emerald green, dark

Table 1. Major oxide compositions of studied tourmaline samples from southwestern Nigeria

Sample	Sample Source	Sample colour	SiO_2 (%)	FeO (%)	CaO (%)	P_2O_5 (%)	MgO (%)	TiO_2 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)
M001	Komu	Pink	93.15	0.01	0.06	0.02	0.01	0.01	6.33	0.31	0.13
M002	Komu	Pinkish red	91.39	0.01	0.07	0.03	0.01	0.01	7.59	0.38	0.52
M003	Komu	Green	89.85	0.87	0.31	0.23	0.01	0.01	7.90	0.67	0.16
M004	Komu	Blue	44.14	0.13	54.99	0.01	0.01	0.08	0.57	0.04	0.05
M005	Komu	Yellow	92.21	0.04	0.01	0.01	0.01	0.07	6.97	0.58	0.13
M006	Komu	Lemon yellow	92.35	0.27	0.10	0.01	0.01	0.01	6.63	0.47	0.17
M007	Komu	Dark blue	84.84	1.89	0.07	0.01	0.01	0.02	11.79	1.01	0.28
M008	Ofiki	Purple	92.50	0.08	1.43	1.33	0.01	0.01	4.00	0.51	0.14
M009	Komu	Yellow green	91.09	0.72	0.20	0.02	0.12	0.04	6.91	0.69	0.22
M010	Komu	Brown	87.94	0.48	0.39	0.22	0.01	0.03	9.82	0.87	0.25
M011	Komu	Green	88.13	0.99	0.41	0.01	0.01	0.02	9.60	0.65	0.20
M012	Komu	Grey	62.47	0.23	31.00	0.01	0.01	0.05	5.80	0.33	0.11
M013	Ofiki	Orange	93.28	0.03	0.85	0.51	0.01	0.02	4.87	0.32	0.12
M014	Ijero	Green blue	89.91	1.26	0.04	0.02	0.01	0.01	7.93	0.67	0.16
M015	Ijero	Light blue	91.72	0.35	0.13	0.01	0.01	0.01	7.20	0.45	0.14
M016	Ijero	Green	87.86	1.11	0.13	0.01	0.05	0.01	9.88	0.77	0.19
M017	Ijero	Yellow green	88.62	0.89	0.18	0.03	0.05	0.02	9.37	0.68	0.16
M018	Ijero	Green blue	90.50	0.59	0.15	0.06	0.01	0.01	7.93	0.55	0.19
M019	Oro	Dark blue	83.73	2.10	0.07	0.01	0.01	0.02	12.69	1.14	0.24
M020	Oro	Dark green	85.25	1.99	0.14	0.01	0.01	0.03	11.37	0.94	0.27
M021	Iganna	Black	87.55	2.02	0.08	0.03	0.17	0.03	9.20	0.74	0.18
M022	Ijero	Blue	91.36	0.66	0.08	0.01	0.01	0.01	7.16	0.47	0.25

Table 2. Summary of major oxide compositions of studied tourmaline samples from southwestern Nigeria

Oxides	Range (%)	Mean ± S.D
SiO_2	44.14 - 93.28	86.36±11.39
FeO	0.01 - 2.10	0.76±0.71
CaO	0.01 - 54.99	4.13±13.12
P_2O_5	0.01 - 1.33	0.12±0.30
MgO	0.01 - 0.17	0.02±0.05
TiO_2	0.01 - 0.08	0.02±0.02
Al_2O_3	0.57 - 12.69	7.80±2.71
Na_2O	0.04 -1.14	0.60±0.26
K_2O	0.05 - 0.52	0.19±0.09

Table 3. Statistical correlation coefficients for major oxides of tourmaline samples from different locations in southwestern Nigeria

	FeO	CaO	P_2O_5	MgO	TiO_2	Al_2O_3	Na_2O	K_2O	SiO_2
FeO	1								
CaO	-0.27	1							
P_2O_5	-0.29	-0.10	1						
MgO	.49*	-0.15	-0.16	1					
TiO_2	-0.13	.69**	-0.19	0.09	1				
Al_2O_3	.78**	.62**	-0.35	0.27	-0.37	1			
Na_2O	.82**	-.56**	-0.12	0.34	-0.22	.91**	1		
K_2O	0.21	-0.42	-0.17	0.08	-0.33	.49*	0.35	1	
SiO_2	0.05	-.97**	0.20	0.07	-.69**	0.42	0.35	0.34	1

* Correlation is significant at the 0.05 level (2-tailed

** Correlation is significant at the 0.01 level (2-tailed) blue, yellow green, green, green blue, green, yellow green, dark blue, and black coloured tourmalines respectively. Taylor and Slack (1984) interpreted the blue to black colors associated with schorl to be dominantly influenced by Fe^{2+} => Fe^{3+} and O^{2-} => Fe^{3+} charge-transfer processes, and the brown hues of dravite by uv-centered O^{2-} => Fe^{2+} and Fe^{2+} => Ti^{4+} processes. FeO is therefore believed to be chiefly responsible for the southwestern Nigerian tourmaline's colour variation. The results established that the FeO content varies directly and proportionately with the depth of color in the greens, and inversely in the pinks and reds, being totally absent, or, if present, only in extremely minute traces in the reds. The darker greens had the most iron, becoming less in the lighter shades and completely undetected in the lightest pink. Samples M021 (2.02%), a schorl and M019 (2.1%), dark blue tourmaline have the highest concentrations of FeO. The results showed FeO in greater concentration in the green and black tourmalines, whereas, on the contrary it was observed to be low in samples M005 (0.04%), M008 (0.08%) and M013 (0.03%), which may most likely be responsible for their pale colours of yellow, purple and orange respectively. The dravite, brown tourmalines, also follow the same trend as other tourmalines with respect to corresponding colours; Fe content again controls the intensity, with hues ranging from brown sample, M010 (0.48%)) down to lemon yellow sample M006 (0.27%), to yellow sample, M005 (0.04%)) and then to orange M013(0.03%)). This is in conformity with widely reported works, the foremost one being Deer et al., (1986), who acknowledged the main controlling factor for colour in tourmaline to be the presence or absence of Fe. Dunn (1977) actually established relationship between a decrease in Fe content and a decrease in colour intensity, an assertion similarly supported by this study (Table 1).

CaO is negatively correlated with all the other major oxides except TiO_2 with which it is positively correlated (Table 3). Strong negative correlation coefficients were obtained between CaO and the oxides Al_2O_3 (-0.62), Na_2O (-0.56), K_2O (-0.42) and SiO_2 (-0.97), clearly revealing features of magmatic deposits for the southwestern Nigerian tourmalines. The strong negative correlation that existed between CaO and Al_2O_3 on one hand and SiO_2 and CaO on the other indicated magmatic origin (Frondel and Collette, 1957). Other pairs of oxides with strong to moderate negative correlations included SiO_2-TiO_2 (-0.69), Al_2O_3-TiO_2 (0.37), K_2O-TiO_2 (-0.33) and K_2O-TiO_2 (-0.33), all of which are related to cations substitutions in the tourmaline structure, the higher the negative correlation coefficients, the greater the ease with which substitutions take place between the concerned cations. A binary plot of SiO_2 against CaO (Fig. 6) revealed a negative correlation between the two oxides, indicating that tourmaline produced within an environment high in CaO is likely to have low concentration of SiO_2. Similarly a plot of Al_2O_3 versus CaO (Fig. 7) showed a negative trend between the two oxides. These two plots also confirm that SiO_2 and Al_2O_3 distributions in tourmalines of southwestern Nigeria are not significantly affected by low concentrations of CaO.

Al_2O_3 is positively correlated with the oxides Na_2O (.91), FeO (.78), K_2O (.49) and SiO_2 (0.42) but negatively correlated with the others (Table 3). The binary plots of Al_2O_3 versus Na_2O (Fig. 8), Al_2O_3 versus K_2O (Fig. 9) and Al_2O_3 against FeO (Fig. 10) all yielded well-defined trends, reflecting positive correlations between the respective pairs of oxides. It therefore also followed that FeO and Na_2O are also positively correlated (Fig. 11). The positive correlations between Al_2O_3 and the alkaline Na_2O and K_2O is in line with the believe of Morgan and London (1989) that the solubility of aluminosilicates phases and components (e.g., Al) in borate fluids increases with increasing fluid alkalinity and may be indicative of changing speciation mechanisms in solution as a function of pH. A remarkable feature noted in the majority of tourmalines from southwestern Nigeria is the direct relationship between total FeO and Al_2O_3. In other studies, the transition from Al-rich to Fe-rich compositions has been linked to increasing distance from a magmatic source coincident with decreasing temperature and increasing differentiation of late magmatic fluids (Caverretta and Puxeddu, 1990). A ternary plot of Al_2O_3 - FeO - MgO (Fig. 12) showed that all the tourmaline samples from southwestern Nigeria plot in the alumina zone, indicating that the tourmalines are alumina rich. Since tourmaline chemistry reflects the diverse compositions of host rock (Demirel, 2004), it therefore follows that the southwestern Nigeria tourmalines are formed in a peraluminous provenances and within high to weak acidic environments. This is further supported by the ternary plot of SiO_2 - FeO - CaO (Fig. 13), where most of the tourmaline samples plot at the SiO_2 apex.

The oxides MgO, TiO_2 and P_2O_5 have each consistently exhibited either negative or very low positive correlation coefficients with all the other oxides except the oxide pairs FeO-MgO (.49) and CaO-TiO_2 (.69) which showed significant positive correlations. The level of affinity among the cations in the respective pair dictates the degree of positive correlation among them. The positive correlation that existed between FeO and MgO may presumably suggest uvite substitutions in the tourmaline samples and/or chemical influence of the mafic country rocks that are prevalent in almost all the tourmaline environments in southwestern Nigeria. The non-reactive nature of P_2O_5 is exhibited by its consistently low positive and negative correlation coefficients with all the other oxides.

Despite the large number of possible substitutions in tourmalines, some generalizations can be made about the relationship between tourmaline composition and the host rock. As can be observed (Table 1), it is apparent that apart from Si, other most important cations allowing for variations in their oxides include Al, Ca, Fe, Na and

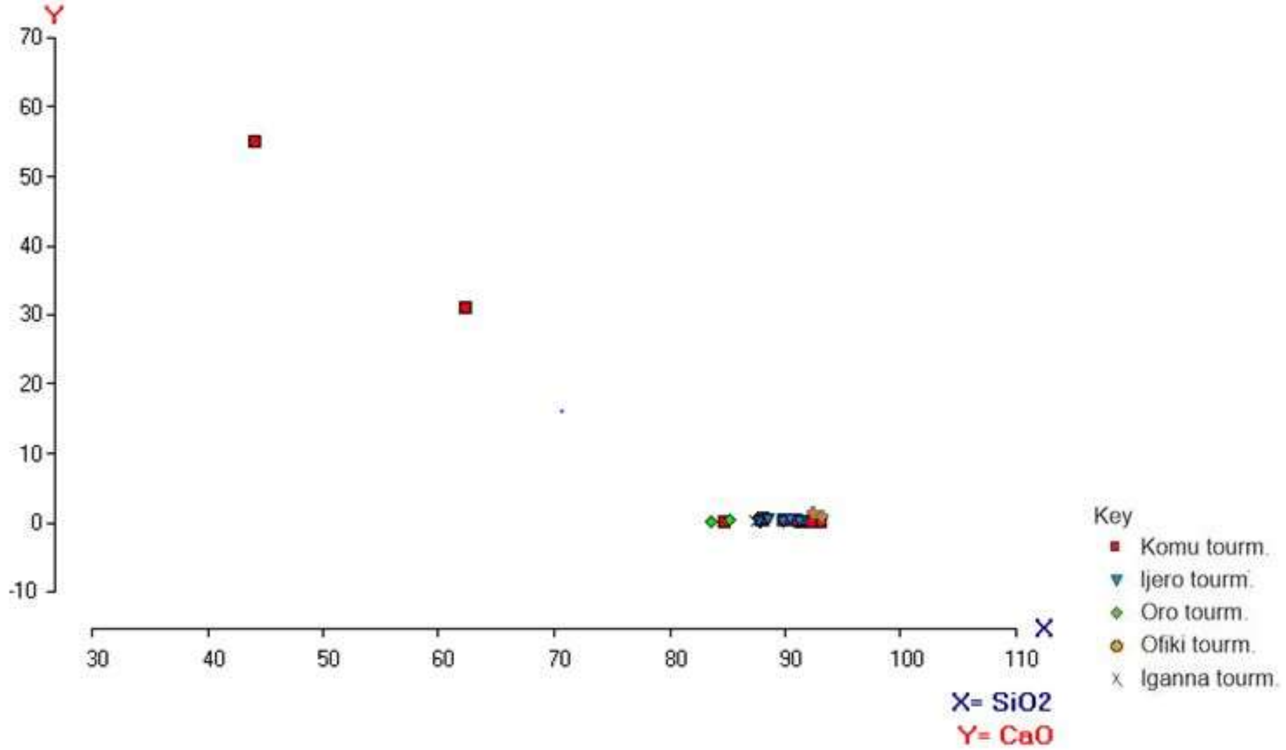

Figure 6. Correlation plot of SiO_2 and CaO for southwestern tourmalines

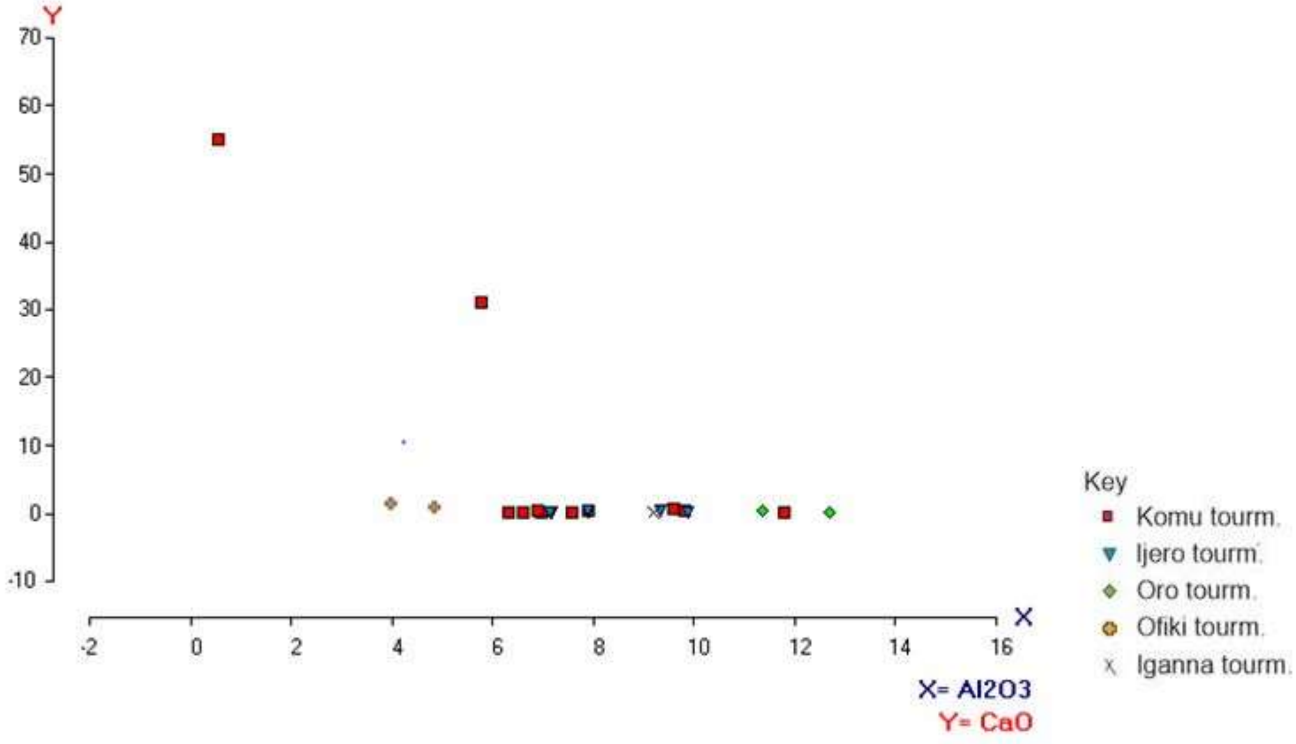

Figure 7. A binary plot of Al_2O_3 and CaO for southwestern tourmaline

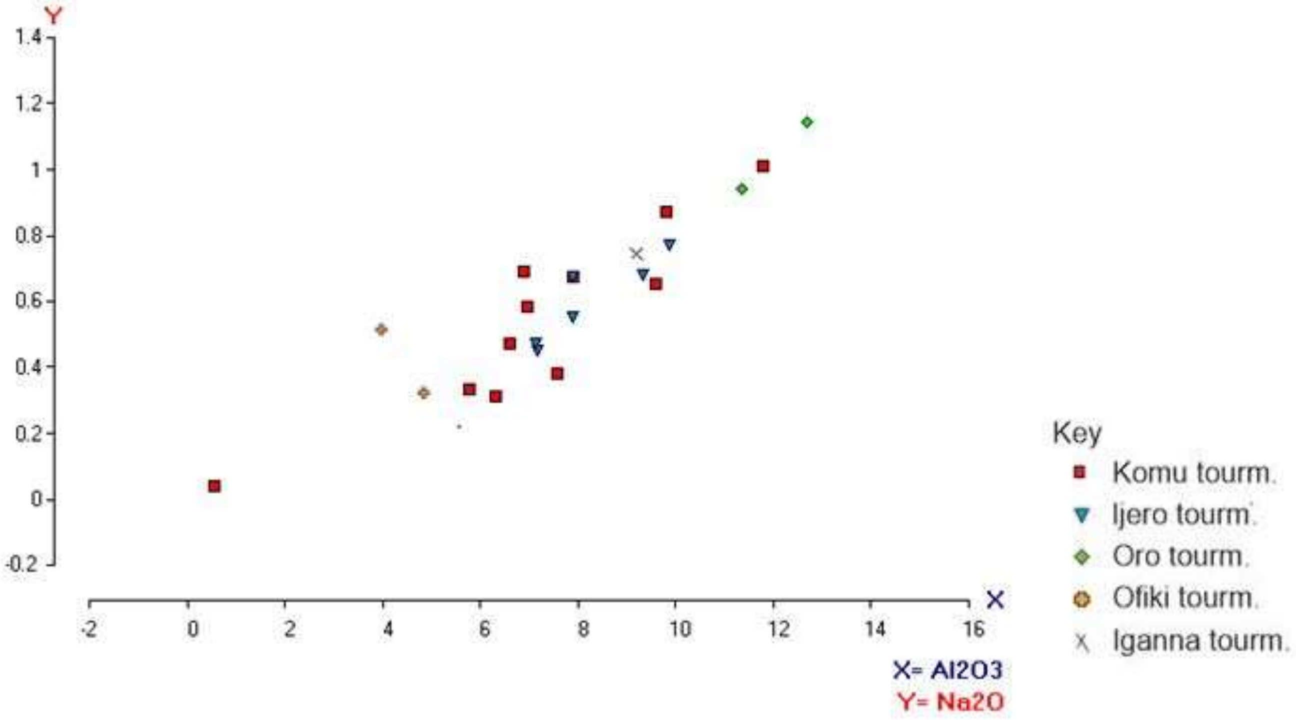

Figure 8. Correlation plot of Al_2O_3 and Na_2O for southwestern tourmalines

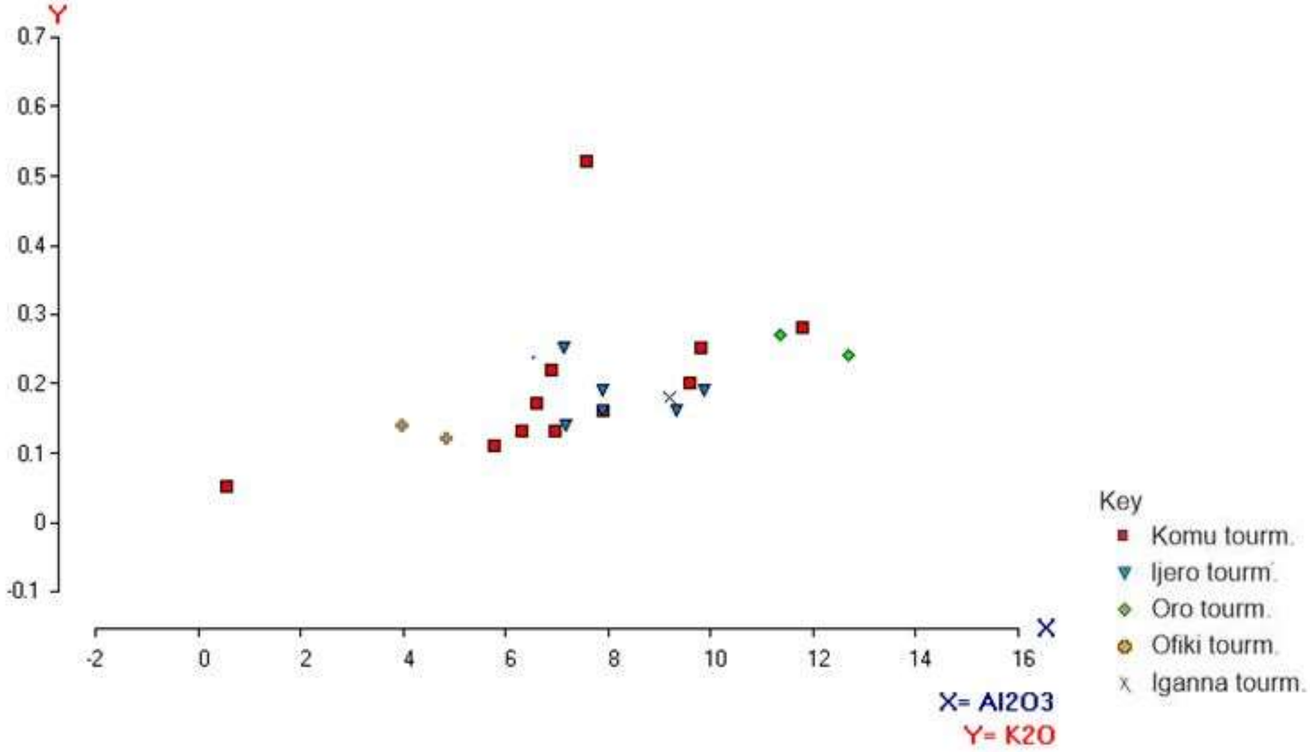

Figure 9. A binary plot of Al_2O_3 and K_2O for southwestern tourmalines

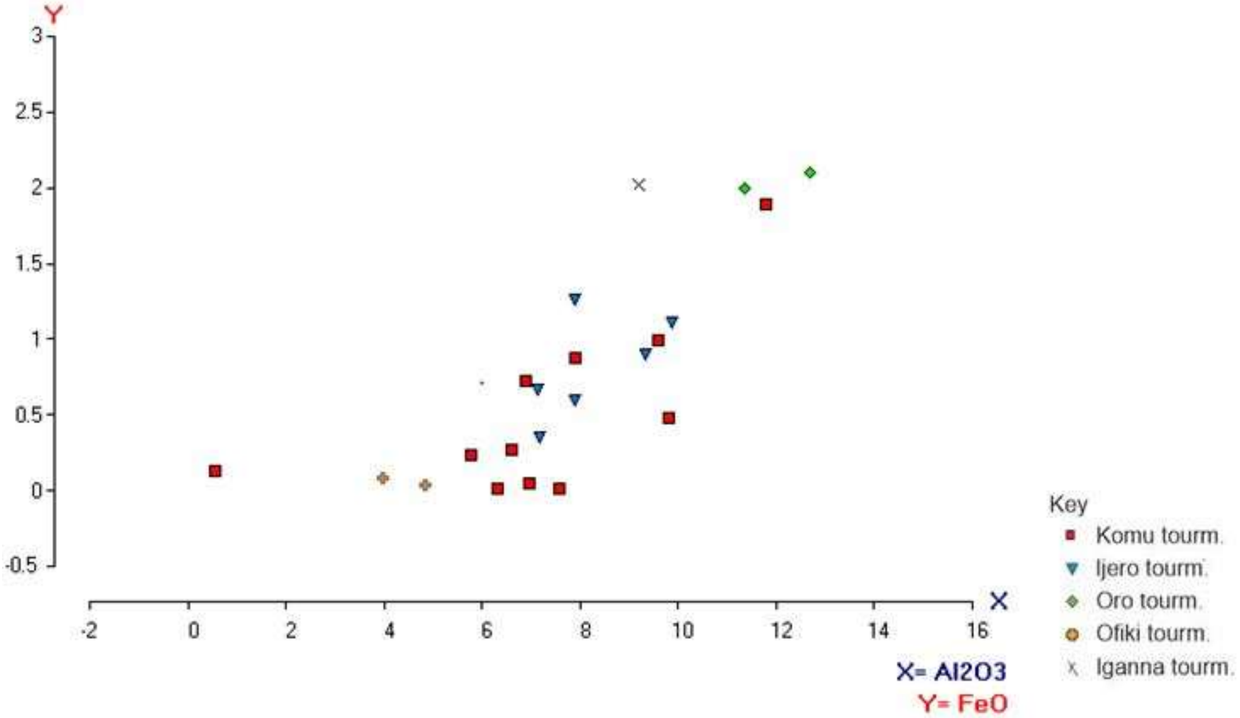

Figure 10. A binary plot of Al_2O_3 and FeO for southwestern tourmalines

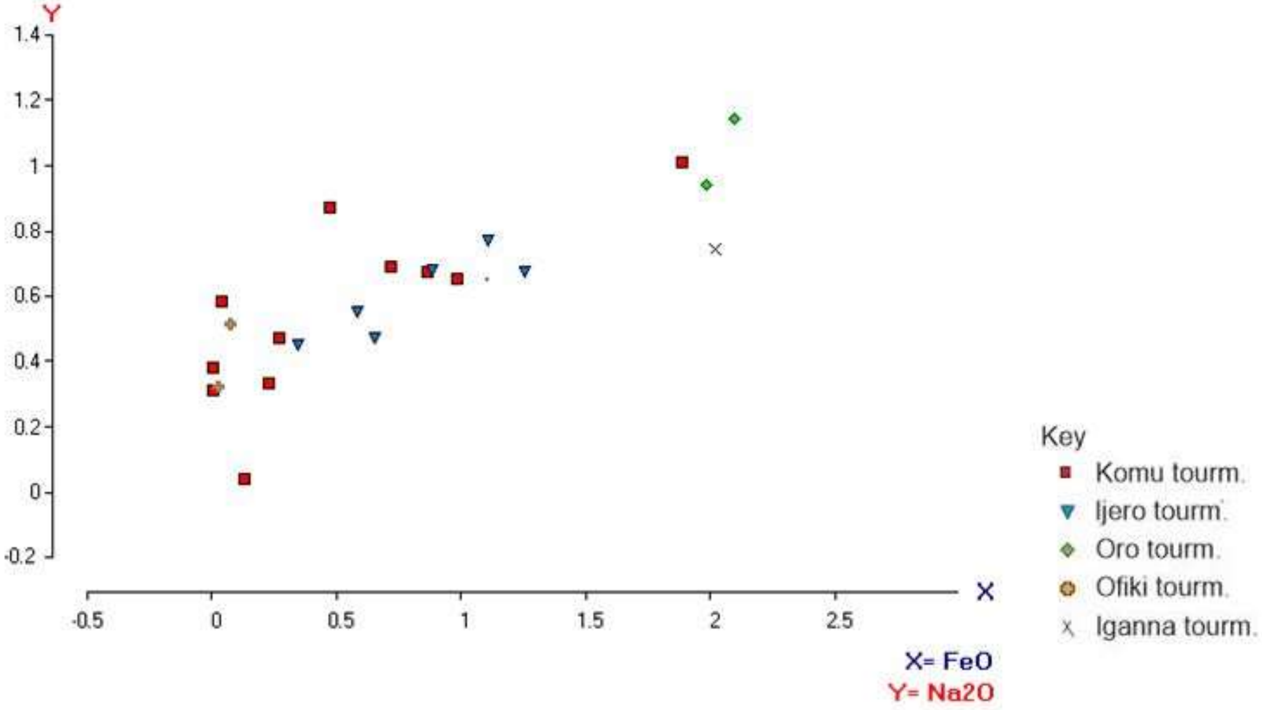

Figure 11. A correlation plot of FeO and Na_2O for southwestern tourmalines

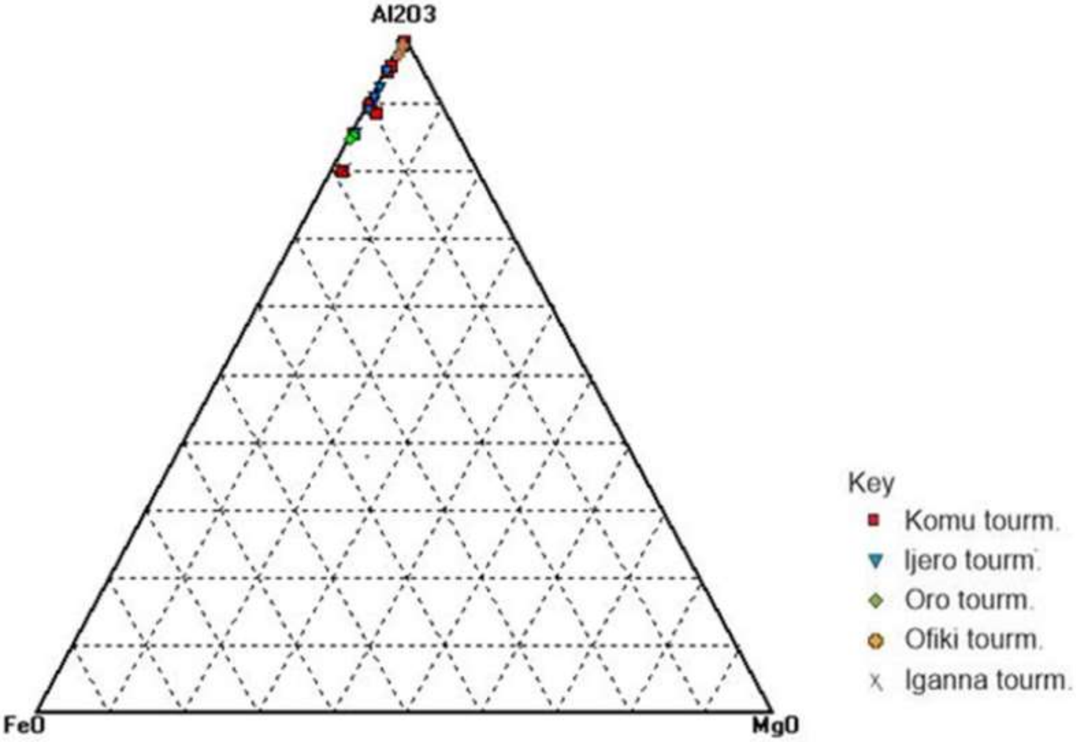

Figure 12. Al_2O_3 - FeO - MgO ternary diagram for southwestern tourmalines

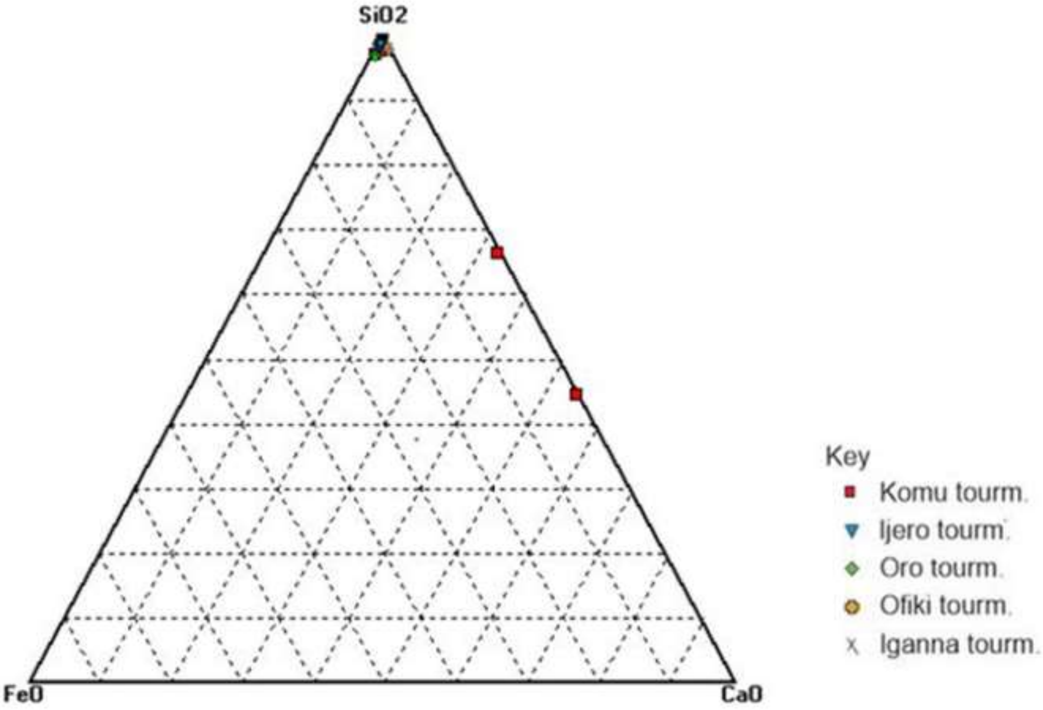

Figure 13. SiO_2 - FeO - CaO ternary diagram for southwestern Nigerian tourmaline

Table 4. Major element compositions (%) of studied tourmaline samples from southwestern Nigeria

Sample	Sample source	Sample colour	Fe	Ca	P	Mg	Ti	Al	Na	K	S	Fe/Fe+Mg
M001	Komu	Pink	0.01	0.04	0.007	0.01	0.005	3.35	0.233	0.11	0.02	0.5
M002	Komu	Pinkish red	0.01	0.05	0.015	0.01	0.008	4.02	0.283	0.43	0.02	0.5
M003	Komu	Green	0.68	0.22	0.099	0.01	0.011	4.18	0.498	0.13	0.02	0.99
M004	Komu	Blue	0.1	39.31	5.000	0.01	0.071	0.3	0.027	0.04	0.02	0.91
M005	Komu	Yellow	0.03	0.01	0.001	0.01	0.06	3.69	0.432	0.11	0.02	0.75
M006	Komu	Lemon yellow	0.21	0.07	0.003	0.01	0.008	3.51	0.347	0.14	0.02	0.95
M007	Komu	Dark blue	1.47	0.05	0.003	0.06	0.015	6.24	0.752	0.23	0.02	0.96
M008	Ofiki	Purple	0.06	1.02	0.58	0.01	0.008	2.12	0.38	0.12	0.02	0.86
M009	Komu	Yellow green	0.56	0.14	0.007	0.07	0.036	3.66	0.511	0.18	0.02	0.89
M010	Komu	Brown	0.37	0.28	0.094	0.01	0.029	5.2	0.647	0.21	0.02	0.97
M011	Komu	Green	0.77	0.29	0.002	0.01	0.017	5.08	0.484	0.17	0.02	0.99
M012	Komu	Grey	0.18	22.16	5.000	0.01	0.046	3.07	0.248	0.09	0.02	0.95
M013	Ofiki	Orange	0.02	0.61	0.223	0.01	0.014	2.58	0.236	0.1	0.02	0.67
M014	Ijero	Green blue	0.98	0.03	0.009	0.01	0.005	4.2	0.494	0.13	0.02	0.99
M015	Ijero	Light blue	0.27	0.09	0.005	0.01	0.004	3.81	0.336	0.12	0.02	0.96
M016	Ijero	Green	0.86	0.09	0.004	0.03	0.011	5.23	0.568	0.16	0.02	0.97
M017	Ijero	Yellow green	0.69	0.13	0.015	0.03	0.017	4.96	0.503	0.13	0.02	0.96
M018	Ijero	Green blue	0.46	0.11	0.028	0.01	0.007	4.2	0.411	0.16	0.02	0.98
M019	Oro	Dark blue	1.63	0.05	0.003	0.01	0.014	6.72	0.847	0.2	0.02	0.99
M020	Oro	Dark green	1.55	0.1	0.003	0.01	0.023	6.02	0.699	0.22	0.02	0.99
M021	Iganna	Black	1.57	0.06	0.012	0.1	0.027	4.87	0.552	0.15	0.02	0.94
M022	Ijero	Blue	0.51	0.06	0.004	0.01	0.009	3.79	0.348	0.21	0.02	0.98

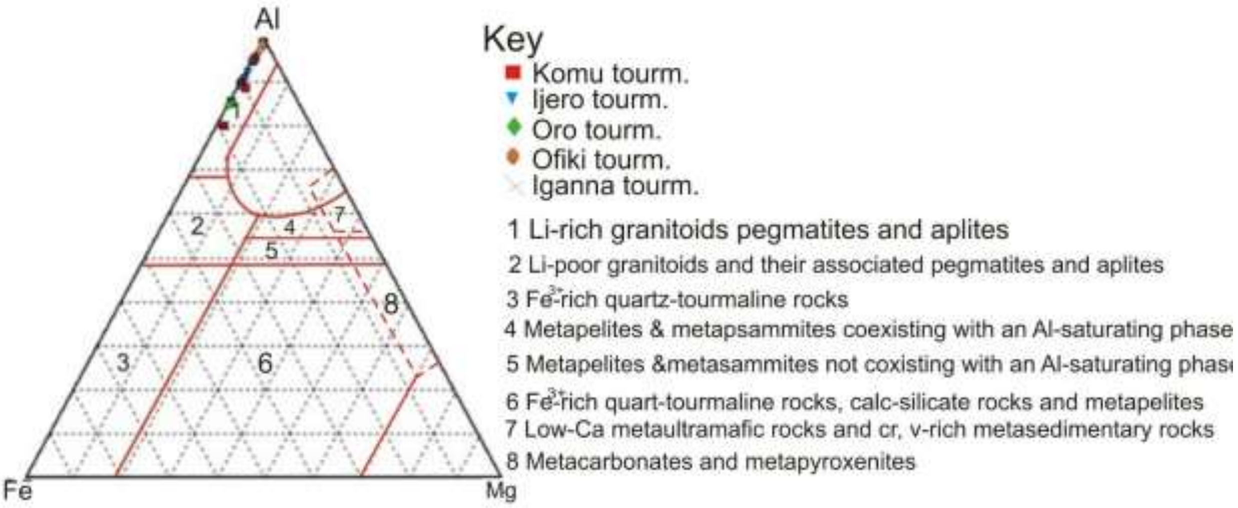

Figure 14. Al - Fe - Mg ternary plot of the southwestern Nigerian tourmalines (After Henry and Guidotti (1985))

Mg. The southwestern Nigeria tourmaline major elements compositions (Table 4) and their mineralogy are virtually dictated by the mineralizing fluid and the environment of deposition, particularly the host rocks' chemistry. Thus comparing modeled and measured tourmaline compositions provides information on the conditions prevailing in its host environment. It therefore follows that if tourmaline compositions from various rock types are plotted on the predefined Al - Fe - Mg and Ca - Fe - Mg ternary plots of Henry and Guidotti (1985), several distinct regions can be defined for tourmalines from different rock types. All the southwestern tourmaline samples plot in the predefined field of Li-rich granitoids pegmatites and aplites in the Al -Fe-Mg plot (Fig. 14) of Henry and Guidotti (1985). The tourmaline samples similarly plot in the field of Li-rich granitoids pegmatites

Table 5. Trace elements compositions of studied tourmaline samples from selected study sites in southwestern Nigeria

Samples	Cu	Pb	Zn	Mn	As	U	Sr	Cd	Sb	Bi	Zr	Sn	Be	Li	Rb	Ta	Nb
M001	3.1	10.41	27	2122	0.9	0.6	3	0.22	0.41	26.91	1	1.6	5	2000	8.8	1.7	1.01
M002	3.21	10.51	42.6	2513	1.3	0.5	6	0.23	1.21	22.84	1.6	2.5	5	2000	84.1	6.4	1.62
M003	1.53	27.15	309.7	1840	0.9	0.2	33	0.16	0.37	2.33	1.6	15.2	2	2000	6.4	0.6	1.05
M004	0.01	14.5	21.7	5206	305.6	124.4	6085	11.72	1.3	7.19	0.1	2	0.5	114.1	7.8	0.4	1.45
M005	7.02	19.05	11	8812	1.4	0.05	0.5	0.09	0.5	26.12	1.4	17.3	3	1941.5	5.7	0.8	1.12
M006	1.02	142.33	132.1	467	0.7	0.2	18	0.35	4.13	1.86	1.6	28.4	4	2000	8.3	1.6	1.83
M007	1.68	31.65	766.9	1498	0.4	0.3	8	0.23	0.8	2.09	2.9	14.9	5	2000	12.1	0.6	1.06
M008	3.76	8.33	31.1	5216	1.4	0.3	146	0.54	0.2	10.98	1.3	5.4	1	1536.8	5	0.3	1.09
M009	6.75	33.89	122.3	3152	0.3	0.2	29	0.09	0.91	86.53	2.2	6.8	3	2000	7.6	0.4	1.34
M010	6.56	178.69	109.4	7720	0.6	1.2	52	0.14	6.34	79.45	3.3	8.8	13	2000	8.5	0.8	2.03
M011	1.7	38.36	342.9	2735	1.1	0.2	5	0.55	5.97	1.77	2.3	14.8	5	2000	7.7	1.1	2.12
M012	11.54	25.39	54.6	3950	18	5.1	4291	9.53	0.85	74.23	0.1	6.5	3	1197.2	7.5	2.3	3.02
M013	8.36	44.06	14.2	2248	7.9	1.5	74	0.81	14.69	153.29	1.1	9.1	5	2000	4.4	3	1.68
M014	0.53	10.14	1704	1041	0.8	0.3	4	0.16	0.21	1.31	1.7	12.6	2	1526.2	15.3	0.8	0.87
M015	0.94	71.91	389.2	674	0.8	0.2	3	1.14	0.47	0.89	1.4	50.4	4	2000	7	1.5	1.8
M016	1.15	32.23	320.4	1093	0.7	0.3	6	0.05	0.34	0.54	2.2	29.8	3	2000	12.8	1.4	2.91
M017	2.18	76.02	377.9	1386	0.6	0.2	26	0.15	3.22	35.08	1.2	12.8	3	2000	6.7	0.9	1.25
M018	1.34	58.27	214.4	1246	1.5	0.3	18	0.12	1.03	7.07	1.7	18.9	2	2000	31.5	0.9	2.41
M019	1.35	16.04	1363.6	2077	0	0.2	5	0.05	0.37	0.63	2.3	12.3	3	2000	11.1	0.6	1.08
M020	1.89	37.97	822.1	1768	0.6	0.3	11	0.14	1.22	0.8	3.5	8.7	3	2000	12.4	0.5	1.11
M021	2.77	8.05	1130.2	3536	0.8	0.2	10	0.05	0.16	9.57	2	0.8	1	1296.8	7.9	0.2	1.14 0.52
M022	1.12	14.29	1164.9	1142	1.6	0.2	6	0.18	0.27	0.71	1.9	25	3	1538.4	97	2.8	3.17

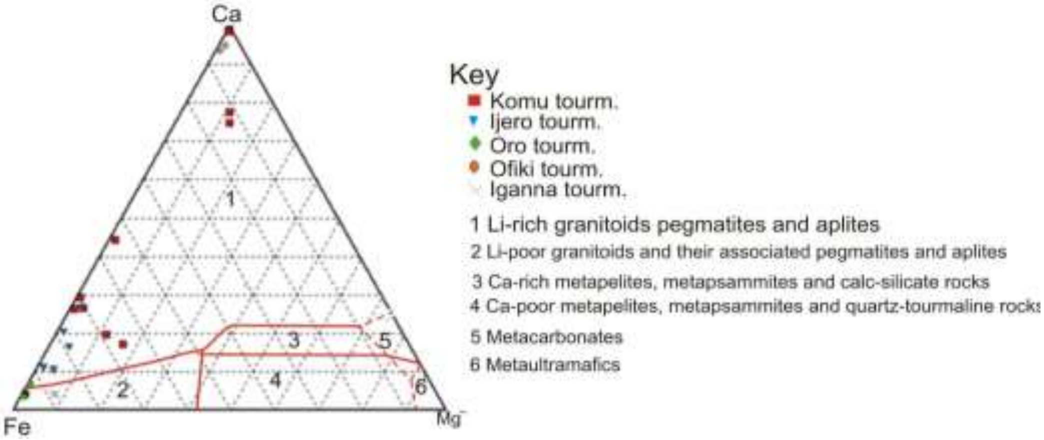

Figure 15. Ca - Fe - Mg ternary plot of the southwestern Nigerian tourmalines (After Henry and Guidotti (1985))

and aplites in the Ca-Fe-Mg plots of Henry and Guidotti (1985) (Fig 15), except two samples that have plotted in the Li-poor granitoids and their associated pegmatites and aplites. The relatively high Fe/Fe+Mg ratio, averaging 0.89 also confirms pegmatitic origin for the southwestern Nigeria tourmalines. Generally, all the southwestern tourmalines are pegmatitic hosted and pegmatite-related tourmalines are higher in Al_2O_3 and Na_2O and lower in CaO, relative to tourmalines from the country rocks. Tourmaline compositions from various localities in southwestern Nigeria generally tend towards or fall within the Al and Fe-rich rocks domain in the Al-Fe-Mg and Ca-Fe-Mg diagrams of Henry and Guidotti (1985), suggesting an important host rock control in the formation of the minerals.

Trace and Rare Earth Elements Geochemistry

Southwestern Nigerian tourmaline samples are enriched in Mn and Li, moderately enriched in large ion lithophile elements, LILE (e.g Rb and Ba), but with low concentrations in high field strength elements, HFSE (e.g Ta and Nb) (Table 5). The moderate enrichment in LILE

Table 6. Summary of trace elements Composition of tourmaline study samples

Element	Range (ppm)	Mean
Cu	0 - 11.54	3.16
Pb	8.05 – 178.69	41.30
Zn	11 – 1704	430.55
Mn	467 – 8812	2792.82
As	0 – 305.6	15.81
U	0 -124.4	6.22
Sr	0 -6085	492.68
Cd	0.05 – 11.72	1.21
Sb	0.16 – 14.69	2.04
Bi	0.54 – 153.29	25.10
Zr	0 - 3.5	1.82
Sn	0.8 – 50.4	13.85
Be	0 – 13	3.55
Li	114 – 2000	1779.59
Rb	4.4 – 97	17.07
Ta	0.2 – 6.4	1.35
Nb	0.52 – 3.17	1.62

Table 7: Chondritic-normalized values of rare elements in study samples

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
M001	1.47	2.13	0.83	0.94	0.51	1.23	0.38	1.91	0.30	1.15	0.45	2.81	0.41	2.65
M002	1.76	2.16	1.65	0.94	0.51	1.23	0.35	1.91	0.30	1.15	0.45	2.81	0.41	2.65
M003	1.76	2.32	1.65	0.94	1.03	1.23	0.77	1.91	0.67	1.15	0.45	2.81	0.41	2.65
M004	7.35	5.37	5.79	2.97	5.13	1.23	5.77	8.51	5.00	1.15	0.45	2.81	0.41	2.65
M005	7.65	6.00	3.31	1.72	1.03	1.23	0.35	1.91	0.33	1.15	0.45	2.81	0.41	2.65
M006	2.35	2.64	1.65	0.78	0.51	1.23	0.77	1.91	0.33	1.15	0.45	2.81	0.41	2.65
M007	2.65	3.46	2.48	1.56	0.51	1.23	0.38	1.91	0.33	1.15	0.50	2.81	0.41	2.65
M008	3.53	4.40	4.13	2.81	8.21	1.23	5.00	6.38	3.67	1.15	1.00	2.81	0.91	2.65
M009	6.76	5.46	4.13	2.50	1.54	1.23	0.77	1.91	0.33	1.15	0.45	2.81	0.41	2.65
M010	5.59	6.23	4.96	3.13	3.08	1.23	1.92	1.91	1.67	1.15	1.00	2.81	0.91	2.65
M011	18.24	15.79	12.40	6.09	7.69	1.23	2.31	1.91	1.00	1.15	0.45	2.81	0.41	2.65
M012	42.06	55.89	66.12	53.75	154.87	6.85	118.46	123.40	77.00	28.21	23.00	18.75	22.27	17.65
M013	18.53	14.49	13.22	8.59	6.67	1.23	2.69	1.91	0.67	1.15	0.45	2.81	0.41	2.65
M014	1.18	1.91	0.83	0.47	0.46	1.23	0.35	1.91	0.30	1.15	0.45	2.81	0.41	2.65
M015	2.65	3.00	1.65	0.63	1.03	1.23	0.38	1.91	0.30	1.15	0.45	2.81	0.41	2.65
M016	2.35	2.65	1.65	0.94	0.46	1.23	0.38	1.91	0.33	1.15	0.45	2.81	0.41	2.65
M017	3.24	3.74	1.65	0.78	1.03	1.23	0.38	1.91	0.30	1.15	0.45	2.81	0.41	2.65
M018	2.65	3.04	1.65	1.25	1.03	1.23	0.77	1.91	0.30	1.15	0.45	2.81	0.41	2.65
M019	1.47	2.25	1.65	0.94	0.46	1.23	0.35	1.91	0.33	1.15	0.45	2.81	0.41	2.65
M020	6.18	4.93	4.13	2.97	2.56	1.23	0.77	1.91	1.00	1.15	0.45	2.81	0.41	2.65
M021	2.94	2.42	2.48	1.56	1.03	1.23	0.77	1.91	0.33	1.15	0.45	2.81	0.41	2.65
M022	2.94	2.35	1.65	1.56	1.03	1.23	0.77	1.91	0.67	1.15	0.45	2.81	0.41	2.65

showed that the tourmaline samples have been formed from granite-related fluids (Goldschmidt, 1937; Kleemann, 1982; Plimer *et al,* 1991). Lithium, as one of the normal constituents of tourmaline is present in varying concentrations in all the studied samples, even in the intensely green and black varieties. Li ranged from 114 to 2000 ppm, with a mean of 1779.59 ppm, while Mn ranged between 467 and 8812 ppm, with a mean of 2792.82 ppm (Table 6). Apparently, it does not seem that lithium is responsible for any colour variation in tourmalines, as there are instances where samples of different colours possess same value of Li, while there are also other instances of samples with similar colour having different concentrations of Li. It may however have assisted other elements such as Mn, which do cause colour variations (Nassau, 1975).

Despite Li being a major tourmaline constituent, it occurs in low concentrations in samples M004

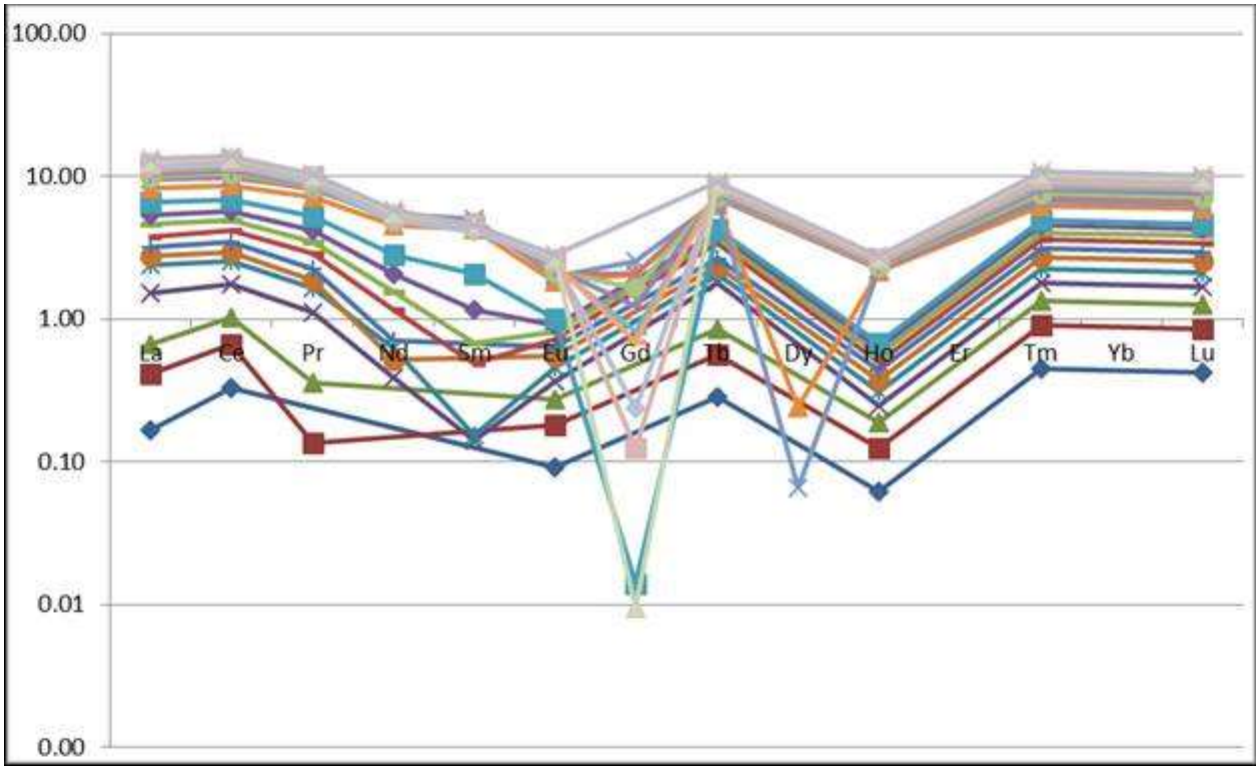

Figure 16. Rare earth elements pattern distributions in the study samples

(114.1ppm) and M012 (1197.2ppm), confirming that these two tourmaline samples must have crystallized from highly factionalized pegmatites. M004 and M012 are particularly enriched in Sr with values of 6085ppm and 4291ppm respectively. M004 is also enriched in As (305.6), U (124.4) and Cd (11.72) in which other samples, except M012 are depleted. The two samples M004 and M012 which were sourced from the same site, Lotonturawa in Komu are also mostly depleted in some high field strength elements such as Zr, Ta and Sn. While M004 has the lowest value of Cu among the tourmaline samples, it is however highest in M012. Above all; M004 is the only tourmaline sample that is exceptionally enriched in all the rare earth elements (REE), especially the heavy REE, that are virtually below detection levels in the other samples (Table 7). This indicates that highly differentiated granites and associated pegmatites have provided the source materials for its enrichment.

The chemical composition of tourmaline has proven useful as a proximity indicator for a range of mineral deposits (Henry and Guidotti, 1985; Slack, 1996; Keller et al., 1999; Jiang et al., 2004). Ore-related tourmalines contain high concentrations of ore metals such as Au, Ag, Pb, and Cu (Shao-Yong et al., 2002). Since gem minerals are usually associated, it therefore follows that sample M013, with a relatively high value of Be (13ppm) can serve as exploration guide for beryl (aquamarine) in its environment of crystallization, so also samples M020, M010 and M007 which contain 3.5ppm, 3.3ppm and 2.9ppm of Zr can be used as tracers for zircon, in their respective environments of crystallization. Bi is enriched in the samples M013 (86.53), M009 (86.53) and M010 (79.45), and so these samples can be used as exploration guides for Bi in their various environments. So also M015, M016 and M006 which contain 50.4ppm, 29.8ppm and 28.4ppm of Sn can be used as exploration tool for cassiterite mineralization, likewise samples high in Ta and Nb can serve as exploration guides for tantalite and columbite mineralizations. It can however be concluded that these study areas lack appreciable tantalite-columbite mineralization as can be deduced from Ta and Nb depletion in the tourmaline compositions.

Results from this study showed an extreme depletion of most heavy rare earth elements (HREE) relative to the light rare earth elements (LREE) in all the samples analyzed (Table 7). Generally the samples display light REE (LREE)-enriched and heavy REE (HREE)-depleted patterns, as shown from the chondrites normalized plot of the rare earth elements (REE) (Fig. 16). This relative abundance of LREE as compared to HREE suggests that the study samples have originated and sourced from the upper continental crust material and not the mantle.

CONCLUSION

The southwestern Nigerian tourmalines are magmatic in origin mostly occurring in miarolitic cavities within pegmatites and along contacts these pegmatites have made with their host rocks and their provenances are believed to be peraluminous, formed within high to weak acidic environments. The abundance of tourmaline in most of the gemstones bearing pegmatites of Southwestern Nigeria is indicative of acidic, boron bearing mineralizing fluids. This study has revealed the wide variation in chemical compositions of tourmalines from some parts of southwestern Nigeria, reflecting systematic changes associated with different types of mineralizing fluids or mineral assemblages and geologic settings in the zone. Their chemistry can be used to provide a clearer understanding of ore-forming processes, related depositional environments, and the location of prospective exploration targets. Compositions of tourmalines from Southwestern Nigeria represent compositional trends towards Li-rich compositions that reflect the compositions of the host lithologies. These results are consistent with relatively oxidized fluids that varied in composition through time, suggesting that tourmaline compositions distinguish different environments of crystallization.

It was further observed that the darker green coloured tourmaline had the most iron, the content becoming less in the lighter shades and becoming extinct in the lightest pink. This further established the fact that the iron content varies directly and proportionately with the depth of color in the greens, and inversely in the pinks and reds, being totally absent or if present, only in extremely minute traces in the reds. This revelation is consistent with widely accepted theories. It is therefore inferred that the different types of colour zoning observed in tourmalines is primarily due to variation in iron content through its length.

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