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## Iron: A Significant Determinant of Colours in Gem Tourmalines from Southwestern Nigeria

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### ABSTRACT

Gem tourmalines from southwestern Nigeria vary highly in composition and display limitless plethora of colours. This study intended to link the chemistry of these tourmalines with their colours. Fifteen differently coloured samples of tourmaline from three localities; Komu, Ijero-Ekiti and Okerimi-Oro were pulverized and analysed through the inductively coupled plasma-mass spectrometry (ICP-MS) method to characterize the chemical compositions. Results showed wide variation among the major oxides,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  with standard deviations of 11.74 and 9.52 respectively and narrow variation for  $\text{Fe}_2\text{O}_3$  with standard deviation of 2.74, while the remaining oxides remained depleted in the studied samples.  $\text{Fe}_2\text{O}_3$  was significantly high in samples R32(4.01%), R35(7.25%), R33(7.65%) and R34(9.22%), which are blue-green, dark-green, dark-blue and dark-blue coloured tourmalines respectively, relatively high in samples R048(2.58%) and R049(2.61%), a green and grey tourmaline respectively and of very low concentrations in samples R046 (0.15%) and R052(1.82%), a pink and red tourmaline respectively. This showed that the blues and the darker greens had the most iron, becoming less in the lighter shades of green and completely depleted in the lightest pink.  $\text{TiO}_2$  and  $\text{MnO}$  values on the other hand have remained virtually very low and fairly constant throughout the analyzed samples despite the varied colours among them. This study showed iron to be chiefly responsible for colour variation among the studied southwestern Nigerian tourmalines.

**Keywords:** Tourmaline, Southwestern Nigeria, Iron, Colours, Major oxides

### Introduction

Tourmaline, a group of boron aluminum cyclosilicate mineral is unique among gem minerals in the great variety of colours in which it occurs. It varies greatly in composition and consequently the colour varies with the chemistry of the crystals (Olatunji and Jimoh, 2016). It is the

most colourful of all gem minerals and varies widely in colour and physical properties but share a common crystal structure. Given the range of elements that can be accommodated by the tourmaline structure, a diversity of tourmaline compositions ensues, giving rise to a large number

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of tourmaline species, but because these species are isostructural, extensive ionic substitutions and solid solution occur between the end-members (Novak *et al*, 2009). The formula of the solid solution may be written as;  $(\text{Na},\text{Ca})_R_3(\text{Al},\text{Fe})_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{O},\text{OH},\text{F})_4$ , with the major variable components giving rise to several mineralogical varieties (Henry *et al*, 2011). In addition to the major-element occupation of the sites, tourmaline also accommodates a range of trace elements. This ability is due to the marked differences in morphology and coordination of the various structural sites in the tourmaline structure, which allows elements of widely varying charge and ionic radius to be incorporated. Three end-members are distinguished; R is predominantly Mg in dravite, (Li + Al) in elbaite and Fe<sup>2+</sup> in schorl (Hawthorne and Henry, 1999). Other substituting ions Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, V<sup>3+</sup>, and F<sup>-</sup> for example, may further complicate the chemistry. There is almost complete solid solution between dravite and schorl, and between elbaite and schorl, forming well marked series, but very little between dravite and elbaite (Ferreira *et al*, 2005). In general, we may expect the depth of colouration in either series to be related to the proportion of schorl. Gem tourmaline displays virtually every possible colour, ranging from colourless to yellow, purple, pink, red, green, blue, brown and most commonly, black (Anthony *et al.*, 1995, Beurlen *et al.*, 2011). Tourmaline's almost limitless colours make it resemble almost any other gem mineral. Its multitude of colours and its hardness combine to make tourmaline a spectacular gemstone (Pezzotta

and Laurs, 2011). Colour may not be constant even within a single crystal as bi-coloured and multicoloured crystals are common, reflecting variations of fluid chemistry during crystallization. Crystals may be pink at one end, green at the other and nearly colourless in between, or pink inside and green on the outside; this type is called watermelon tourmaline (Jimoh, 2018). Multicoloured tourmaline is unique as no other gemstone resembles it. Chromophoric metallic cations, intervalence charge transfers (I.V.C.T.) and the effects of natural irradiation are responsible for the nearly limitless plethora of colours displayed by elbaite and other gem quality tourmaline species (Fonseca, 2008). Giller (2003), in his work analyzed some crystals of tourmaline from Africa, including suites of gem-quality faceted tourmaline from Nigeria to determine their mineralogy and minor element chemistry and showed that these tourmalines are elbaite, liddicoatite, rossmanite and schorl, while Fe, Mn and Ti are their principal chromophores. Tourmaline 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. In Nigeria, particularly in the southwest, the most common and characteristic occurrences of euhedral gem tourmaline minerals are in granitic pegmatites where they are found frequently associated with other gem minerals, and they crystallize almost exclusively from rare-elements and in miarolitic class, Lithium, Cesium and Tantalum (LCT)-family pegmatites (Olatunji

and Jimoh, 2016). Studies have revealed 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; MacDonald *et al.*, 1993; Selway *et al.*, 1998). This paper is intended to investigate the contribution of iron to colours in some studied gem tourmaline crystals from southwestern Nigeria.

### Materials and Methods

The southwestern part of Nigeria which lies from latitudes 6°30'N to 9°00'N and between longitudes 2°45'E and 6°00'E, comprises the study areas and it is mainly underlain by crystalline rocks, collectively referred to as the Southwestern Nigerian Basement Complex (Fig. 1). Fifteen differently coloured flawless crystals of gem tourmaline were selected as studied mineral samples (Fig. 2) from three localities; Komu, Ijero-Ekiti and Okerimi-Oro, known to contain some of the most important and productive gem tourmaline mineral producing deposits within southwestern Nigeria. The colours of these samples included pink, red, green, grey and blue. Each of the crystals was inspected for clarity, zoning, and surface deposit. It was then crushed by wrapping carefully in a paper and striking it with a hammer. A sufficient amount of gem-quality tourmaline chips were separated using cutting pliers and pulverized to fine grained powder using a steel impact mortar and pestle. Each powdery sample thus obtained was analysed through inductively coupled plasma-

mass spectrometry (ICP-MS) method to determine the chemical compositions.

### Geologic setting

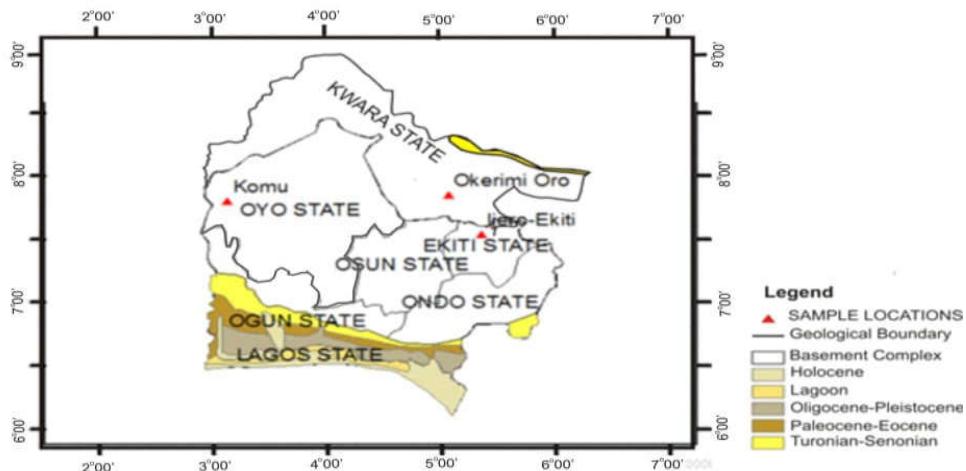
The areas under study are underlain by rocks of the Basement Complex of Nigeria (Fig. 1), a part of the African crystalline shield occurring within the Pan African mobile belt that lies between the West African and Congo Cratons and south of the Tuareg Shield (Black, 1980). Grant (1970) established an orogenic belt of similar age in the Ghana-Togo-Dahomey area in the eastern margin of the Craton. The Nigerian Basement Complex which occupies about half the landmass of the country, Nigeria is a polycyclic terrain that suffered its most pronounced deformation and mobilization during the Pan-African age (600 Ma). The Pre-Cambrian rocks consist predominantly of folded gneisses, migmatites, supracrustal rocks largely of Greenschist to amphibolite facies, Pan African granites and Undeformed dykes (Adetunji *et al.*, 2016).

On the basis of structural, lithostratigraphy and geochemical data, the Precambrian rocks of Nigeria can be classified into four age groups, corresponding to the four major Orogenies that have punctuated the Precambrian history of Africa. It has been suggested that the major orogenic events; Liberian (2,600 - 3,000Ma), Eburnean (2,000 - 2,400Ma), Kibaran (1,100 Ma), and pan-African (450 - 750Ma) did take place, resulting in what is now known as the Basement Complex of Nigeria, though most workers consider the first two events as the same. Obaje 2009 distinguished four major petro-lithological units within the Basement

Complex of Nigeria, namely; the Migmatite - Gneiss Complex (MGC), the Schist Belts (Metasedimentary and Metavolcanic rocks), the

Older Granites (Pan African granitoids) and the Undeformed Acid and Basic Dykes.

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**Figure 1:** Geological map of southwestern Nigeria showing sample locations (Okeyode, 2012).



**Figure 2:** Samples of tourmaline crystals obtained from various localities used for ICP-MS analysis. a): Komu tourmaline samples, b): Ijero-Ekiti tourmaline samples, c): Okerimi-Oro tourmaline samples.

The Migmatite - Gneiss Complex has a heterogeneous assemblage comprising migmatites, orthogneisses, paragneisses and a series of basic and ultrabasic metamorphosed rocks. Petrographic evidence indicates that the Pan-African reworking led to re-crystallization of many of the constituent minerals of rocks of the Migmatite - Gneiss Complex by partial melting with majority of the rock types displaying medium to upper amphibolites facies metamorphism. Gneisses vary in mineralogical composition and character, with two types recognizable in the Basement Complex; the biotite gneiss and the hornblende biotite gneiss (Okunlola and Udoudo, 2005). 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, migmatites and other similar lithological units. The Migmatite - Gneiss Complex has ages ranging from Pan-African to Liberian (Adetunji *et al*, 2016).

The Schist Belts which comprise low grade, metasediments-dominated belts, trending North-South are best developed in the western half of Nigeria. They are considered to be Upper Proterozoic supracrustal assemblages of low to medium grade meta-sedimentary rocks with subordinate mafic and ultramafic rocks which have been in-folded into the Migmatite-Gneiss-Quartzite Complex (Turner, 1983). The lithological 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). Quartzites are the most obvious of the meta-sedimentary rocks and they occur prominently as ridges and vary in texture from massive quartzites to quartz schist. The various types of schist occur as lowland between quartzite ridges and do not occur as continuous outcrops. Concordant bands, lenses and sheets of amphibolites, biotite and hornblende schist and meta-gabbroic rocks are found within the gneisses. The geochronology of the schist belts remains problematic although the ages of the intrusive cross-cutting Older Granites provide a lower limit of 750 Ma (Obaje, 2009).

The Older Granites which are referred to as the 'intrusive suites' 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 (Olatunji and Jimoh, 2017). The Pan-African intrusive suite comprises mainly granites and granodiorite, with subordinate pegmatite and aplites. Affiliated 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). There are three main groups of the Older Granites; an early phase comprising of granodiorite and quartz diorite, a main phase consisting of coarse porphyritic hornblende

granite, syenite and lastly the coarse porphyritic biotite granite (Okunlola and Udoudo, 2005).

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:

- a) Felsic dykes that are associated with Pan African granitoids on the terrain such as the muscovite, tourmaline- and beryl-bearing pegmatites, micro-granites, aplites and syenite dykes (Dada, 2006)
- b) 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. The general trend of all dykes observed is between NE-SW and ENE-WSW (Jones and Hockey, 1964; Rahaman (1973).

### **Results and discussions**

A total number of 9 major oxides were determined for the studied tourmaline samples and these included;  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ , (Table 1). Result of the analysed samples showed high enrichment in both  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  with mean values of 45.68% and 34.40% respectively, but depletion in the remaining oxides (Table 2).  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  have average values of 3.26% and 1.91% respectively, while the other oxides exhibited very low values. The major oxides analysis of the tourmaline samples also showed pronounced variability in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  distributions with standard

deviations of 11.74 and 9.52 respectively, while  $\text{Fe}_2\text{O}_3$  exhibited limited variability with standard deviation of 2.74 (Table 2). The wide compositional variation can be explained in terms of the heterogeneity in compositions of their mineralising fluids and host rocks brought about by the diversity in their geologic settings since the chemistry of tourmaline reflects the diverse compositions of host rock and mineralising fluids, as well as differences in temperature and pressure of formation (Demirel *et al.*, 2009).

$\text{Fe}_2\text{O}_3$  content of the studied tourmaline samples ranged from 0.15% (R046 and R047, both pink tourmalines from Komu) to 9.22% (R34, a dark blue tourmaline from Oro) (Table 1). Whereas  $\text{Fe}_2\text{O}_3$  was found to be of very low concentrations in samples R046, R047(0.15%) and R051(0.18%) which are pink tourmalines from Komu, and R052(1.82%), a red tourmaline from Ijero-Ekiti, relatively high in samples R048(2.58%) and R049(2.61%), a green and grey tourmaline respectively from Komu, R054(2.65%) and R055(2.75%), another green and grey tourmaline respectively from Ijero-Ekiti, it was significantly high in samples R32(4.01%), R35(7.25%), R33(7.65%) and R34(9.22%), which are blue-green, dark-green, dark-blue and dark-blue coloured tourmalines respectively from Okerimi-Oro.

**Table 1:** Major oxides compositions of studied tourmaline samples from selected study sites in southwestern Nigeria

		Analyte	<i>SiO<sub>2</sub></i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>Fe<sub>2</sub>O<sub>3</sub></i>	<i>MgO</i>	<i>CaO</i>	<i>Na<sub>2</sub>O</i>	<i>K<sub>2</sub>O</i>	<i>TiO<sub>2</sub></i>	<i>MnO</i>	<i>Sum</i>	
Page   3453	Sample	Sample source	Sample colour										
	<b>R046</b>	<b>Komu</b>	<b>Pink</b>	40.40	41.96	0.15	0.02	0.44	1.84	0.16	0.02	0.25	85.23
	<b>R047</b>	<b>Komu</b>	<b>Pink</b>	40.02	41.01	0.15	0.02	0.43	1.80	0.17	0.02	0.25	83.88
	<b>R048</b>	<b>Komu</b>	<b>L. Green</b>	39.70	38.63	2.58	0.04	0.33	2.39	0.19	0.05	2.74	86.63
	<b>R049</b>	<b>Komu</b>	<b>Gray</b>	39.80	39.07	2.61	0.04	0.33	2.41	0.18	0.05	2.73	87.22
	<b>R050</b>	<b>Komu</b>	<b>L. Gray</b>	39.66	38.49	2.58	0.04	0.34	2.38	0.19	0.05	2.71	86.42
	<b>R051</b>	<b>Komu</b>	<b>Pink</b>	40.32	41.35	0.18	0.02	0.50	1.81	0.17	0.02	0.26	84.64
	<b>R052</b>	<b>Ijero</b>	<b>Red</b>	63.87	19.39	1.82	0.01	0.17	1.22	0.20	0.02	0.03	89.44
	<b>R053</b>	<b>Ijero</b>	<b>L. Green</b>	63.56	19.19	2.68	0.29	0.06	0.68	0.21	0.02	0.20	89.45
	<b>R054</b>	<b>Ijero</b>	<b>L. Green</b>	65.28	18.27	2.65	0.19	0.08	0.51	0.28	0.02	0.01	89.42
	<b>R055</b>	<b>Ijero</b>	<b>B. Green</b>	64.83	20.30	2.75	0.28	0.07	0.76	0.25	0.02	0.28	89.54
	<b>R31</b>	<b>Oro</b>	<b>L. Green</b>	37.49	41.74	2.61	0.06	0.22	1.98	0.05	0.04	0.20	87.95
	<b>R32</b>	<b>Oro</b>	<b>B. Green</b>	37.74	40.60	4.01	0.02	0.40	2.33	0.05	0.02	0.94	89.60
	<b>R33</b>	<b>Oro</b>	<b>D. Blue</b>	37.40	38.48	7.65	0.07	0.11	2.84	0.05	0.03	0.88	90.49
	<b>R34</b>	<b>Oro</b>	<b>D. Blue</b>	37.02	38.56	9.22	0.08	0.09	2.80	0.05	0.03	0.49	91.31
	<b>R35</b>	<b>Oro</b>	<b>D. Green</b>	38.05	38.92	7.25	0.04	0.18	2.88	0.05	0.02	0.69	91.47

\*Results are in %

**Table 2:** Summary of major oxides compositions of studied tourmaline samples from selected study sites in southwestern Nigeria

<b>Oxides</b>	<b>Range</b>	<b>Mean ± S. D</b>	<b>Median</b>
<b><i>SiO<sub>2</sub></i></b>	37.02 - 65.28	45.68 ± 11.74	39.80
<b><i>Al<sub>2</sub>O<sub>3</sub></i></b>	18.27 - 41.96	34.40 ± 9.52	38.63
<b><i>Fe<sub>2</sub>O<sub>3</sub></i></b>	0.15 - 9.22	3.26 ± 2.74	2.61
<b><i>MgO</i></b>	0.01 - 0.29	0.08 ± 0.09	0.04
<b><i>CaO</i></b>	0.06 - 0.50	0.25 ± 0.15	0.22
<b><i>N<sub>2</sub>O</i></b>	0.51 - 2.88	1.91 ± 0.79	1.98
<b><i>K<sub>2</sub>O</i></b>	0.05 - 0.28	0.15 ± 0.80	0.17
<b><i>TiO<sub>2</sub></i></b>	0.02 - 0.05	0.03 ± 0.01	0.02
<b><i>MnO</i></b>	0.01 - 2.74	0.84 ± 1.01	0.02

\*Results are in %

It was observed that while the highest  $\text{Fe}_2\text{O}_3$  concentrations were found in the blue tourmalines, relatively higher  $\text{Fe}_2\text{O}_3$  values were found in the greens, the values were very low in the red and pinks. It can therefore be inferred that the variation in  $\text{Fe}_2\text{O}_3$  concentrations of the tourmaline samples has adverse effects on type and intensity of colouration in tourmalines.  $\text{Fe}_2\text{O}_3$  is quite high in the various shades of green and blue coloured tourmalines, ranging between 2.58% to 9.22%. Samples R35(7.25%), a dark green tourmaline, R33(7.65%) and R34(9.22%) all dark blue tourmalines from Oro have the highest concentrations of  $\text{Fe}_2\text{O}_3$ , with Fe content causing the greens and blues and also controlling colour intensity, thereby confirming it as the principal chromophores of the studied tourmaline. Generally, as the green become more intense in color,  $\text{Fe}_2\text{O}_3$  content increases. The results showed  $\text{Fe}_2\text{O}_3$  in greater concentration in the green and blue tourmalines, whereas, on the contrary it was observed to be low in samples R046, R047, R051 and R052 which are pink and red tourmalines. The red-coloured tourmalines are slightly more Fe-rich than the pink, while the dark green and blue are much more Fe-rich than the light green. The results established that the  $\text{Fe}_2\text{O}_3$  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 pinks. Iron is therefore believed to be chiefly responsible for tourmaline's colour variation in the studied tourmaline samples. The darker greens

and blues had the most iron, becoming less in the lighter shades of green and completely depleted in the lightest pink. 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.

Tourmaline colour is directly related to its transition elements contents, especially  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  (Simmons *et al.*, 2011). Of these three chromophoric transition metal cations responsible for colouring in tourmalines, only Fe is seen to be the most dominant and active in the studied southwestern Nigeria tourmaline samples. As Fe content increases, hues become darker and colours change to grey, green and blue. Although  $\text{Fe}^{2+} \Rightarrow \text{Ti}^{4+}$  charge-transfer has been suggested as the cause for blue colour in tourmalines (Bacik *et al.*, 2015), it does not seem so in the studied southwestern Nigerian tourmalines. The  $\text{TiO}_2$  value has remained virtually very low and sometimes fairly constant throughout the analyzed samples despite the varied colours among them.  $\text{TiO}_2$  ranged in the southwestern tourmalines between 0.02% and 0.05%, with a mean value of 0.03%. The amounts of  $\text{TiO}_2$  are not significant in these samples and do not seem to result in any noticeable colour changes among them. All the blue and green

tourmaline samples have very low  $\text{TiO}_2$  concentrations but relatively high  $\text{Fe}_2\text{O}_3$  value, suggesting that Fe is the primary chromophores controlling colour intensities in the southwestern Nigeria tourmalines. The overall low  $\text{TiO}_2$  content of these samples may be related to low initial Ti value of the parent pegmatitic magma or the incorporation of this element into earlier formed mineral phases. Taylor and Slack (1984) interpreted the blue to black colours associated with schorl to be dominantly influenced by  $\text{Fe}^{2+} \Rightarrow \text{Fe}^{3+}$  and  $\text{O}^{2-} \Rightarrow \text{Fe}^{3+}$  charge-transfer processes, and the brown hues of dravite by uv-centered  $\text{O}^{2-} \Rightarrow \text{Fe}^{2+}$  processes. According to Brown and Wise (2001),  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  is the principle causes of green hues in elbaite.

$\text{MnO}$  in the studied tourmalines ranged from 0.01% to 2.74% with a mean value of 0.84%.  $\text{MnO}$  value was found to be very low in Komu pink tourmaline samples, R046 and R047 (0.25%) but highest in another Komu green tourmaline, R048 (2.74%), whereas a green tourmaline, R054 was found to contain the lowest  $\text{MnO}$  value of 0.01%. This is contrary to the general assumptions of Rossman (1997) and Brown and Wise (2001) that Mn is the cause of pink hues in tourmaline and that the intensity of the pink colour is thought to be directly related to the quantity of Mn in the structure. Rossman (1997) however postulated that  $\text{Mn}^{2+}$ , being a much weaker absorber than  $\text{Fe}^{2+}$ , its low concentrations of between 1.0 to 3.0% might usually not be enough to impart a colour to Li-Al tourmaline. The low values of

$\text{TiO}_2$  and  $\text{MnO}$  in the studied samples may most likely be the cause of their inactiveness in the tourmalines.

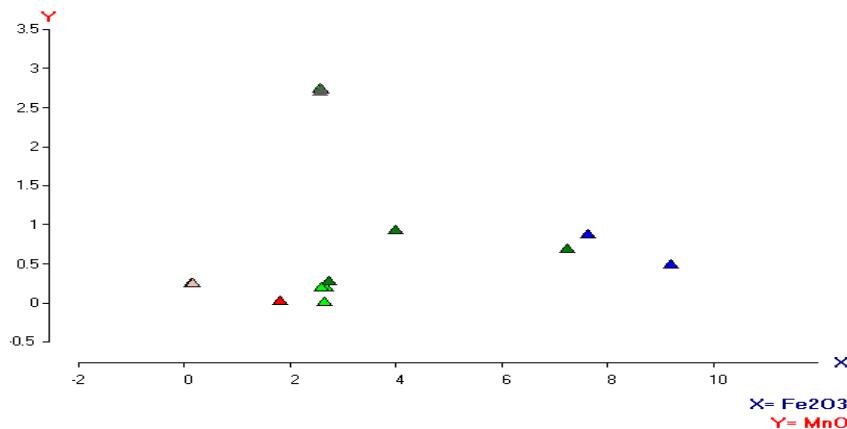
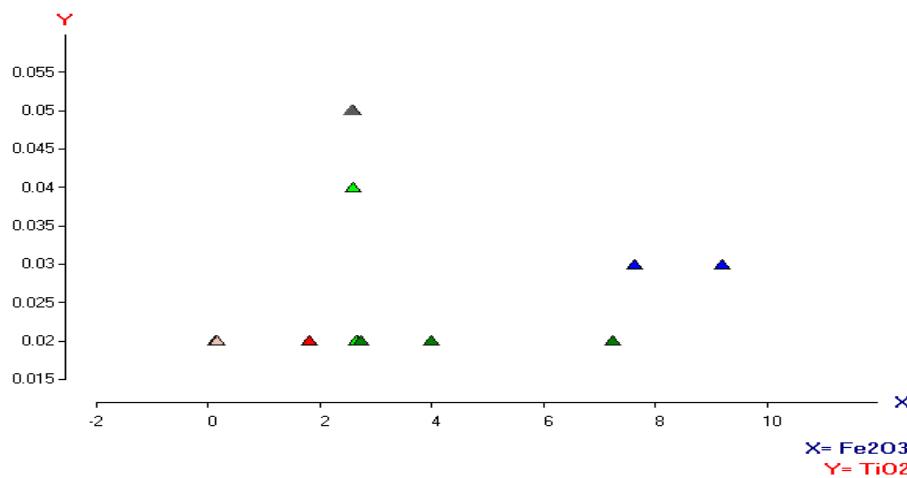
Despite the low values of the chromophoric transition elements (Fe, Mn and Ti) in the studied tourmaline samples, they are positively correlated to one another, and they equally exhibited similar relationships towards each of the alkalis (Table 3). While they were positively correlated to  $\text{Na}_2\text{O}$ , they showed weak negative correlation to  $\text{K}_2\text{O}$ . The low transition elements contents of the studied tourmaline samples have probably resulted from their low content in the late-stage magma from which these minerals were crystallized. The binary plots of  $\text{Fe}_2\text{O}_3$  against  $\text{MnO}$  (Fig. 3),  $\text{Fe}_2\text{O}_3$  versus  $\text{TiO}_2$  (Fig. 4) and  $\text{Fe}_2\text{O}_3$  against  $\text{Na}_2\text{O}$  (Fig. 5) presented positive correlations between the respective oxides and also clearly showed that the green and blue tourmalines are more Fe-rich than the red and pinks. Figures 3 and 4 also showed two grey and one light green tourmaline samples possessing the highest values of  $\text{MnO}$  and  $\text{TiO}_2$  and another light green tourmaline having the lowest values for these oxides. These figures also displayed two pink and one red tourmaline with lowest  $\text{Fe}_2\text{O}_3$  values also containing some of the lowest values of  $\text{TiO}_2$  and  $\text{MnO}$ . All these clearly indicate that both Ti and Mn have not shown any adverse effects on colours in the southwestern Nigerian tourmalines, or if any, their chromophoric effects must have been subdued by the vivid chromophoric effects of Fe.

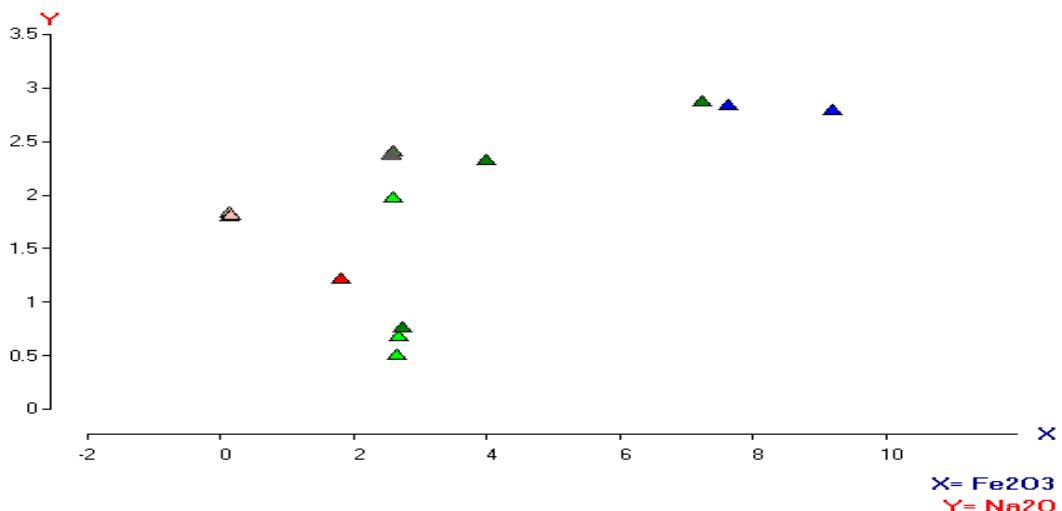
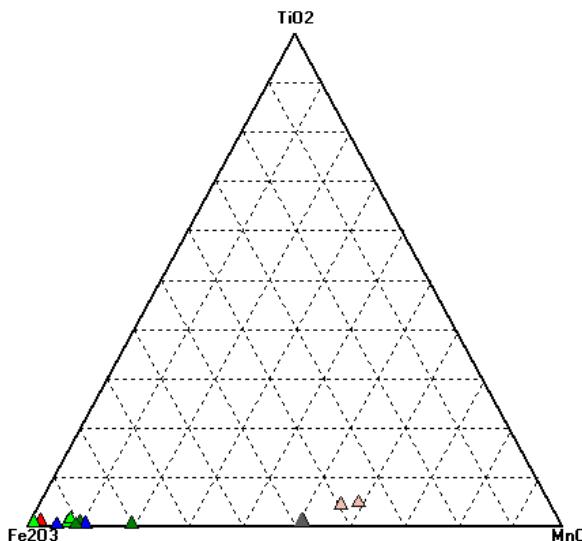
**Table 3:** Statistical correlation coefficients for major oxides of studied tourmaline samples from different locations in southwestern Nigeria

	<i>SiO<sub>2</sub></i>	<i>Al<sub>2</sub>O<sub>3</sub></i>	<i>Fe<sub>2</sub>O<sub>3</sub></i>	<i>MgO</i>	<i>CaO</i>	<i>Na<sub>2</sub>O</i>	<i>K<sub>2</sub>O</i>	<i>TiO<sub>2</sub></i>	<i>MnO</i>	
Page   3456	<i>SiO<sub>2</sub></i>	1								
	<i>Al<sub>2</sub>O<sub>3</sub></i>	-0.37	1							
	<i>Fe<sub>2</sub>O<sub>3</sub></i>	-0.46	-0.41	1						
	<i>MgO</i>	0.01	-0.56*	0.63*	1					
	<i>CaO</i>	-0.17	0.82**	-0.65**	-0.81**	1				
	<i>Na<sub>2</sub>O</i>	-0.84**	0.31	0.41	-0.10	0.20	1			
	<i>K<sub>2</sub>O</i>	0.86**	-0.64*	-0.30	0.25	-0.36	-0.73**	1		
	<i>TiO<sub>2</sub></i>	-0.54*	0.08	0.08	0.16	0.06	0.57*	-0.15*	1	
	<i>MnO</i>	-0.54*	0.19	0.24	-0.08	0.29	0.74**	-0.29	.62*	1

\*\*. Correlation is significant at the 0.01 level (2-tailed).

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

**Figure 3:** Binary plot of Fe<sub>2</sub>O<sub>3</sub> versus MnO for the studied southwestern Nigerian tourmaline samples

**Figure 4:** Binary plot of  $\text{Fe}_2\text{O}_3$  versus  $\text{TiO}_2$  for the studied southwestern Nigerian tourmaline samples**Figure 5:** Binary plot of  $\text{Fe}_2\text{O}_3$  versus  $\text{Na}_2\text{O}$  for the studied southwestern Nigerian tourmaline samples**Figure 6:**  $\text{TiO}_2$  –  $\text{Fe}_2\text{O}_3$  –  $\text{MnO}$  ternary diagram for the studied southwestern Nigerian tourmaline samples

The separation of colours with respect to Fe is significant. As  $\text{Fe}_2\text{O}_3$  value increases, colours change to hues of green and blue. It was observed that some of these Fe-rich blue and green tourmalines also contain about the same or more quantities of  $\text{MnO}$  and  $\text{TiO}_2$  than the red and pinks. The  $\text{TiO}_2$ - $\text{Fe}_2\text{O}_3$ - $\text{MnO}$  chromophoric ternary plot

(Fig. 6) showed all the green and blue tourmaline samples plotting in the  $\text{Fe}_2\text{O}_3$ -field with no sample plotting in the  $\text{TiO}_2$ -field. While the green and grey Komu tourmalines have plotted halfway along the  $\text{Fe}_2\text{O}_3$ - $\text{MnO}$  line due to their equal enrichment in both  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$ , the remaining three Komu pink tourmaline samples plot a little into the  $\text{MnO}$  zone due to their slightly higher  $\text{MnO}$  value. The pink tourmalines are  $\text{Fe}_2\text{O}_3$ -poor but not necessarily  $\text{MnO}$ -rich and pink tourmalines which have more  $\text{Fe}_2\text{O}_3$  than  $\text{MnO}$  usually contain very low quantities of both oxides. Such tourmalines usually result in high colour intensity, just like the Ijero red tourmaline which has plotted in the  $\text{Fe}_2\text{O}_3$ -field.  $\text{Fe}_2\text{O}_3$ -rich green and blue tourmalines usually contain as much  $\text{MnO}$  as the  $\text{Fe}_2\text{O}_3$ -poor pink tourmalines. It is rare for tourmalines with greater  $\text{MnO}$  contents than  $\text{Fe}_2\text{O}_3$  to plot in the  $\text{MnO}$ -field due to the weaker absorber nature of  $\text{Mn}^{2+}$ . In all of the studied samples, colour is controlled mainly by

Fe and not by Mn or Ti. Regardless of the quantity, the respective Fe contents dictate the observed colour hues in the samples. The green and blue tourmalines which are rich in  $\text{Fe}_2\text{O}_3$  and low in  $\text{TiO}_2$  and  $\text{MnO}$  are proof that high Fe content alone can cause blue hues instead of the  $\text{Fe}^{2+}\leftrightarrow\text{Ti}^{4+}$  and I.V.C.T. as suggested by Rossman (1997). It can therefore be established that among the southwestern Nigeria tourmalines, colour is principally controlled by Fe and not Mn or Ti.

### Conclusions

This study established that of the three chromophoric transition metal cations (Fe, Mn and Ti) responsible for coloring in tourmalines, only Fe is seen to be the most dominant and active among the studied southwestern Nigeria gem tourmaline samples with the Fe content varying directly and proportionately with the depth of colour in the greens and blues, and inversely in the pinks and red. It was observed that while the highest  $\text{Fe}_2\text{O}_3$  concentrations were found in the blue tourmalines, relatively higher  $\text{Fe}_2\text{O}_3$  values were found in the greens, the values were very low in the red and pinks. It can therefore be inferred that the variation in  $\text{Fe}_2\text{O}_3$  concentrations of the tourmaline samples has adverse effects on type and intensity of colouration in tourmalines. The colour of gem-quality tourmaline is largely controlled by the Fe content. As Fe content increases, hues become darker and colours change to grey, green and blue. Fe causes light-green, dark-green, grey, blue-green and blue colours as Fe-content increases. Iron is therefore believed to be chiefly responsible for tourmaline's colour variation in the studied tourmaline samples.

The darker greens and blues had the most iron, becoming less in the lighter shades of green and completely depleted in the lightest pink.

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