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# Geochemical Characterization and Gemological Suitability of African Gem Tourmalines, Nigerian Tourmalines: A Case Study

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#### Abstract

Tourmaline, a versatile gem-mineral with a diverse array of colours, has long captivated gem enthusiasts and researchers alike. Nigeria is a significant source for gem-quality tourmalines, highly prized for their vibrant hues. This study presents a comprehensive geochemical analysis of Nigerian tourmalines, aiming to elucidate their compositional variations and gemological significance. Analytical results revealed moderate SiO<sub>2</sub> (av. 45.68%) and Al<sub>2</sub>O<sub>3</sub> (av. 34.40%), but depletion in the other major oxides. Incompatible elements are significantly concentrated in a few of the analyzed samples, making Cs the most variable (0.05 - 8863.00ppm), suggesting different petrogenetic processes and sources of magmatic or hydrothermal fluids, thus providing insights into the genesis and evolution of the host rocks. Elevated Be values (>10,000ppm) were observed for some samples, confirming tourmaline's use as an exploratory tool for other mineralizations. All the studied tourmaline samples plot into the fields of Li-rich granitoid pegmatites and aplites of the Al-Fe-Mg plot.

Key word: Tourmaline, Nigeria, Gem-mineral, Geochemical analysis, Pegmatite

### **1.0 Introduction**

Gemstones have captivated humanity for ages, revered for their beauty, durability, rarity, and symbolic significance. Among these treasures of the earth, tournaline stands out as one of the most diverse and enchanting gemstones, offering a spectrum of colours and unique properties. Within the vast continent of Africa, tourmaline deposits have drawn significant attention from gemologists, geologists, and miners alike. Nigeria, with its rich geological heritage, holds promise as a source of tournalines, presenting an intriguing case study for understanding their geochemical characteristics and gemological suitability. Tournaline, a group of boron aluminum cyclosilicate mineral, with a typically complex chemical formula  $Na(Mg,Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$ , is categorized as a semi-precious gemstone with special beauty (colour) and physical properties, making it suitable for adornment and decorative purposes. It is the most colourful of all gemstones and varies widely in colour and physical properties but share a common crystal structure. It has a complex range of chemical composition with major and trace elements substituting for one another in the crystal structure. The tournaline's complex composition reflects changes in its chemical and physical environment and therefore makes it wellsuited to explore the conditions under which it formed, the varied mineral compositions allowing for conditions to be pinpointed more precisely (Henry and Guidotti, 1985). Understanding the geochemical signatures of tournalines is crucial for unraveling their provenance and genesis.

In Nigeria, the most common and characteristic occurrences of euhedral gem tourmaline are in granitic

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pegmatites, particularly the mineralized zones, where they are usually associated with other gem minerals like beryl and spodumene, and metallic minerals such as tantalite-columbite and cassiterite alongside the rock-forming minerals like quartz, felspars and muscovite (Jimoh, 2018). Studies have revealed that a number of tournaline species such as schorl, elbaite, liddicoatite, magnesiofoitite, rossmanite and olenite crystallize almost exclusively from rare-elements and in miarolitic class, LCTfamily pegmatites (Selway *et al.*, 1998). Pegmatites within the Precambrian Basement Complex rocks of Nigeria have been categorized in terms of rare elements (e.g. Nb, Ta, Li, W, Sn, Be, B, Cs, Rb) mineralization as mineralized and non-mineralized (Adetunji *et al*, 2016). This study embarks on an exploration of African gem tournalines, focusing on the specific case of Nigerian tournalines. Through a combination of geochemical analysis and gemological assessment, we aim to elucidate the chemical distribution and its significance to the gemological properties of these gemstones. By so doing, we seek to provide valuable insights into their origin, formation processes, and potential for use in jewelry and other applications, which have never been undertaken for Nigerian tournalines.

# 2.0 Materials and Methods

A number of 25 quality tourmaline crystals ranging in colour from colourless, pink, red, green, and blue were purchased from several mines across Nigeria for this study. These specimens were thoroughly washed and immersed in methylated spirit to remove contaminations on the crystal faces. 15 of these crystal samples (Fig. 1a) were individually prepared and analyzed using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) method to quantify their major and trace elemental contents. The remaining ten samples which all have some natural faces (Fig 1b) were subjected to different gemological investigations such as colour examination, hardness and specific gravity to ascertain their suitability as gemstones. The hardness was determined via the Mohs Scales of Hardness by using materials of known hardness such as felspar and topaz to scratch each of the crystals. Specific gravity (SG) and refractive indices (RIs) were measured by standard gemological instruments. The ten crystals were latter taken through lapidary processes and subsequently mounted as jewelries (Fig. 4)

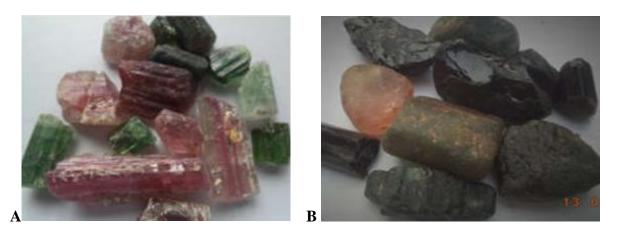


Figure 1: The photographs of Nigerian gem tourmaline crystals used for the study; A: Samples used for ICP-MS analysis, B: Samples for gemological properties tests

### **2.1 Geological Setting**

Nigeria is underlain by three major litho-petrological components, namely; 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 Precambrian pegmatites, particularly the rare-metal pegmatites, which are homes to the gem tourmalines belong to the Older Granite suite, a

member of the Nigerian Basement Complex. Other members of the group include; the Migmatite-Gneiss-Quartzite Complex and the Schist Belt. The Basement Complex of Nigeria, which is Precambrian in age 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). It is a polycyclic terrain which suffered its most pronounced deformation and mobilization during the Pan-African age (600 Ma). Different ages have been ascribed to the Nigerian Basement Complex using different radiometric dating methods such as Rb/Sr, K/Ar and Th/Pb. Grant (1970) observed that the majority of the radiometric ages obtained fall in the range of 600 Ma, which corresponds to the Pan-African thermo-tectonic event. It consists predominantly of folded gneisses, schist and quartzite into which have been emplaced granitic and to a lesser extent, more basic material. It is intruded by the Mesozoic calc-alkaline ring complexes (Younger Granites) of the Jos Plateau, and is unconformably overlain by the Cretaceous and younger sediments, occupying the remaining half the landmass of the country (Fig. 2).

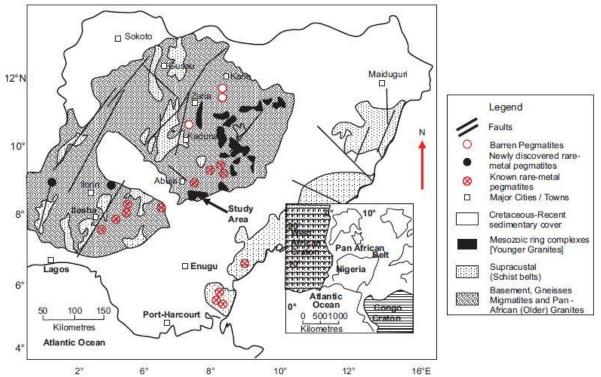


Figure 2: Geological map of Nigeria showing the regional fractures and location of areas of rare-metal and barren pegmatites (After Garba, 2003)

Three principal subdivisions are recognizable within the basement complex. Elueze (2000) gave these subdivisions as: -

- The ancient Migmatite Gneiss Quartzite Complex,
- The Schist Belts, and
- The Pan African plutonic series.

The Migmatite–Gneiss–Quartzite Complex represents the oldest recognizable rocks and most widespread making up about 60% of the surface area of the Nigerian Basement Complex (Rahaman and Ocan, 1978). It has a heterogeneous assemblage comprising migmatites, orthogneises, paragneisses and a series of basic and ultrabasic metamorphosed rocks. Much of the migmatization of the gneiss complex is believed to be associated with the latter phases of older granite activity but there is evidence that the onset of intrusive activity found the gneiss complex already highly metamorphosed. The schist

belts which are best developed in the western part of Nigeria, west of 8°E longitude consist of supracrustal assemblage of low to medium grade metasedimentary rocks with subordinate mafic and ultramafic rocks. These roughly north-south trending rocks consist of quartzites, amphibolites, micaschist, calc-silicate rocks, marbles, phyllites, pelites, meta-conglomerate iron formations and subordinate meta-igneous rocks (Elueze, 1992). Geochronological studies of Ajibade et al (1987) put the age of the Schist Belts to Pan-African, setting their deformation and metamorphic histories to the periods of Pan-African orogeny (500Ma – 800Ma). Referred to as the 'Pan African plutonic series', the Older Granites, which occur intricately associated with the Migmatite-Gneiss Complex and the Schist Belts, into which they generally intruded are believed to have been emplaced during the Pan-African orogeny (Harper et al, 1973). They comprise mainly granites and granodiorite, with subordinate pegmatite and Aplite.

# 3.0 Results and Discussions

Results of the analyzed Nigerian tournaline samples show high compositional variability, a reflection of diversity in the chemistry of their host rocks and mineralizing fluids, as well as differences in temperature and pressure of formation (Demirel et al., 2009). Giller (2003), while analyzing tournaline samples from six African countries of Nigeria, Namibia, Mali, Tanzania, Congo and Mozambique showed that the Nigerian samples are the most chemically diverse population of samples.  $SiO_2$  and  $Al_2O_3$  are moderately enriched in all the samples with their respective values in the range of 37.02% to 65.28% and 18.27% to 41.96% (Table 1), and their mean and standard deviation values of 45.68%  $(\pm 11.74)$  and 34.40%  $(\pm 9.52)$  (Table 2). Fe<sub>2</sub>O<sub>3</sub> value varies considerably among the tournalines, ranging from 0.15% to 9.22%, with the mean and standard deviation values of 3.26% and  $\pm 2.74$ respectively, thereby causing the obvious differences in the colours of the tourmaline crystals. As  $Fe_2O_3$ value increases, colours change to hues of green and blue, suggesting that Fe is the primary chromophores controlling colour intensities in Nigerian tourmalines (Jimoh, 2018). According to Brown and Wise (2001),  $Fe^{2+}$  or  $Fe^{3+}$  is the primary causes of green hues in elbaite, and Deer *et al.* (1986) actually acknowledged the main controlling factor for colour in tourmalines to be the presence or absence of Fe. Though the remaining major oxides are depleted in the analyzed tourmaline samples, their distributions reflect their respective host rock lithologies and also depend on the presence, absence or amount of the other major oxides they coexist with. MgO value range from 0.01% to 0.29% with a mean value of 0.08%. Giller (2003) reported a Mg signature for Congolese tournaline samples with MgO value as high as 0.46%, indicating that the mineralizing fluid contained high Mg concentration or was contaminated by Mg-rich host rock.

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R31	R32	R33	R34	R35	R046	R047	R048	R049	R050	R051	R052	R053	R054	R055
				1										
37.49	37.74	37.40	37.02	38.05	40.40	40.02	39.70	39.80	39.66	40.32	63.87	63.56	65.28	64.83
41.74	40.60	38.48	38.56	38.92	41.96	41.01	38.63	39.07	38.49	41.35	19.39	19.19	18.27	20.30
2.61	4.01	7.65	9.22	7.25	0.15	0.15	2.58	2.61	2.58	0.18	1.82	2.68	2.65	2.75
0.06	0.02	0.07	0.08	0.04	0.02	0.02	0.04	0.04	0.04	0.02	0.01	0.29	0.19	0.28
0.22	0.40	0.11	0.09	0.18	0.44	0.43	0.33	0.33	0.34	0.50	0.17	0.06	0.08	0.07
1.98	2.33	2.84	2.80	2.88	1.84	1.80	2.39	2.41	2.38	1.81	1.22	0.68	0.51	0.76
0.05	0.05	0.05	0.05	0.05	0.16	0.17	0.19	0.18	0.19	0.17	0.20	0.21	0.28	0.25
0.04	0.02	0.03	0.03	0.02	0.02	0.02	0.05	0.05	0.05	0.02	0.02	0.02	0.02	0.02
0.20	0.94	0.88	0.49	0.69	0.25	0.25	2.74	2.73	2.71	0.26	0.03	0.20	0.01	0.28
87.95	89.60	90.49	91.31	91.47	85.23	83.88	86.63	87.22	86.42	84.64	89.44	89.45	89.42	89.54
	37.49 41.74 2.61 0.06 0.22 1.98 0.05 0.04 0.20	37.49         37.74           41.74         40.60           2.61         4.01           0.06         0.02           0.22         0.40           1.98         2.33           0.05         0.05           0.04         0.02           0.20         0.94	37.49         37.74         37.40           41.74         40.60         38.48           2.61         4.01         7.65           0.06         0.02         0.07           0.22         0.40         0.11           1.98         2.33         2.84           0.05         0.05         0.05           0.04         0.02         0.03           0.20         0.94         0.88	37.49         37.74         37.40         37.02           41.74         40.60         38.48         38.56           2.61         4.01         7.65         9.22           0.06         0.02         0.07         0.08           0.22         0.40         0.11         0.09           1.98         2.33         2.84         2.80           0.05         0.05         0.05         0.05           0.04         0.02         0.03         0.03           0.20         0.94         0.88         0.49	37.49         37.74         37.40         37.02         38.05           41.74         40.60         38.48         38.56         38.92           2.61         4.01         7.65         9.22         7.25           0.06         0.02         0.07         0.08         0.04           0.22         0.40         0.11         0.09         0.18           1.98         2.33         2.84         2.80         2.88           0.05         0.05         0.05         0.05         0.05           0.04         0.02         0.03         0.03         0.02           0.20         0.94         0.88         0.49         0.69	37.49         37.74         37.40         37.02         38.05         40.40           41.74         40.60         38.48         38.56         38.92         41.96           2.61         4.01         7.65         9.22         7.25         0.15           0.06         0.02         0.07         0.08         0.04         0.02           0.22         0.40         0.11         0.09         0.18         0.44           1.98         2.33         2.84         2.80         2.88         1.84           0.05         0.05         0.05         0.05         0.16         0.02           0.20         0.94         0.88         0.49         0.69         0.25	37.49         37.74         37.40         37.02         38.05         40.40         40.02           41.74         40.60         38.48         38.56         38.92         41.96         41.01           2.61         4.01         7.65         9.22         7.25         0.15         0.15           0.06         0.02         0.07         0.08         0.04         0.02         0.02           0.22         0.40         0.11         0.09         0.18         0.44         0.43           1.98         2.33         2.84         2.80         2.88         1.84         1.80           0.05         0.05         0.05         0.05         0.05         0.16         0.17           0.04         0.02         0.03         0.03         0.02         0.02         0.02           0.20         0.94         0.88         0.49         0.69         0.25         0.25	37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58           0.06         0.02         0.07         0.08         0.04         0.02         0.02         0.04           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39           0.05         0.05         0.05         0.05         0.02         0.02         0.05           0.20         0.94         0.88         0.49         0.69         0.25         0.25         2.74	37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61           0.06         0.02         0.07         0.08         0.04         0.02         0.02         0.04         0.04           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41           0.05         0.05         0.05         0.05         0.16         0.17         0.19         0.18           0.04         0.02         0.03         0.03         0.02         0.02         0.05         0.05           0.20         0.94         0.88         0.49         0.69         0.25         0.25         2.74         2.73	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18           0.06         0.02         0.07         0.08         0.04         0.02         0.02         0.04         0.04         0.02           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81           0.05         0.05         0.05         0.05         0.16         0.17         0.19         0.18         0.19         0.17           0.04         0.02         0.03         0.03         0.02         0.02         0.05         0.05         0.05         0.05 <t< th=""><th>37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32         63.87           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35         19.39           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18         1.82           0.06         0.02         0.07         0.08         0.04         0.02         0.04         0.04         0.02         0.01           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50         0.17           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81         1.22           0.05         0.05         0.05         0.05         0.16         0.17         0.19         0.18         0.19         0.17         0.20           0.04         0.02         0.03         0.03</th><th>37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32         63.87         63.56           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35         19.39         19.19           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18         1.82         2.68           0.06         0.02         0.07         0.08         0.04         0.02         0.04         0.04         0.04         0.02         0.01         0.29           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50         0.17         0.06           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81         1.22         0.68           0.05         0.05         0.05         0.16         0.17         0.19         0.18         0.19         0.17</th><th>37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32         63.87         63.56         65.28           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35         19.39         19.19         18.27           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18         1.82         2.68         2.65           0.06         0.02         0.07         0.08         0.04         0.02         0.04         0.04         0.04         0.02         0.01         0.29         0.19           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50         0.17         0.06         0.08           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81         1.22         0.68         0.51           0.05         0.05         0.05</th></t<>	37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32         63.87           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35         19.39           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18         1.82           0.06         0.02         0.07         0.08         0.04         0.02         0.04         0.04         0.02         0.01           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50         0.17           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81         1.22           0.05         0.05         0.05         0.05         0.16         0.17         0.19         0.18         0.19         0.17         0.20           0.04         0.02         0.03         0.03	37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32         63.87         63.56           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35         19.39         19.19           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18         1.82         2.68           0.06         0.02         0.07         0.08         0.04         0.02         0.04         0.04         0.04         0.02         0.01         0.29           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50         0.17         0.06           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81         1.22         0.68           0.05         0.05         0.05         0.16         0.17         0.19         0.18         0.19         0.17	37.49         37.74         37.40         37.02         38.05         40.40         40.02         39.70         39.80         39.66         40.32         63.87         63.56         65.28           41.74         40.60         38.48         38.56         38.92         41.96         41.01         38.63         39.07         38.49         41.35         19.39         19.19         18.27           2.61         4.01         7.65         9.22         7.25         0.15         0.15         2.58         2.61         2.58         0.18         1.82         2.68         2.65           0.06         0.02         0.07         0.08         0.04         0.02         0.04         0.04         0.04         0.02         0.01         0.29         0.19           0.22         0.40         0.11         0.09         0.18         0.44         0.43         0.33         0.33         0.34         0.50         0.17         0.06         0.08           1.98         2.33         2.84         2.80         2.88         1.84         1.80         2.39         2.41         2.38         1.81         1.22         0.68         0.51           0.05         0.05         0.05

Table 1: Compositions of the studied Nigerian gem tourmaline samples

#### ILORIN JOURNAL OF SCIENCE

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Trace Lements (ppm)															
B	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000	>2000
Ba	23	15	14	17	20	419	421	179	161	194	735	278	95	182	84
Be	179	22	16	26	37	239	402	516	354	675	555	>10000	>10000	>10000	>1000
Co	0.3	0.1	0.8	0.6	0.3	0.2	0.3	0.3	0.3	0.3	0.2	0.1	0.4	0.5	0.7
Cs	1	1.2	0.2	0.5	0.1	4.2	4.0	7.3	5.8	8.3	7.8	8863	240.6	292.0	226.4
Ga	130.9	136.6	118.8	58.3	58.7	154.3	155.2	200.0	201.2	202.0	156.7	47.8	28.2	29.0	36.3
Hf	0.2	0.2	0.1	0.1	0.2	0.1	0,1	0.4	0.3	0.5	0.2	0.2	0.2	0.1	0.2
Nb	19.4	2.6	0.9	0.7	1.6	8.1	8.2	1.6	1.6	1.7	8.4	0.9	1.5	2.3	1.3
Rb	2.2	3.1	0.6	0.8	0.7	7.6	8.0	10.0	9.4	10.8	9.1	921.1	41.6	110.0	41.7
Sn	146	29	21	20	20	128	126	23	23	24	127	8	2	1	3
Sr	7.4	9.5	10.3	50.3	24.8	12.9	12.9	24.4	25.9	27.1	19.8	9.1	9.4	9.6	10.5
Ta	96.2	5.8	1.6	2.3	5.8	5.3	5.8	1.6	1.5	1.5	4.9	3.0	0.7	0.5	0.6
Th	0.3	0.2	0.1	0.1	0.2	0.9	0.9	0.5	0.4	0.4	1.3	0.4	0.4	1.2	0.6
U	1.2	0.1	0.05	0.05	0.05	0.1	0.2	0.4	0.3	0.4	0.2	0.2	0.05	0.2	0.4
V	12	9	10	4	4	4	4	4	4	4	4	4	4	16	13
W	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.7	1.3	0.25	0.9	0.25	0.25	0.25
Zr	5.1	5	2.9	3.8	8.4	4.3	5.0	6.9	7.8	10.4	5.6	6.4	5.3	6.6	6.6
Y	0.6	0.6	0.3	0.6	0.4	1.2	1.4	1.1	1.0	0.9	2.6	0.9	1.0	1.2	1.2
La	2.1	1.8	0.9	1.2	1.1	1.3	1.4	1.8	2.0	1.8	1.8	1.3	1.1	1.8	1.7
Ce	2.5	1.4	1.2	1.5	1.5	2.3	1.7	3.1	2.7	3.1	3.2	2.2	2.2	3.4	3.5
Pr	0.22	0.15	0.12	0.15	0.16	0.24	0.24	0.31	0.30	0.31	0.26	0.23	0.20	0.37	0.35
Nd	0.9	0.4	0.3	0.5	0.5	1.1	1.0	1.2	0.7	1.6	1.1	0.8	1.2	2.0	1.4
Sm	0.17	0.03	0.07	0.03	0.03	0.23	0.21	0.26	0.24	0.30	0.24	0.16	0.24	0.51	0.41
Eu	0.03	0.01	0.01	0.03	0.03	0.05	0.04	0.03	0.04	0.02	0.04	0.02	0.05	0.04	0.06
Gd	0.13	0.08	0.03	0.06	0.08	0.24	0.28	0.21	0.22	0.29	0.29	0.21	0.22	0.46	0.33
Tb	0.03	0.01	0.01	0.01	0.01	0.04	0.03	0.04	0.04	0.03	0.06	0.02	0.02	0.04	0.04
Dy	0.14	0.06	0.07	0.1	0.09	0.21	0.23	0.21	0.18	0.14	0.27	0.09	0.12	0.13	0.20
Но	0.02	0.01	0.01	0.01	0.01	0.03	0.04	0.04	0.02	0.03	0.06	0.03	0.02	0.03	0.04
Er	0.04	0.02	0.04	0.02	0.04	0.08	0.07	0.07	0.06	0.06	0.18	0.05	0.02	0.03	0.06
Tm	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
Yb	0.03	0.03	0.03	0.03	0.03	0.10	0.08	0.10	0.09	0.08	0.15	0.08	0.12	0.06	0.11
Lu	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01

 Table 2: Summary of major oxides compositions of studied Nigerian gem tourmaline samples (%)

Oxides	Range	$Mean \pm S.D$	Median
SiO <sub>2</sub>	37.02 - 65.28	$45.68 \pm 11.74$	39.80
Al <sub>2</sub> O <sub>3</sub>	18.27 - 41.96	$34.40 \pm 9.52$	38.63
Fe <sub>2</sub> O <sub>3</sub>	0.15 - 9.22	$3.26\pm2.74$	2.61
MgO	0.01 - 0.29	$0.08\pm0.09$	0.04
CaO	0.06 - 0.50	$0.25 \pm 0.15$	0.22
$N_2O$	0.51 - 2.88	$1.91 \pm 0.79$	1.98
$K_2O$	0.05 - 0.28	$0.15 \pm 0.80$	0.17
TiO <sub>2</sub>	0.02 - 0.05	$0.03 \pm 0.01$	0.02
MnO	0.01 - 2.74	$0.84 \pm 1.01$	0.02

Dunn (1977) reported that MgO would not cause major colour change in tourmalines, but would have influence on the presence or otherwise and concentration of other oxides/elements. The general low value of  $K_2O$  throughout the studied tourmaline samples may also be attributed to the fact that tourmaline structures do not easily accommodate K, mostly due to its large ionic radius which limits its substitutions for smaller cations at the X-site. The high values of Na<sub>2</sub>O relative to  $K_2O$  observed among

the studied tournalines could have resulted from massive cationic substitution of the  $K^+$  by the  $Na^+$  at the X-site of the solid solutions of the tournalines.

Plots of some major oxides of the analyzed tournalines revealed compositional variations, mineralization trends, and suggest geochemical tools for future geochemical sampling procedures. The major oxides compositions of tournalines being controlled by the host rock lithology. The ternary plot of Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-MgO (Fig. 3a) show the tourmalines samples plotting in the alumina field, while that of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> (Fig. 3b) show equal enrichment in both silica and alumina by most samples. Since tourmaline chemistry reflects the diverse compositions of its host rock (Demirel et al., 2009), it therefore follows that the Nigerian tourmalines have formed from peraluminous provenances and within high to weak acidic environments. Thus, the general chemistry displayed by the Nigerian tourmalines is typical of gem-quality tournaline from LCT-family pegmatites. Adequate concentration of Al is necessary and required for tourmaline crystallization, as Grew (1996) proved that in highly alkaline and/or silica- or aluminum-undersaturated conditions, tourmaline growth is inhibited and other borosilicates form instead. Maximum concentrations of the oxides; SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are therefore required for tourmaline crystallization in an environment. The host rock lithologies of the Nigerian tourmaline samples correlate well with the pre-defined fields in the Al-Fe-Mg and Ca-Fe-Mg plots of Henry and Guidotti (1985), whereby several distinct regions are defined for tournalines from different rock types. All the studied tourmaline samples plot into the fields of Li-rich granitoid pegmatites and aplites of the Al-Fe-Mg plot (Fig. 4a) of Henry and Guidotti (1985) and majority of the samples also plot in the field of Li-rich granitoids pegmatites and aplites of the Ca-Fe-Mg plot (Fig. 4b) of Henry and Guidotti (1985). The relatively high Fe/Fe+Mg ratio, averaging 0.89 also confirms pegmatitic origin for the Nigeria tourmalines. Pegmatite-related tourmalines are systematically higher in Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O and lower in CaO and MgO, relative to tournalines from the country rocks. This has been adequately reflected in the compositions of the analyzed Nigerian tourmaline samples as evidenced also by the ternary Ca-Fe-Mg plot (Fig. 4b).

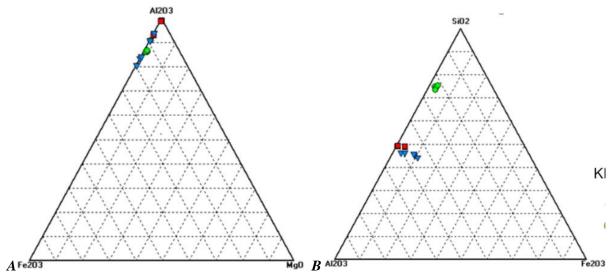


Figure 3: Triangular diagrams of; (A) Al<sub>2</sub>O <sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-MgO and (B) SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> for the analyzed Nigerian tourmaline samples.

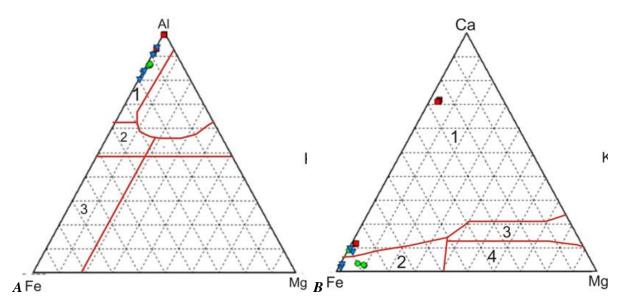


Figure 3: Ternary plots (A) Al - Fe - Mg ternary plot (1:Li-rich granitoids pegmatites and aplites, 2:Li-poor granitoids and their associated pegmatites and aplites, 3:Fe<sup>3+</sup> rich quartz-tourmaline rocks) (B) Ca - Fe - Mg (1:Li-rich granitoids pegmatites and aplites, 2:Li-poor granitoids and their associated pegmatites and aplites, 3:Ca-rich metapsammites and calc-silicate rocks, 4:Ca-poor metapelites, metapsammites and quartz-tourmaline rocks) of the Nigerian tourmaline samples (After Henry and Guidotti (1985))

Based on the fact that the analyzed tournalines have actually evolved from LCT-family pegmatitic melts, they are not expected to have appreciable Mg, unless this element has been introduced via contaminations from more mafic country rocks or other Mg-bearing rocks (Selway *et al.*, 1998).

The analyzed Nigerian tourmalines samples show high compositional variation in trace elements with most of them highly enriched in incompatible elements, particularly the large ion lithophile elements (LILE), but low in the high field strength elements (HFSE), indicating that the tourmaline samples have indeed crystalized from granite related melt (Plimer et al, 1991). Boron for instance, measures above 2000ppm in each of the analyzed sample, indicating tourmaline as a boron cyclosilicate mineral, while Cs exhibits the most variable concentration (0.05 - 8863.00ppm), suggesting different petrogenetic processes and sources of magmatic or hydrothermal fluids. A few of the samples contain beryllium measuring above 10000ppm, an indication of their associations with beryl, a chief beryllium mineral, thereby giving credence to the use of tourmaline as prospecting guides or tools in mineral exploration (Jimoh, 2018). As a potential indicator mineral, tourmaline has a wide range of chemical compositions, and can modify its chemical composition to reflect the presence of mineral of economic interest.

### **Gemological Observations**

Gemstones are minerals or rocks that can be cut, shaped, and polished into beautiful stones that can be used in jewelry and for collections. Gems can be composed of various minerals, but their beauty, durability and rarity make a gem highly valued. Of the several properties that contribute to the beauty of a gem, colour is a major factor, and colour is a combination of its hue, tone and saturation, and this is evaluated during general observation using a magnifying lens. A full range of colours are observed to be available among Nigerian tourmalines. It exhibits remarkable diversity in colour, ranging from vivid reds, and greens to delicate pinks and blues, and this diversity is attributed to variations in chemical composition, as well as structural defects and impurities within the crystal lattice (Jimoh and Olatunji, 2019). Tourmaline color is directly related to its transition elements contents, especially Mn<sup>2+</sup>, Mn<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> and Ti<sup>4+</sup> (Simmons *et al.*, 1998). Of these 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 in the studied Nigeria tourmaline samples (Jimoh, 2018). As Fe contents increase, hues become darker and colors change to green, grey and blue. There is no correlation between the degree of colour of Nigerian tourmaline samples and their Mn contents (Giller 2003). With the aid of the Rayner Refractometer the refractive index (RI) of the studied tourmalines was measured to range from 1.62 to 1.64 with a birefringence up to 0.039. Gem durability is a combination of three properties; hardness, toughness, and stability. These properties are a testimony to the longevity of a gem. While each of the tourmaline crystals was observed to scratch orthoclase feldspar, they were scratched by topaz. It was therefore deduced that the Nigerian tourmalines measure 7 to 7.5 on the Mohs scale of hardness. This means that they are quite hard and resistant to scratches with no cleavages, and as such they are extremely durable. The specific gravity (SG) of the samples which was measured using the hydrostatic weighing method gave an average value of 3.06. Rarity, the third characteristic is a valued quality of gemstones. High-quality Nigerian tourmalines free from inclusions are super rare and come at a very high price.

Further investigations such as the "Four Cs" of gem grading which stand for color, clarity, cut, and carat (weight) can only be undertaken after the tournalines are cut and polished (Fig. 5) which mostly depends on the skills of the lapidaries. How cutters orient the rough can greatly impact the appearance of the finished gem. Cutting style is also a part of color management. The choice of cut can lighten or darken a gem, which will considerably affect both the appearance and the value of the stone. The shape, number, and location of facets influence the brilliance of the gem. Unpolished, loose tournalines simply look like ordinary rocks; cutting and polishing allows them to have brilliance and sometimes colour (leading to their value) that can't be found in other types of stones. Its multitude of colours and its hardness combine to make tournaline a spectacular gemstone (Pezzotta and Laurs, 2011).



Figure 5: Facetted Nigerian gem tourmalines; A: Some facetted tourmalines, B: Mounted facetted tourmaline

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