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MAJOR OXIDES GEOCHEMISTRY OF TOURMALINE FROM SELECTED GEM-MINERAL DEPOSITS IN SOUTHWESTERN NIGERIA

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Abstract

Tourmaline occurs in associations with other gem minerals such as beryl, topaz, garnet and kunzite alongside rock-forming minerals like quartz, feldspar and muscovite in various gem mineral deposits across southwestern Nigeria. These occurrences of tourmaline in varieties of colors resulting from its range in chemical compositions remain puzzling, more so when there is a lack of sufficient information on the chemistry of the Nigerian tourmalines. This study is aimed at the major oxides investigation of tourmalines from selected gem-mineral deposits in southwestern Nigeria and how the chemistry can be used to infer their environment and processes of mineralization. A total of 22 differently colored tourmaline samples obtained from different locations in southwestern Nigeria were prepared and analyzed, using the inductively coupled plasma - mass spectrometry (ICP-MS) to determine the elemental constituents. Komu and Ijero-Ekiti, being the two areas with highest concentrations of the study samples were specially chosen and mapped, at least to reveal the geology of some gem mineral deposits in the area. Results of the geochemical analysis of the tourmaline samples showed enrichment in SiO2 and Al2O3, but depletion in the remaining major oxides. However, a few of the tourmaline samples showed unusual enrichment in CaO, revealing the fact that the samples have crystallized from highly fractionated melt. The major oxide compositions of the tourmalines exhibited wide and distinct variations, especially in SiO2, Al2O3 and CaO, indicating magmatic origin for the southwestern Nigerian tourmalines. Similarly, the strong negative correlations observed between CaO and the oxides Al2O3, Na2O, K2O and SiO2 in the tourmaline samples, coupled with the relatively high Fe/Fe+Mg ratio, averaging 0.89,clearly reinforced magmatic sourcing for the tourmalines. Almost all the southwestern tourmaline samples plot in the predefined field of Li-rich granitoidpegmatites and aplites in the Al-Fe-Mg and Ca-Fe-Mg plots. Southwestern Nigerian tourmalines are thus magmatic in origin with their chemistry reflecting control by host rocks and granitic-pegmatitic fluid. The study also revealed that the intensity of coloration in tourmalines can be linked to the presence or otherwise of iron concentration. The iron content varies directly and proportionately with the depth of color in the greens, and inversely in the pinks and reds.

Key words

Southwestern Nigeria, Tourmaline, Major oxides, Pegmatite, Host rock, Magmatic origin

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INTRODUCTION

Tourmaline, a group of boron aluminum cyclosilicate mineral, with a typical complex chemical formula $Na(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$, is categorized as a semi-precious gem mineral with special beauty (color) and physical properties making it suitable for adornment and decorative purposes. Tourmaline varies greatly in composition, and consequently the colour varies with the chemical composition of the crystals. Its multitude of colors and hardness combine to make tourmaline a spectacular gemstone (Pezzotta and Laurs, 2011). Natural gem minerals being constituents of rocks are formed through various geological processes. Tourmaline therefore occurs in a variety of geological environments, generally found as minor accessory phases in rocks such as granitic pegmatites, low- to high-grade metamorphic rocks and clastic sedimentary rocks. However, hydrothermal depositions comprise some of the most common and diverse occurrences worldwide. In Nigeria, particularly in the southwest, the most common and characteristic occurrences of euhedral gem tourmalineare in pegmatites and as detrital grains in alluvial deposits, where they must have been deposited after weathering has released them from their parent pegmatites. Gem quality tourmalines crystallize almost exclusively from rare-elements and LCT-family pegmatites. Recent work has shown that a number of tourmaline species such as schorl, elbaite, liddicoatite, magnesiofoitite, rossmanite and olenite occur in these types of pegmatites (Hawthorne et al., 1993; Selway et al., 1998; MacDonald et al., 1993). In most gemstone deposits of southwestern Nigeria, crystals of different colors of tourmaline occur in miarolitic cavities within granitic pegmatites and along the contacts between these pegmatites and their host (usually mafic) rocks, frequently associated with other gem minerals such as beryl, topaz, garnet, kunzite and amethyst, alongside other rock-forming minerals such as feldspars, quartz and micas. Prominent locations in southwestern Nigeria where various colors of tourmaline are found and currently being exploited include Komu, Ijero-Ekiti, Ofiki and Oro.

With the formula $XY_3Z_6(BO_3)_3Si_6O_{18}(O,OH,F)_4$, the tourmaline group is one of the most chemically variable silicates, having many recognized mineral species (Hawthorne and Henry, 1999) and an extremely wide range of cation sizes and charges that can occupy the X, Y, and Z sites. Added to these properties, the large P-T stability field of tourmaline, its propensity to develop and retain chemical zoning, and its resistance to alteration and weathering, all make tourmaline an excellent mineral archive and therefore a good indicator mineral of its environment of deposition. Tourmaline’s complex composition reflects changes in its chemical and physical environment which, combined with its refractory nature and wide range of stability, makes it well-suited to explore the conditions under which it formed (Henry and Guidotti, 1985). A tourmaline’s large stability range, in both pressure and temperature, facilitates its widespread occurrence. Moreover, tourmaline has a crystal structure that accommodates major and trace elements of widely varying ionic charge and radius, making it an excellent monitor of the major and trace-element make-up of its local environment of growth. No known study is available in this part of the world, on the use of tourmalines in the compositional and/or evolutional study of its host environment, particularly its host pegmatite. In southwestern Nigeria, tourmaline mineralizations are widespread, occurring in many geologic settings but limited geological environments with widely varying types of mineral assemblages and chemical compositions, making this area an exceptional locality for studying controls on tourmaline chemistry. The study of tourmaline in these settings has the potential to constrain the origin(s) of this puzzling style of mineralization and can yield insights on the diversity of conditions under which tourmaline forms, thus giving insight into the evolutional history and composition of the host rock, particularly the parent pegmatite. Consequently, tourmaline could be an extremely useful petrogenetic indicator mineral if sufficient background information is attained so that the chemical signatures of tourmaline could be properly interpreted. This required a significant amount of allied investigations of tourmaline in disparate fields, which this study intends to undertake. This study therefore seeks to investigate the major oxide compositions of some southwestern Nigeria Tourmalines and to use the information obtained therefrom to infer the chemical composition and evolutional history of the host rocks.

MATERIALS AND METHODS

The study involved systematic geological mapping of two areas, Komu and Ijero-Ekiti, which contain majority of the studied samples, at least to ascertain the geology of some tourmaline deposits in southwestern Nigeria. Twenty-two samples of various colors of tourmaline, including rubellite, elbaite, dravite, indicolite and schorl (Table 1, Fig. 1) were obtained at different mining sites in southwestern Nigeria and prepared for geochemical analysis. Each of the crystal was inspected for clarity, zoning, and surface deposit. It was 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 pieces thus obtained were selected individually using a 10 power magnifying lens. The particles were handled by tweezers to avoid contaminations. The selected particles were then ground in a thoroughly cleaned new agate mortar. The crushing process was continued until the tourmalines were reduced to fine-grained powder. The powder thus obtained was again examined with a magnifying lens and any suspicious particles were removed.

The geochemical analyses of the twenty-two (22) prepared samples of tourmaline from different locations in the study area were done at ACME Laboratories in Vancouver, Canada. Major elements concentrations were determined by $LiBO_2$ fusion and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). An ICP-MS technique 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.

GEOLOGICAL SETTING

Nigeria is underlain by three major litho-petrological units, the Basement Complex (Pan-African and older (Precambrian), ≥600 Ma), Younger Granites (Jurassic, 200 – 145 Ma) and Sedimentary Basins (Cretaceous to Recent, ≤ 145 Ma). The study area which lies within the southwestern part of Nigeria is mainly underlain by crystalline rocks, collectively referred to as the Southwestern Nigerian Basement Complex. The Basement Complex of Nigeria, of which the Southwestern Nigeria Basement Complexis part, occupies about half the landmass of the country, Nigeria and it is a polycyclic terrain with a complex geologic history as a result of the different episodes of rock formation spanning Archean to Lower Proterozoic (Fig. 2). It forms a part of the African crystalline shield which occurs within the Pan African mobile belt that lies between the West African and Congo Cratons and south of the Tuareg Shield (Black, 1980). 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 materials. Three principal subdivisions are recognizable within the Basement Complex. Elueze (2000) gave these subdivisions as:-

- The ancient migmatite gneiss complex,
- The Schist belts, and
- The Pan African plutonic series.

Themigmatite gneiss complexis the most widespread, making up about 60% of the surface area of the Nigerian Basement Complex (Rahaman and Ocan, 1978) and it is therefore generally considered as the basement complex sensu strict (Rahaman, 1988; Dada, 2006). It has a heterogeneous assemblage comprising migmatites, orthogneises, paragneisses, granite-gneiss and a series of basic and ultra basic metamorphosed rocks. Petrographic evidence indicates that the Pan-African reworking led to re-crystallization of many of the constituent minerals of the Migmatite - Gneiss Complex by partial melting with majority of the rock types displaying medium to upper amphibolites facies metamorphism. The gneiss-migmatites have yielded Achaean and Proterozoic ages (Annor, 1995; Okonkwo and Ganev, 2012) and bears imprints of the Liberian (ca. 2700Ma), Eburnean (ca2000Ma) and Pan African (ca. 600Ma) tectonic events (Oversby, 1975; Turner, 1983,Rahaman, 1988, Dada, 1998).

Table 1: Studied tourmaline samples obtained from various locations in southwestern Nigeria

Sample	***Location***	***Mining site***	***Colour***	***Variety***
M001	Komu	Abuja leather	Pink	Rubellite
M002	Komu	Abuja leather	Pinkish-red	Rubellite
M003	Komu	Abuja leather	Green	Verdelite
M004	Komu	Loton turawa	Blue	Indicolite
M005	Komu	Abuja leather	Yellow	Elbaite
M006	Komu	Abuja leather	Lemon yellow	Elbaite
M007	Komu	Abuja leather	Dark blue	Indicolite
M008	Ofiki	Budo Are	Purple	Elbaite
M009	Komu	Abuja leather	Yellow green	Elbaite
M010	Komu	Abuja leather	Brown	Dravite
M011	Komu	Ajet	Green	Verdelite
M012	Komu	Loton turawa	Grey	Elbaite
M013	Ofiki	Budo-Are	Orange	Elbaite
M014	Ijero	Oke-Kusa	Green blue	Indicolite
M015	Ijero	Oke-Kusa	Light blue	Indicolite
M016	Ijero	Oke-Kusa	Green	Verdelite
M017	Ijero	Oke-Kusa	Yellow green	Elbaite
M018	Ijero	Oke-Kusa	Green blue	Indicolite
M019	Oro	Ijomu-Oro	Dark blue	Indicolite
M020	Oro	Ijomu-Oro	Dark green	Verdelite
M021	Iganna	Iganna	Black	Schorl
M022	Ijero	Ijero	Blue	Indicolite

Figure 1: Studied southwestern Nigerian tourmaline samples

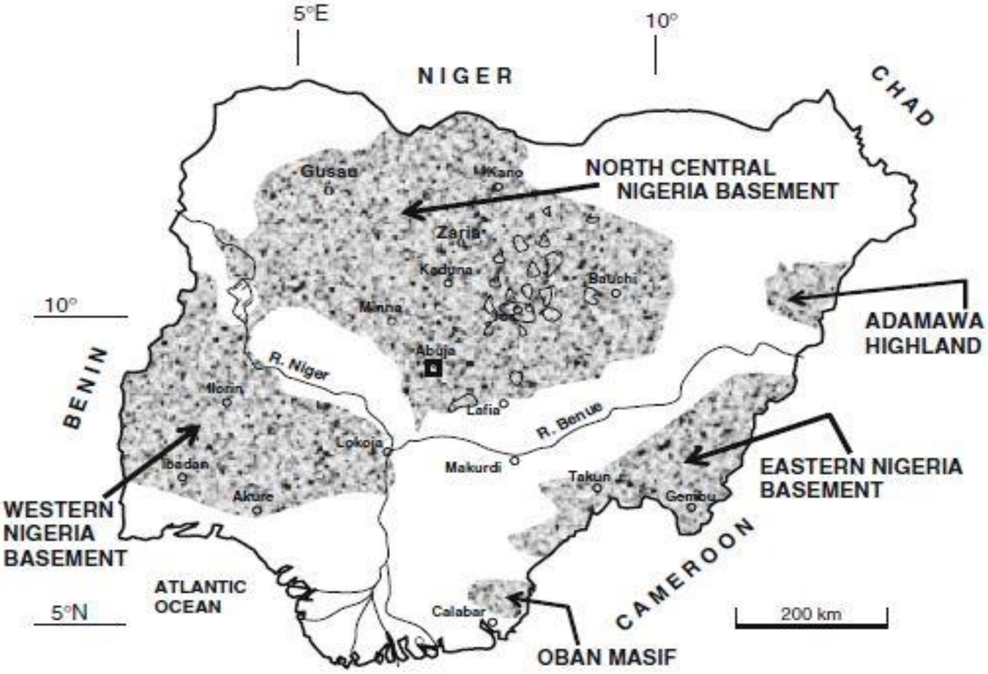

Figure 2: Geological map of Nigeria, showing the Basement Complex (after Obaje, 2009)

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 oldermigmatite-gneiss complex (Turner,1983). The litho logical variations of the schist belts include quartzites, amphibolites, pelitic and mica-schists, calc-silicate rocks, marbles, phyllites, meta-conglomerate iron formations and subordinate meta-igneous rocks (Elueze, 1992).

The Pan African plutonic series, termed 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 dikes believed to belong to the terminal stage of the Pan-African orogenic event in Nigeria (Olarewaju, 1999).

LOCAL GEOLOGY

The two study areas, Komu and Ijero-Ekiti arelithologically similar, being underlain by amphibole and pelitic schists which have been intruded by pegmatites of various forms. Komu study area, which lies between latitudes 8° 16' 12'' N and 8° 17' 29'' N and longitudes 2° 59' 18'' E and 3° 01' 07'' E is mainly underlain by amphibole and pelitic schists which have been mostly intruded semi-discordantly by pegmatites (Fig. 3). Field evidence showed observable lateral compositional and textural variations of the schist. There is an increase in the quartzo-feldspathic content and a decrease in the amphibole content of the rock towards the west, hence more of the outcrops are preserved in this axis while in the eastern part,the area is devoid of any appreciable rock exposures due to intense weathering of the schist. Rocks are rarely exposed in the central portion, except in mining excavations and along stream channels. The Komu 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). Like the schist belt, 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 schists. In most instances, they occur aspegmatitic dikes making visible contacts with the older rock bodies, while in some others they are found as intrusive bodies forming isolated plutons within the study area. Thus two lithologically and chronologically different groups of Precambrian pegmatites are distinguishable in the area. The simple, usually barren massive quartz-microcline pegmatites with minor muscovite and accessory tourmalines, which usually occur as isolated intrusive bodies and the complex NNE-SSW trending, tourmaline-bearing pegmatites generally revealed to have intruded discordantly the amphibole schist as dikes and veins of various width and mainly observable in most mining excavations in the study area.

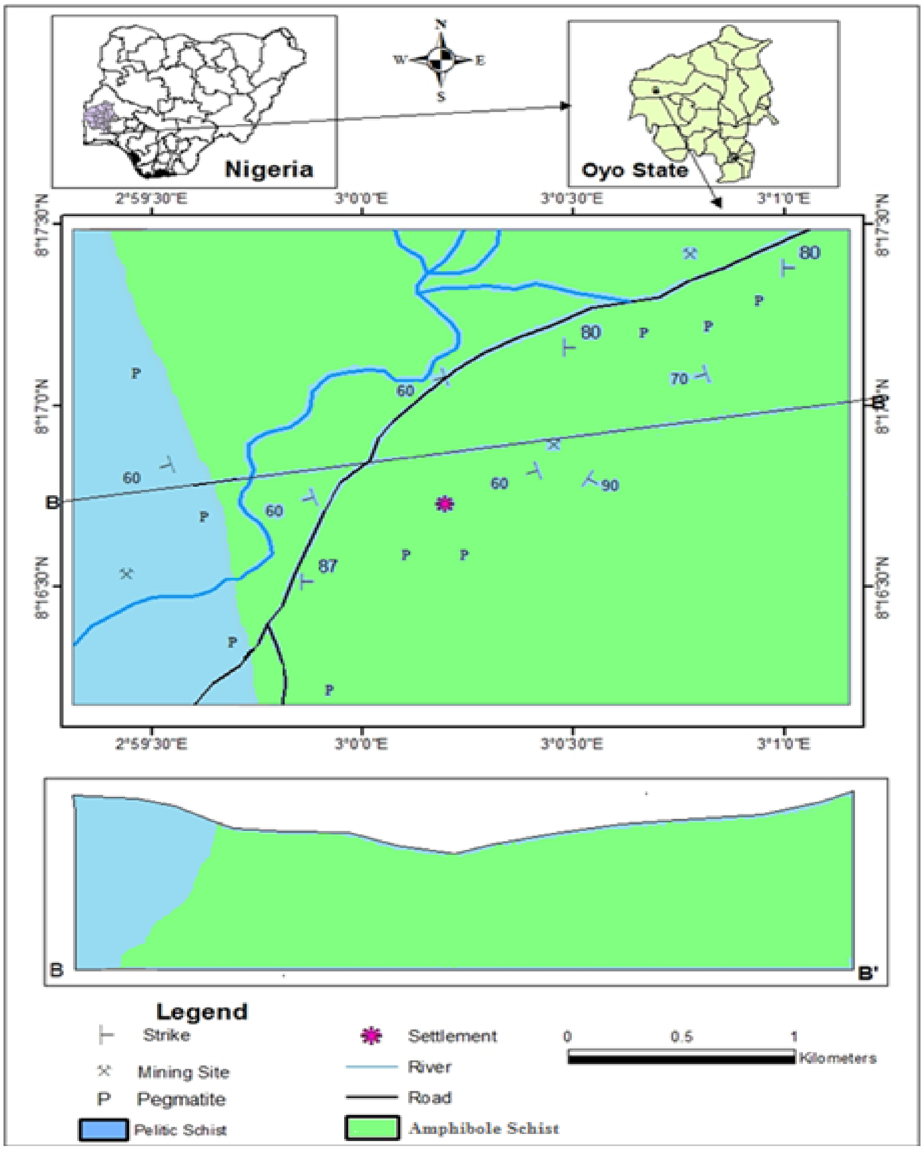

Figure 3: Geological map of Komu study area

The tourmaline-bearing pegmatite has been described by Dada (2006) as a member of the felsic dikes that are associated with Pan African granitoids on the terrane. They belong tothe undeformed acid and basic dikes 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 therefore believed to be part of the late Pan African rare metals granitic pegmatites (Jacobson and Webb, 1946; Wright, 1970). They are younger than the simple massive quartz - microcline pegmatites which are usually 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 *al*., 1977; Rahaman et al., 1983; Dada eta*l*., 1987; Matheis and Caen-Vachette, 1983; Umeji and Caen-Vachette, 1984; Akande and Reynolds, 1990).An older Pan African magmatic event in Southwestern Nigeria has however been reported by the obtained U-Pb Zircon age of 709 +27/-19 for pegmatites in Ede (Adetunji et al., 2016). Results of the rock ages showed that the pegmatities' emplacement in southwestern Nigeria occurred mainly after the peak of the Pan-African orogenic event in this area.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 pegmatites' mineralization is closely associated with the fractures in the Pan-African belt (Kuster, 1990; Ekweme and Matheis, 1995; Garba, 1992, 2003).

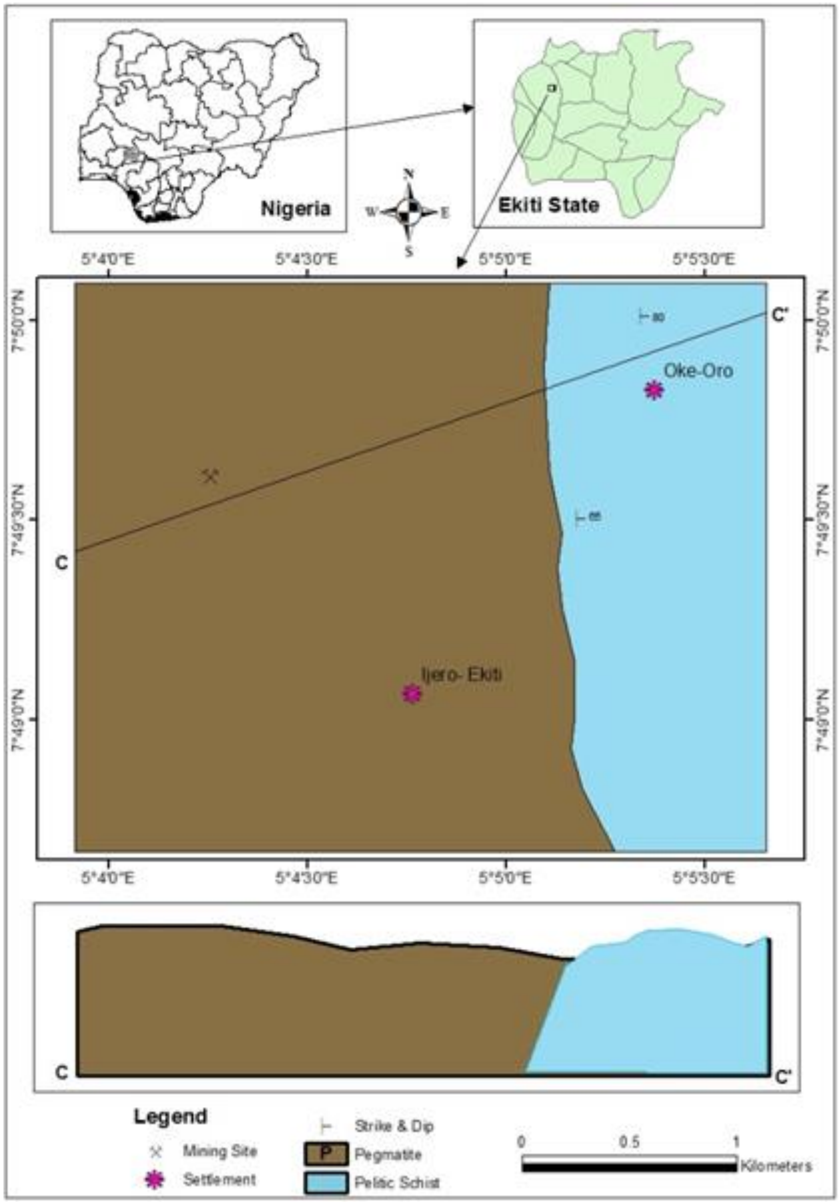

Figure 4: Geological map of Ijero-Ekiti study area

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 mainly characterized by pegmatites and meta-sedimentary rocks, consisting of dark colored 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-bearing Precambrian pegmatites, making the older rocks sparsely seen, falsely revealing the pegmatite as the dominant rock type in the areas. However, at the eastern part underlain mainly by the quartz-feldspathic pelitic schist, the rocks are well exposed (Fig. 4). The Ijero pegmatites which cover more than two-thirds of the total landmass are most times tabular and expansive in nature. This 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 DISCUSSION

Results of the southwestern Nigerian tourmalines showed enrichments in SiO_2 and Al_2O_3, but depletions in the remaining oxides (Table 2). SiO_2 concentrations ranged from 44.14% (M004) to 93.28% (M013) with a mean value of 86.36%, whileAl_2O_3ranged from 0.57% (M004) to 12.69% (M019) with a mean value of 7.8%. Wide compositional variations were observed in the oxidesSiO_2, CaOand Al_2O_3, with standard deviations of 11.90%, 13.12% and2.70%respectively, while the remaining oxides showed very narrow variability (Table 3). The wide compositional variability of the three oxides has resulted from the compositional heterogeneity of the mineralizing fluids and diversity in geologic settings and chemistry of the host rock environments of crystallization of the tourmalines. Previous studies have shown that the composition of tourmaline typically reflects the environment in which it crystallized (Henry and Guidotti, 1985; Slack, 1996). CaO concentrations ranged from 0.01% (M005) to 54.99% (M004) with a mean value of 4.13%. The sear extremely contrasting values, which may essentially be due to the huge contrast in geological backgrounds of the environments of crystallization of the respective tourmaline samples, most probably brought about by the compositional heterogeneity of their host rocks.$Al_2O_3$is adequately concentrated in the southwestern tourmaline, since an adequate concentration of Al is necessary and required for tourmaline crystallization, as Grew (1996) proved that in highly alkaline and silica- or aluminum-under saturated conditions, tourmaline growth is inhibited, and other borosilicates form instead. It therefore follows that maximum concentrations of the oxides SiO_2 and Al_2O_3 are required for tourmaline crystallization in an environment.

The compositional variations of the oxidesSiO_2, CaO and Al_2O_3 do not seem to be apparently responsible for any difference in the physical properties, particularly the color of tourmalines, but they are observed to adversely influence the distribution of other major oxides. An inverse relationship seems to exist between SiO_2andCaOon one side, as revealed in samples M004 and M012 and on the other side between $Al_2O_3$and CaO. Relatively low SiO_2values of 44.14% and 62.47% were encountered in samplesM004 and M012 as opposed to their enormous enrichments of 54.99% and 31.00% in CaO respectively, reflecting the fact that the presence of CaO has negative effects on SiO_2concentrations.Kabata-Pendias (2001) indeed reported the existence of several interferences between Si and other ions such as P^{5+}, Al^{2+}, Ca^{2+} and Fe^{2+} occurring in environments that modify its behavior. The chemical compositions of these two tourmaline samples, M004 and M012, sourced from Lotonturawa mining site in Komu can therefore be said to be distinctly different from the others, indicating that the mineralizing fluid from which these samples have crystallized must have resulted from highly fractionated melt. It can therefore be deduced that the fluid responsible for the formation of the two samples was enriched in Ca but deficient in Si. The enrichment or depletion of any element(s) in various gem fields reflects the geology, geochemistry and mineralogy of the source regions. 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-plagioclase (anorthite) content of the pegmatite housing the tourmaline minerals or could be due to contaminations from the host rock that is rich in such mafic minerals like pyroxene and amphibole.

FeO composition in the southwestern Nigerian tourmaline samples ranged from 0.01% to 2.1% with a mean value of 0.76%. Whereas FeO was found to be highly depleted in samples M001(0.01%) and M002 (0.01%) which are pink and pinkish-red tourmalines 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 blue, yellow, green, green-blue, green, yellow-green, dark blue, and black coloured tourmalines respectively (Table 2). While samples which appear green and dark have higher values of FeO, the values are low in samples that are pink and pale in color. It therefore implies that the variation in FeO concentrations of the samples have adverse effects on type and intensity of colouration in tourmalines. 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 Iron oxide. 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, also follows the same trend as other tourmalines with respect to corresponding colors; 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%)). 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. This is in conformity with widely reported works, the foremost one being Deer et al. (1966), who acknowledged the main controlling factor for color in tourmaline to be the presence or absence of Fe. Dunn (1977) actually established a relationship between a decrease in Fe content and a decrease in color intensity, an assertion similarly supported by this study.

TiO_2, Na_2O, K_2O, and MgOwere found to remain fairly constant in all the samples analyzed.TiO_2 is believed to be a substitute for iron and silicon (Hawthorne and Henry, 1999).Although Fe^{2+} => Ti^{4+} charge-transfer has been cited as the cause for blue colour in kyanite and dumortierite (Parkin et al., 1977; Platonov et al., 2000), it is not likely true for tourmalines. This is because TiO_2 has been observed to be constantly of low values throughout the analyzed tourmaline samples, including the blues while the blue tourmaline samples are found to be relatively rich in FeO, suggesting that Fe is probably among the primary chromophores responsible for deep blue colors in tourmalines. K_2O is evenly distributed in all the samples analyzed, but found to be a little more enriched in sample M002 (0.52%). The analyzed samples showed poor enrichment in P_2O_5, except samples M008 and M013, sourced from the same site which showed relatively high values of 1.33% and 0.51% respectively, confirming an entirely different environment of deposition and mineralizing fluid for the samples.

Table 2: 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	Emerald 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 3: 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

CaO is negatively correlated with all the other oxides except TiO_2 with which it is positively correlated (Table 4). 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 might be 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. Al_2O_3 is positively correlated with the oxides Na_2O, FeO, K_2O and SiO_2 but negatively correlated with the others. Very strong positive correlation coefficients were established among the oxide pairs; Al_2O_3-Na_2O (.91) andAl_2O_3-FeO (.78), while the oxide pairs Al_2O_3-K_2O (.49) and Al_2O_3-SiO_2 (0.42) exhibit moderate positive correlations.

Binary plots of some oxide pairs of the southwestern Nigerian tourmalines revealed compositional variations, mineralization trends, and suggest geochemical tools for future geochemical sampling procedures. There are discernable positive correlations between Al_2O_3 and Na_2O (Fig. 5), Al_2O_3 versus K_2O (Fig. 6), Al_2O_3 against FeO (Fig. 7) and FeO versus Na_2O (Fig. 8), all yielding well-defined trends. The positive correlation between Al_2O_3 and the alkaline, Na_2O and K_2O is in line with the belief 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. The activity of Al_2O_3 or equivalent aqueous species also contributes to tourmaline stability and formation, which are favored 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).A ternary plot of Al_2O_3 - FeO - MgO (Fig. 9) showed that all the analyzed 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 et al., 2004), it therefore follows that the pegmatites housing the southwestern Nigeria tourmalines have per aluminous provenance and are formed within high to weak acidic environments. However, a remarkable feature noted in the majority of tourmalines from southwestern Nigeria is the direct positive 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).

Table 4: 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)

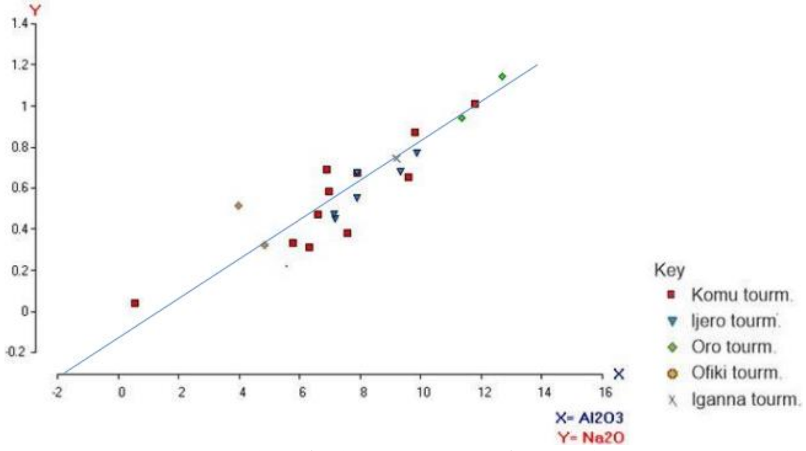

Figure 5: Correlation plot of Al_2O_3 and Na_2O for southwestern tourmalines

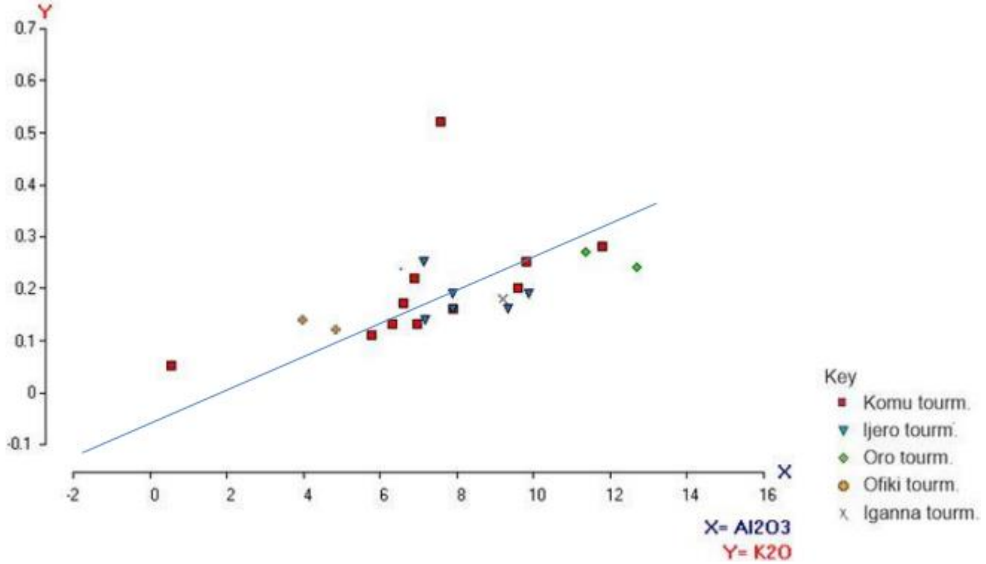

Figure 6: A binary plot of Al_2O_3 and K_2O for southwestern tourmalines

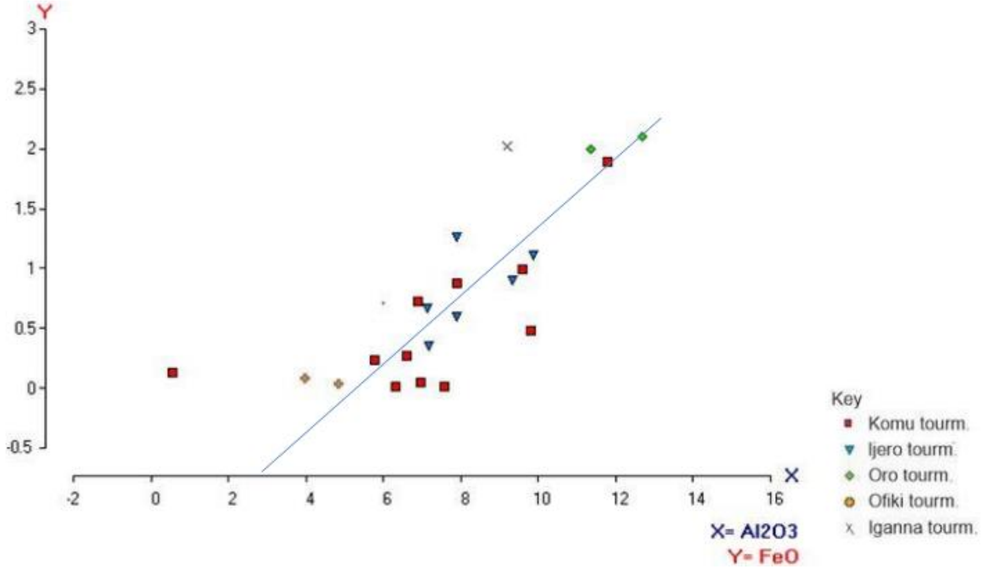

Figure 7: A binary plot of Al_2O_3 and FeO for southwestern tourmalines

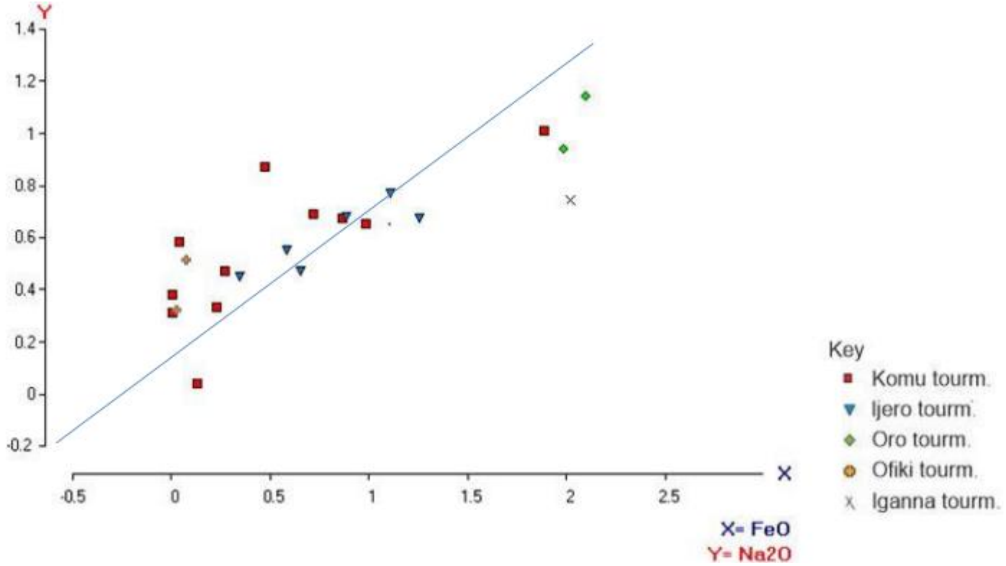

Figure 8: A correlation plot of FeO and Na_2O for southwestern tourmalines

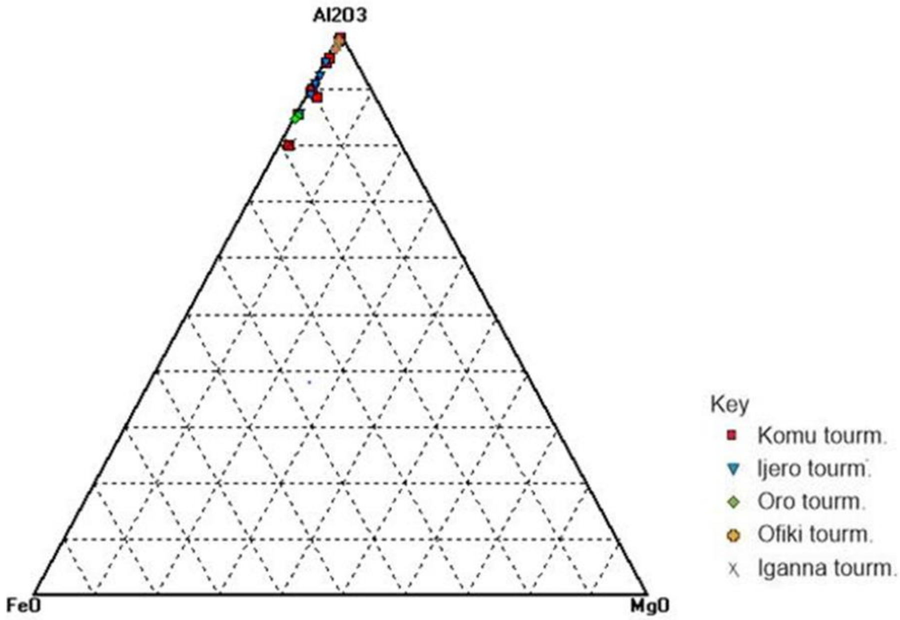

Figure 9: Al_2O_3 - FeO - MgO ternary diagram for southwestern tourmalines

The oxides MgO, TiO_2 and P_2O_5 have each consistently exhibited either negative or very low positive values of correlation coefficients with all the other oxides except the oxide pairs FeO-MgO (.49) and CaO-TiO_2 (.69) which showed significant positive correlations (Table 4). The level of affinity among the cations in the respective pairs is indicated by the degree of positive correlation. The positive correlation that existed between FeO and MgO may presumably suggest uvite substitutions in the tourmaline samples and chemical influence of the mafic host country rocks that are prevalent in almost all the tourmaline environments in southwestern Nigeria. Dunn (1977) however reported that MgO would not cause a color change, but would have an influence on the presence or otherwise and amount of other oxides/elements. The non-reactive nature of P_2O_5 is exhibited by its consistently low positive or negative values of correlation coefficients with all the other oxides.

The major elements composition of the southwestern Nigerian tourmaline samples (Fig. 5) exhibits distinct variations reflecting the environment of formation. The composition and therefore mineralogy of tourmalines 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. The host rock lithologies of the southwestern Nigerian tourmaline samples correlate well with the pre-defined fields in the Al-Fe-Mg and Ca-Fe-Mg plots (Fig. 10 and 11) of Henry and Guidotti (1985). All the tourmaline samples fall into the fields of Li-rich granitoid pegmatites and aplites of the Al-Fe-Mg plot (Fig 10) of Henry and Guidotti (1985) and majority of the samples also plot in the Ca-Fe-Mg plot (Fig. 11) of Henry and Guidotti (1985), except only three that have plotted in the Li-poor granitoids and associated pegmatites and aplites. It therefore follows that the southwestern Nigerian tourmalines are pegmatitic in origin, and this is also confirmed by the relatively high Fe/Fe+Mg ratio, averaging 0.89.

Table 5: Major element compositions (%) of studied tourmaline samples from southwestern Nigeria

			Fe	*Ca*	*P*	*Mg*	*Ti*	*Al*	*Na*	*K*	*S*	*Fe/Fe+Mg*
Sample	**Sample source**	**Sample colour**										
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

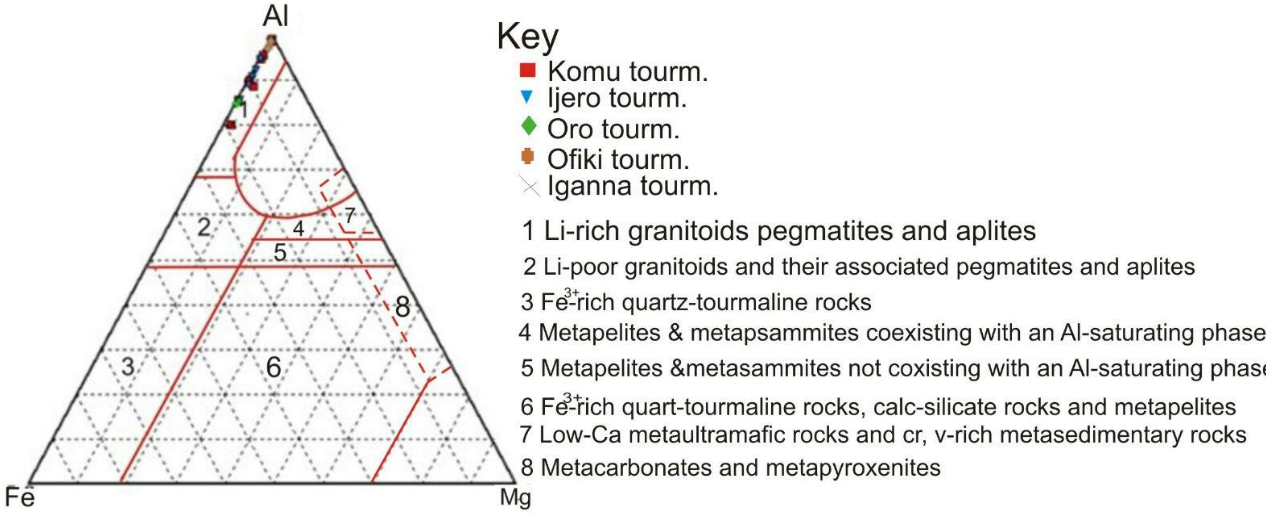

Figure 10: Al - Fe - Mg ternary plot of the southwestern Nigerian tourmalines (After Henry and Guidotti (1985))

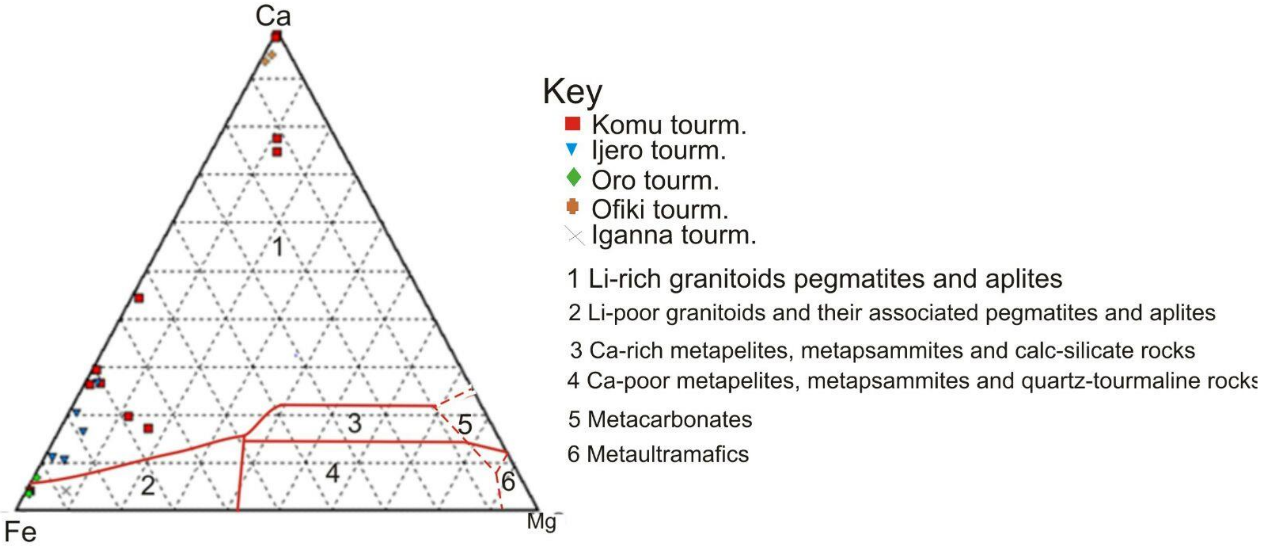

Figure 11: Ca- Fe - Mg ternary plot of the southwestern Nigerian tourmalines (After Henry and Guidotti (1985))

CONCLUSION

The southwestern Nigerian tourmalines showed wide compositional variability particularly in the oxidesSiO_2, CaOand Al_2O_3, resulting from the compositional heterogeneity of the mineralizing fluids and diversity in geologic settings and chemistry of the host rock environments of crystallization of the tourmalines. The inverse correlations existing between CaO and the oxides Al_2O_3, Na_2O, K_2O and SiO_2, clearly reveal features of magmatic deposits for the southwestern Nigerian tourmalines. A ternary plot of Al_2O_3 - FeO - MgO showed that the southwestern Nigeria tourmalines are alumina-rich, indicating per aluminous provenances for their host rocks, which also have lithologies correlating well with the pre-defined field of Li-rich granitoids pegmatites and aplites of the Al-Fe-Mg and Ca-Fe-Mg plots of Henry and Guidotti (1985).The relatively high Fe/Fe+Mg ratio, averaging 0.89 also confirms pegmatitic origin for these tourmalines. The abundance of tourmaline and lack of significant amounts of other borosilicates in most of the gemstones deposits of Southwestern Nigeria is indicative of acidic fluids with high Al activities and sufficient ferromagnesian components necessary for tourmaline crystallization and formation. The results of the geochemical analysis of the southwestern tourmalines also 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 southwestern Nigerian tourmalines are magmatic in origin occurring in miarolitic cavities within pegmatites and along the contacts which these pegmatites have made with their host rocks.

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