

Rare Earth Elements And Rare Elements concentration In Two Pegmatite Fields Within North-Central Nigerian Precambrian Basement Complex: Implication For Mineralization

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Abstract

The Precambrian pegmatites of Akwanga (field 1) and Keffi (field 2) area were studied for their rare earth elements and rare elements (rare metals) concentration. A total of 12 whole rock samples were analysed for major, trace and rare earth elements using inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analytical technique. Rare earth element (REE) is an emerging alternative energy technology, such as electric vehicles, energy-efficient lighting, and wind power. Ce, Pr, Nd, Sm, Eu, Gd and Y in field 1 is less than field 2 as (4.06 < 5.48), (0.83 < 2.52), (2.95 < 10.65), (0.72 < 2.23), (0.22 < 0.34), (0.69 < 2.30) and (4.90 < 14.18) respectively while La, Tb, Dy, Ho, Er, Th, Yb and Lu in field 1 greater than field 2 as (4.25 > 2.40), (0.15 > 0.14), (0.75 > 0.53), (0.21 > 0.13), (0.40 > 0.32), (1.71 > 1.18), (0.51 > 0.35) and (0.09 > 0.05) respectively. The anomalous concentration of Neodymium (10.65 ppm) and Yttrium (14.18 ppm) in the study area is close and can be compared with international published works on REE. Rare elements data show that the rare metal Ta, Nb, Cs and Sn increases from field 1 to 2 with tantalum ranges from 1.49 to 78.32 ppm, niobium (12–25.15 ppm), cesium (8.56 – 16.05) and Tin ranges from 10.25 – 52.50. Meanwhile Binary plots revealed that most of the samples plot in the barren field than in the mineralized field.

Keywords: ICP-AES, Anomalous, Rare Earth Elements, Rare Elements and Pegmatite

1. Introduction

The purpose of this paper is to describe and compare rare earth elements and rare elements in two pegmatite fields. The research area is located within the basement complex rocks of north central Nigeria (Fig. 1). Pegmatite fields 1 is found in Akwanga area while pegmatite field 2 in Keffi area both in Nasarawa State and are separated with distance approximately 68.007km in a ENE-SSW trend (Fig. 2). This trend is in accordance with pegmatite zone of (Kinnaird, 1984). Rare Earth Elements was first

named in 1794, it is "rare" because they were originally thought to be present in the earth's crust only in small amounts and "earth" because as oxides, when first discovered they had an earthy appearance. Rare Elements (Rare Metal) - the term rare is based on the difficulty in finding economic concentrations of these elements. The rare earth elements (REE) are fifteen elements with atomic numbers 57 through 71, from lanthanum to lutetium ("lanthanides") while yttrium with atomic number (39) is chemically similar to the lanthanide elements and thus added as rare earth elements. These Elements are

essential for a diverse and expanding array of high-technology applications but industrial demand is relatively small in tonnage terms. Meanwhile, Rare Elements are unique elements that contrary to REE are not grouped based on similar chemical behaviour. The rare elements are strategic elements, generally metals that are of important to a country's economy or defense. The list varies with country but includes Ta, Nb, Be, Sb and W. An important class of rareelement pegmatites

is the complex-type pegmatites of the LCT (Li–Cs–Ta) family (~Cerný and Ercit, 1989). This type of pegmatite contains extremely high concentrations of Rb, Cs, Be, Ta, Nb, and Sn as well as (Li, P, F, and B). The LCT pegmatites are typically associated with latetectonic peraluminous granites, and their emplacement is controlled at least in part by shear zones (Cerný, 1989a & 1989b; London, 2008).

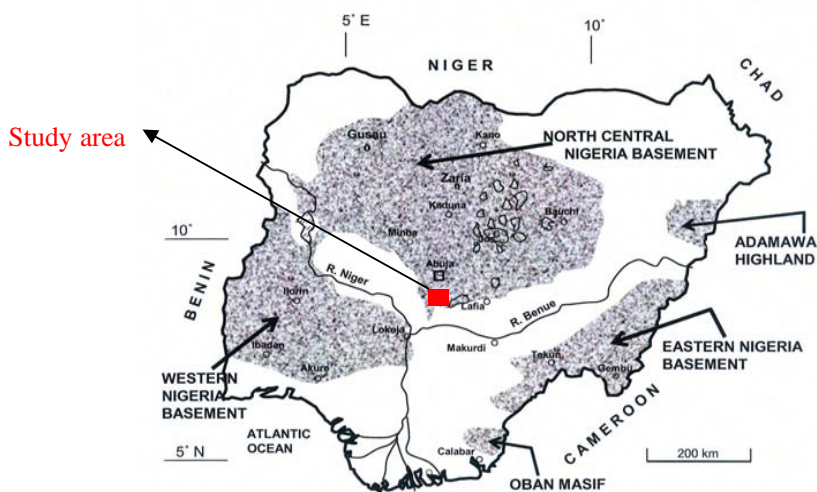


Fig. 1: Basement geology of Nigeria (In Obaje, 2009)

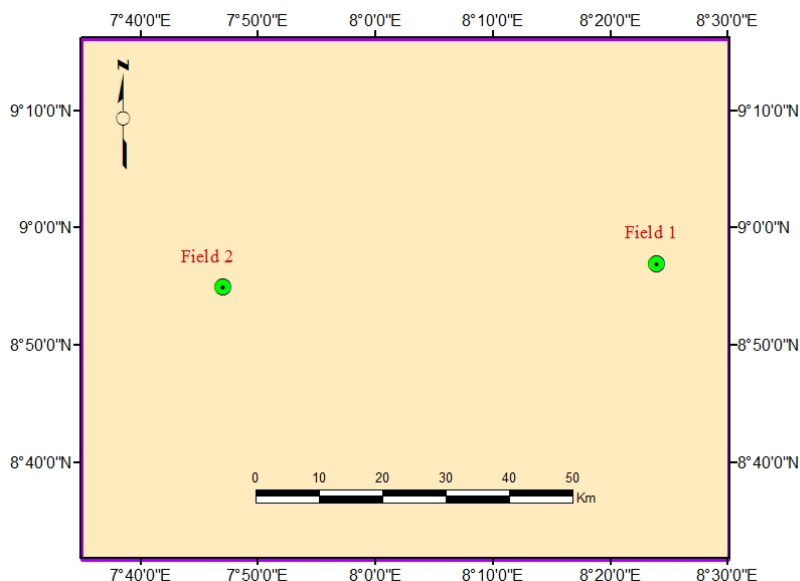


Fig. 2: Showing the two study fields; Field 1 and Field 2

2. The Nigerian basement complex

The Nigerian basement complex forms a part of the Pan-African mobile belt and lies between the West African and Congo Cratons and south of the Tuareg Shield (Black, 1980). The basement complex is one of the three major litho-petrological

components that make up the geology of Nigeria (Fig. 3). Rahaman (1988) in the recent advances to the study of the Nigeria Basement Complex subdivides the basement complex rocks into six major groups. They are;

1. Migmatite – gneiss – quartzite complex
2. Slightly migmatized to non-migmatized metasediment and meta-igneous rocks.
3. Chanockitic, gabbroic and dioritic rocks
4. Members of the older granite suites
5. Metamorphosed to unmetamorphosed calc-alkaline volcanics and hypabyssal rocks.
6. Unmetamorphosed dolerite dykes, basic dyke and syenite dyke.

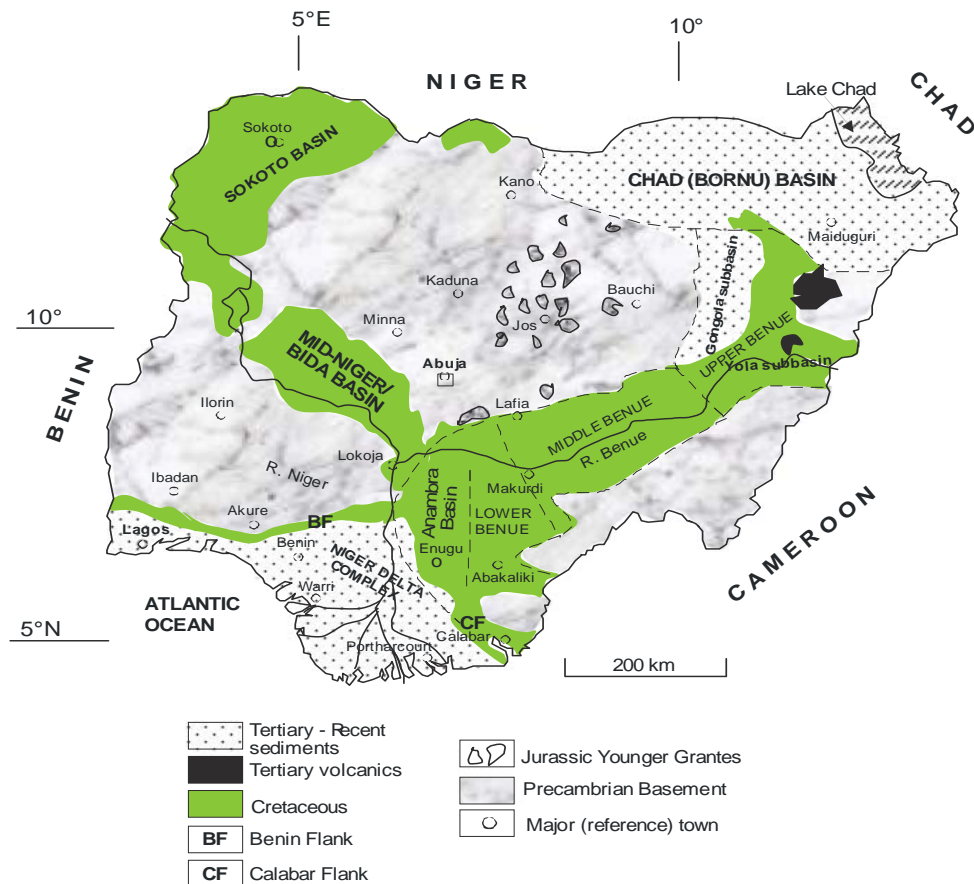


Fig.3: Geological sketch map of Nigeria showing the major geological components; Basement, Younger Granites, and Sedimentary Basins (Obaje, 2009)

3. Methodology

The study areas were traversed and fresh whole rock pegmatite samples were collected from chipping off the host rock using a hammer. The locations include exposed pegmatite outcrops which are mostly flat lying and others in form a ridgewith no visible contact with host rock in field 1. The thick overburden of laterite in this area must have been responsible for lack of exposed contact between pegmatite with the host rock. However, pegmatite

veins were clearly studied with sharp contact with the host rock, migmatite and biotite gneisses around Gwangi and Gunje in field 2. Representative samples were clearly labeled and transported for processing and analysis. Eight whole rock pegmatite samples in field 1 and four in field 2 for elemental analysis were pulverized, sieved on the 80 microns mesh and then about 10 grams put into clean sealed envelopes for geochemical analysis at Acme analytical Laboratory, Vancouver, Canada.

4. Data Presentation

Table 1: Major Element Data of Field 1 and Field 2 pegmatite in percent (%) ICP-AES (P, Pg. = Whole rock Pegmatite)

Field 1								
Oxides	L1(P)	L2(P)	L3(P)	L4(P)	L5(P)	L6(P)	L7(P)	L8(P)
Al ₂ O ₃	16.39	14.83	14.02	16.03	13.71	14.69	15.33	12.61
CaO	0.08	0.49	0.14	1.68	0.63	0.78	0.05	0.95
Na ₂ O	1.91	6.39	2.34	4.25	4.02	3.39	2.3	3.87
K ₂ O	10.46	1.19	5.7	5.25	2.84	6.73	9.36	3.35
A/CNK	1.32	1.84	1.71	1.43	1.83	1.35	1.31	1.54
Field 2								
Oxides	L9(Pg)	L10(Pg)	L11(Pg)	L12(Pg)				
Al ₂ O ₃	20.20	19.12	35.00	37.45				
CaO	0.65	0.13	0.23	1.22				
Na ₂ O	5.01	3.58	2.51	3.51				
K ₂ O	2.01	6.35	3.01	3.26				
A/CNK	2.63	1.90	6.09	4.69				

Table 2: REEs (yellow) and REs (green) in Field 1: P = Whole rock Pegmatite (Unit in ppm)

Elements	L1(P)	L2(P)	L3(P)	L4(P)	L5(P)	L6(P)	L7(P)	L8(P)
Be	24	1	3	1	2	7	<1	4
Cs	26.3	2	4.1	5.6	3.2	6.6	17.2	3.5
Ga	27.6	31	39.8	19	34.2	20.9	13.8	16.8
Hf	0.7	<0.1	0.2	0.5	0.5	0.7	0.3	0.4
Nb	11.7	18.5	37.5	2	22.1	2.1	3.5	3.1
Rb	1175.3	127.6	524.7	135.7	230.9	203.8	427.3	141.8
Sn	20	7	20	<1	14	2	13	5
Ta	5.3	2.5	2.9	0.7	1.9	0.9	1.3	1.7
Th	0.7	0.8	2.4	1.3	2.3	4.1	<0.2	1.9
Zr	7.1	1.8	3.3	16.1	6.8	22.3	2.8	10

Y	0.3	1.7	5.7	2.8	16	5.7	1.4	5.6
La	0.4	1.1	1.9	3.5	19.3	2.1	1.1	4.6
Ce	0.6	3	4	6.8	9.2	2.9	1.4	4.6
Pr	0.07	0.24	0.45	0.8	3.46	0.43	0.21	1
Nd	<0.3	1.2	1.3	2.9	11.4	1.4	0.4	4.7
Sm	0.13	0.29	0.71	0.74	2.14	0.66	0.16	0.96
Eu	0.03	<0.02	<0.03	0.67	0.39	0.29	0.02	0.29
Gd	0.07	0.35	0.72	0.59	2.17	0.65	0.2	0.8
Tb	0.02	0.07	0.22	0.1	0.42	0.16	0.04	0.18
Dy	<0.05	0.33	1.09	0.4	2.01	1.08	0.11	0.95
Ho	<0.02	0.55	0.16	0.1	0.52	0.16	0.04	0.11
Er	0.04	0.09	0.42	0.3	1.36	0.45	0.1	0.47
Yb	<0.05	0.22	0.53	0.38	1.78	0.42	0.23	0.44
Lu	0.01	0.22	0.06	0.05	0.23	0.08	0.04	0.05
Ratios								
K	86833.4	9878.7	47318.4	43582.7	23576.2	55868.9	77701.7	27809.9
K/Rb	73.9	77.4	90.2	321.2	102.9	274.8	181.8	196.1
K/Nb	7422	534	1262	21791	1067	26604	22200	8971

Table 3: REEs (yellow) and REs (green) in Field 2: Pg = Whole rock Pegmatite (Unit in ppm)

Elements	L9(Pg)	L10(Pg)	L11(Pg)	L12(Pg)
Be	10	2	6	9
Cs	8.4	5.3	45.3	5.2
Ga	33.8	20.2	40.8	34.4
Hf	0.8	1	1.5	3.4
Nb	29.5	6.6	37.3	27.2
Rb	163.6	364.2	434.9	176.4
Sn	19	12	137	42
Ta	13.7	61	185	53.6
Th	1.1	0.4	0.7	2.5
Ce	6.3	2.3	2.8	10.5
La	3.3	1.2	1.3	3.8
Zr	15.7	14.6	10.7	179.7
Y	7.3	1.6	1	46.8
Pr	0.63	0.25	0.26	8.95
Nd	1.6	1	1.2	38.8
Sm	0.61	0.17	0.23	7.91
Eu	0.06	0.03	0.02	1.26
Gd	0.85	0.18	0.26	7.91
Tb	0.22	0.05	0.04	0.23
Dy	1.28	0.31	0.29	0.23
Ho	0.21	0.03	0.03	0.23
Er	0.59	0.09	0.06	0.57
Yb	0.53	0.16	0.13	0.58
Lu	0.07	<0.01	0.02	0.08
Ratios				
K	16686	52715	24988	29138
K/Rb	102	145	58	165
K/Nb	566	7987	670	1071

Table 4: Averages of Rare Earth Elements (REEs) and Rare Elements (REs) of Whole rock Pegmatite in Field 1&2

Elements	Symbols	Average Rare Earth Elements (ppm)		Elements	Symbols	Average Rare Elements (Rare Metal) (ppm)	
		Field 1	Field 2			Field 1	Field 2
Lanthanum	La	4.25	2.40	Beryllium	Be	5.38	6.75
Cerium	Ce	4.06	5.48	Cesium	Cs	8.56	16.05
Praseodymium	Pr	0.83	2.52	Gallium	Ga	25.39	32.30
Neodymium	Nd	2.95	10.65	Germanium	Ge	-	-
Samarium	Sm	0.72	2.23	Hafnium	Hf	0.43	1.68
Europium	Eu	0.22	0.34	Indium	In	-	-
Gadolinium	Gd	0.69	2.30	Lithium	Li	-	-
Terbium	Tb	0.15	0.14	Niobium	Nb	12.56	25.15
Dysprosium	Dy	0.75	0.53	Rubidium	Rb	370.89	284.78
Holmium	Ho	0.21	0.13	Tin	Sn	10.25	52.50
Erbium	Er	0.40	0.32	Tantalum	Ta	1.49	78.32
Thulium	Th	1.71	1.18	Zirconium	Zr	8.78	55.18
Ytterbium	Yb	0.51	0.35				
Lutetium	Lu	0.09	0.05				
Yttrium	Y	4.90	14.18				

Table 5: Estimates of the Crustal abundances of rare earth elements (unit of measure in ppm)

Elements	Symbols	Mason and Moore (1982)	Jackson and Christianson (1993)	Wedepohl (1995)	McGill (1997)	Average Rare Earth Elements (ppm)	
						This Study	
						Field 1, N=8	Field 2, N=4
Lanthanum	La	30	29	30	5 to 18	4.25	2.40
Cerium	Ce	60	70	60	20 to 46	4.06	5.48
Praseodymium	Pr	8.2	9	6.7	3.5 to 5.5	0.83	2.52
Neodymium	Nd	28	37	27	12 to 24	2.95	10.65
Samarium	Sm	6	8	5.3	4.5 to 7	0.72	2.23
Europium	Eu	1.2	1.3	1.3	0.14 to 1.1	0.22	0.34
Gadolinium	Gd	5.4	8	4	4.5 to 6.4	0.69	2.30
Terbium	Tb	0.9	2.5	0.65	0.7 to 1	0.15	0.14
Dysprosium	Dy	3	5	3.8	4.5 to 7.5	0.75	0.53
Holmium	Ho	1.2	1.7	0.8	0.7 to 1.2	0.21	0.13
Erbium	Er	2.8	3.3	2.1	2.5 to 6.5	0.40	0.32
Thulium	Th	0.5	0.27	0.3	0.2 to 1	1.71	1.18
Ytterbium	Yb	3.4	0.33	2	2.7 to 8	0.51	0.35
Lutetium	Lu	0.5	0.8	0.35	0.8 to 1.7	0.09	0.05
Yttrium	Y	33	29	24	28 to 70	4.90	14.18

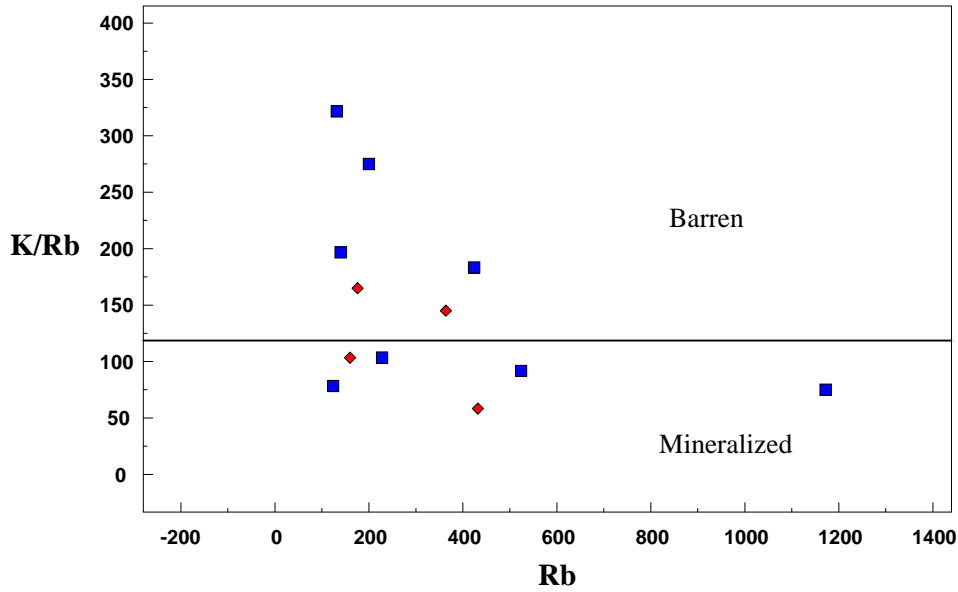


Fig.4: K/Rb Vs Rb plot, discrimination line separates the field of rare metal pegmatite from the barren class (After Staurov et al., 1969). Data of field 1 in square blue and field 2 in red, also for fig. 5-7

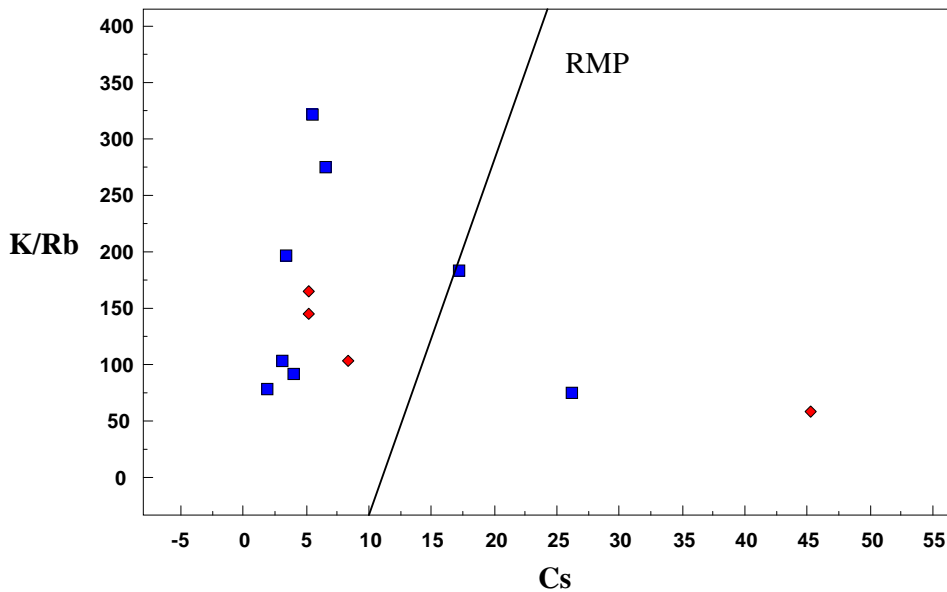


Fig. 5: Plot of relationship among K/Rb and Cs, the discrimination line RMP separates mineralized from non-mineralized pegmatites. Most of the data plot in the non-mineralized zone (After Moller and Morteani, 1987)

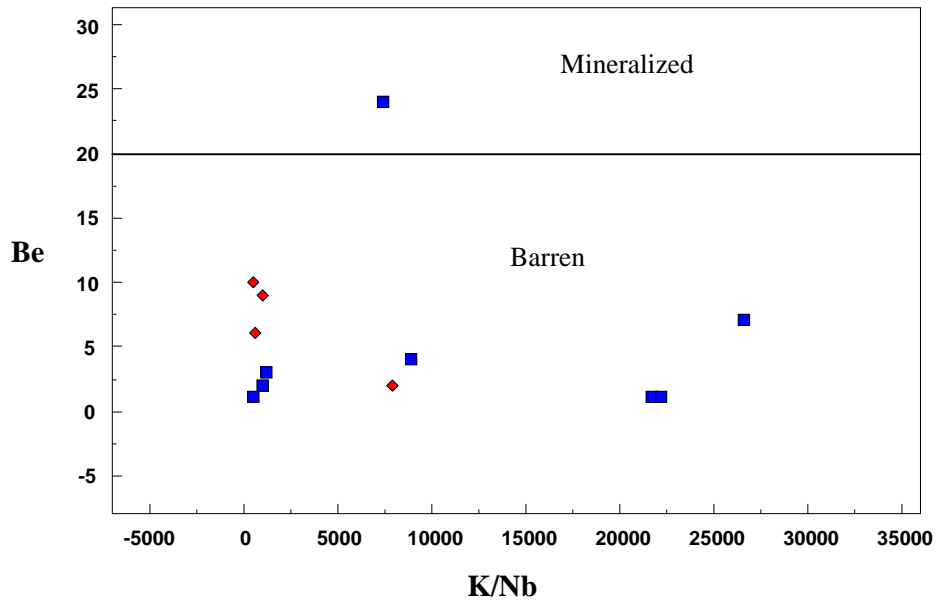


Fig. 6: Be vs K/Nb distribution pattern falls below the mineralization zone (Beus, 1966)

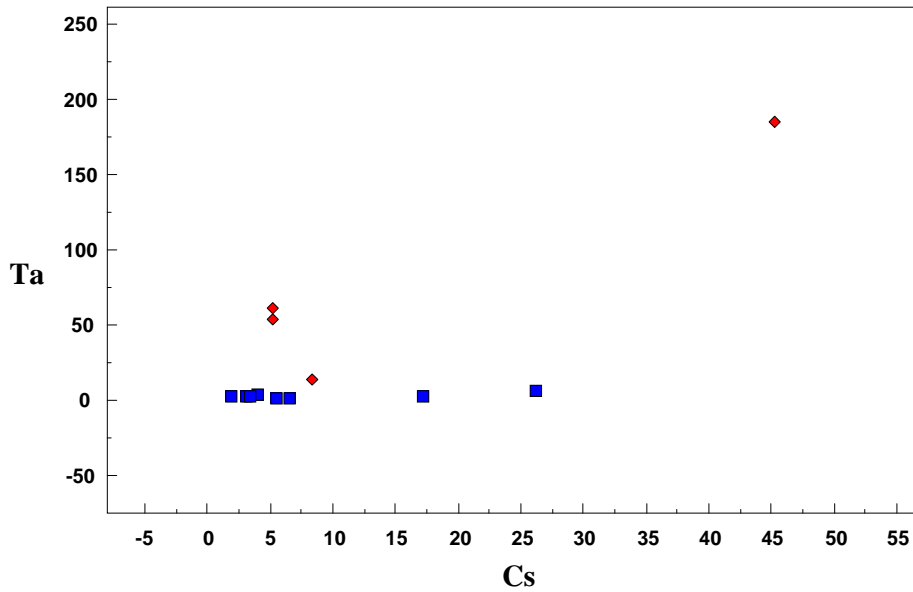


Fig. 7: Ta vs Cs of the study area plots far below mineralized pegmatite, TKS Tanco, Canada (After Moller and Morteani, 1987)

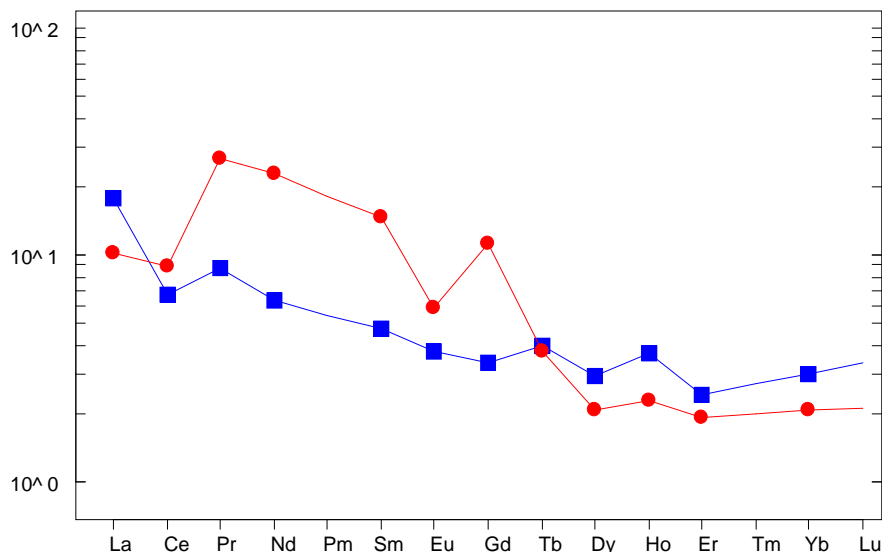


Fig. 8: Chondrites normalized plots of average rare earth elements (REE) in field 1 (square blue) field 2 (round red) after (Sun and McDonald, 1989)

5. Discussion and Conclusion

Whole rock pegmatite samples from the study areas were studied for their major oxides. Computation from table 1 for field 1&2 reveal that the whole rock pegmatite sample can be classified as peraluminous i.e. $(Al_2O_3 > CaO + Na_2O + K_2O)$. Table 2 & 3 shows the result of rare earth elements and rare earth (rare metals) for field 1& 2 respectively. Attempt was made in table 4 to juxtapose results of rare earth elements in field 1 & 2 and also for rare elements in field 1 & 2. According to Taylor and McLennan (1985) Cerium is the most abundant REE, and it is actually more common in the Earth's crust than is copper or lead and all of the REE except promethium are more abundant than silver or mercury. Rare earth elements (REE) in magnets (needs Pr and Nd), in metal alloys and for batteries (needs La, Ce, Pr and Nd) while in petroleum refining (needs La and Ce) and for many current and emerging alternative energy technologies, such as electric vehicles, energy-efficient lighting, and wind power. Ce, Pr, Nd, Sm, Eu, Gd

and Y in field 1 is less than field 2 as $(4.06 < 5.48)$, $(0.83 < 2.52)$, $(2.95 < 10.65)$, $(0.72 < 2.23)$, $(0.22 < 0.34)$, $(0.69 < 2.30)$ and $(4.90 < 14.18)$ respectively while La, Tb, Dy, Ho, Er, Th, Yb and Lu in field 1 greater than field 2 as $(4.25 > 2.40)$, $(0.15 > 0.14)$, $(0.75 > 0.53)$, $(0.21 > 0.13)$, $(0.40 > 0.32)$, $(1.71 > 1.18)$, $(0.51 > 0.35)$ and $(0.09 > 0.05)$ respectively. The anomalous concentration of Neodymium (10.65 ppm) and Yttrium (14.18 ppm) in the study area is close and can be compared with works of (Mason and Moore, 1982; Jackson and Christianson, 1993; Wedepohl, 1995; McGill, 1997) as shown in table 5. The rare elements data (table 4) show that the rare metal Ta, Nb, Cs and Sn increases from field 1 to 2. Tantalum ranges from 1.49 to 78.32 ppm, niobium (12–25.15 ppm), cesium (8.56 – 16.05) and Tin ranges from 10.25 – 52.50. The K/Rb Vs Rb plot (Staurov et al., 1969) (Fig. 4) which separates barren fractionation sequence and mineralized pegmatite show potential for rare metals in the study area as almost 50% of the samples plots within the mineralized zone, but plot of K/Rb Vs

Cs (Fig. 5) show a lot of the pegmatite samples plotting in the barren field than in the mineralized field. Further evaluation of level of mineralization of the pegmatites using the Be vs K/Nb (fig. 6) and Ta vs Cs (fig. 7) according to (Beus, 1966; Moller and Morteani, 1987) respectively shows that the samples plot far below the boundary of mineralization. Chondrite normalized plot of the rare earth element (REE) of the study area shows negative Ce (Fig. 8) and the presence of this trend confirmed a late stage or metasomatic fluids in the genesis of the rocks. Also,

negative Europium (Eu) signature which according to Taylor et al. (1986) suggests fractionation and indicates late metasomatic effect.

In conclusion, geochemical studies of whole rock pegmatite samples in the study area show that the pegmatites are peraluminous in composition. Rare earth elements analysis shows mineable potential and can be further explored for higher concentration, while rare metal mineralization shift from field 1 to field 2 for further exploration as well.

Reference

- Beus, A. A., 1966: Geochemical exploration for endogenic deposits of rare elements on the example of tantalum. Nedra, Moscow, Engl. Transl. GSE Libr, Ottawa.
- Black, R., 1980: Precambrian of West Africa. Episodes 4:3–8.
- Cerny, P., 1989a: Characteristics of pegmatite deposits of Tantalum. In: *Lanthanides, tantalum and niobium*. P. Moller, P. Cerny and F. Saupe (eds.), Springer- Verlag, Berlin, 145-154.
- Cerny, P., 1989b: Exploration strategy and methods for pegmatite deposits of tantalum. In: Moller, P., Cerny, P. and Saupe, F. (eds). *Lanthanides, Tantalum and Niobium: Society for Geology Applied to Mineral Deposits, Special Publication 7*, Springer-Verlag, 271-299 pp.
- Cerny, P. & Ercit, T.S., 1989: Mineralogy of niobium and tantalum: crystal chemical relationships, paragenetic aspects and their economic implications. In *Lanthanides, Tantalum, and Niobium* (P. Moller, P. Cerny & F. Saupe, eds.). Springer-Verlag, Berlin (27-79).
- Kinnaird, J.A., 1984: Contrasting styles of Sn-Nb-Ta-Zn mineralization in Nigeria. *J Afr Earth Sci* 2:81–90
- London, D., 2008: *Pegmatites*, Canadian Mineralogist Special Publication 10. Quebec: Mineralogical Association of Canada.
- Moller, P. and Morteani, G., 1987: Geochemical guide for tantalum pegmatite *Economic Geology*, 12, 1885- 1897
- Obaje, N.G., 2009: *Geology and mineral sources of Nigeria*. Springer Dordrecht Heidelberg London New York, 221pp.<http://dx.doi.org/10.1007/978-3-540-92685-6>.
- Rahaman, M. A., 1988: Recent advances in the study of the basement complex of Nigeria. In: *Geological Survey of Nigeria (ed) Precambrian Geol Nigeria*, pp 11–43
- Staurov, O.D., Stolyarov, L.S. and Isochewa, E.I., 1969: Geochemistry and origin of Verkh Iset Granitoid massif in central Ural. *Geochem Intern.* 6 1138-1146
- Taylor, S.R., McLennan, S., 1985. *The Continental Crust: Its Composition and Evolution*: Blackwell, Oxford, 312 p.
- Taylor, S.R., Rudnick, R.L., McLennan, S.C. and Eriksson, K.A., 1986: Rare earth element patterns in Archean high-grade metasediments and their tectonic significance *Geochim. Cosmochim. Acta*, 50, 2267-2279