

## Concentrations of Rare Earth and Valuable Elements in Mkuju Uranium Cores for Recovery

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## Abstract

Rare earth elements and valuable elements within Mkuju uranium core samples were analysed using EDXRF. Mean elemental concentrations for selected elements including Al, P, K, Ti, V, Mn, Fe, Y, Mo, Ag, Ba, La, Ce, and U were determined as 96445.79 µg/g, 547.19 µg/g, 25296.88 µg/g, 5926.33 µg/g, 116.26 µg/g, 455.02 µg/g, 60.1 µg/g, 142.34 µg/g, 15.8 µg/g, 493.98 µg/g, 67.53 µg/g, 118.68 µg/g, and 128.37 µg/g respectively. The Rare Earth elements: Y, La and Ce and valuable elements: Mo, Ag and U have enrichment factor of EF >1.5 which indicates that, these elements were formed from rocks through geological processes and can be mined at a profit. The valuable elements AL, P, K, Ti, V, Mn, Fe and Ba have enrichment factor of EF  $\leq$  1.5 which indicates that, these elements were formed from natural weathering processes. It is concluded that, despite the low concentration of the Rare Earth and valuable elements, the possibility of recovering both valuable and Rare Earth elements in Mkuju deposit is significant.

Keywords: Rare Earth; Valuable Elements; Mkuju; EDXRF

## Introduction

Tanzania witnessed extensive uranium exploration investments which lead to discoveries of several sites with economically viable uranium deposits at Bahi, Manyoni and Mkuju. Currently the Mkuju River Project located in Ruvuma region, southern Tanzania is the most advanced project. Uranium is mainly used for production of electricity and powering of submarines. Although uranium ores from many parts of the world are known to also contain Rare Earth Elements (REE) which include the lanthanide series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) plus Sc and Y. These REE are reported to have magnets properties which are essential for emerging alternative energy technologies, such as electric vehicles, energy-efficient lighting and wind power (Rene 2008, Long et al. 2012, Zakrzewska et Uranium ore also found to contain valuable elements which are significant in terms of volume consumed and monetary value such as Al, Cu, Fe, Pb, Ni, Zn, Co, Mo, Sn, Pt, Pd, Au and Ag. For this reason, some uranium mining nations like Australia, China, United States of America (USA) and Poland extract U-238 as primary product and recovers some of Rare Earth and valuable elements as secondary products from uranium mines (Keegan et al. 2008, Frąckiewicz et al 2012 and Zakrzewska et al. 2014). In Africa there are several uranium mining

al. 2014 and Chen and Graedel 2015).

In Africa there are several uranium mining countries as well as countries with potential uranium deposits. One of the countries with potential uranium deposits is Zambia. As Zambia is in the stage of extracting uranium and following the realisation of the presence of other elements that associated with uranium ore, Zambia has modified the uranium mining licenses to include extraction of other valuable elements such as copper (Kinnaird and Nex 2016). It has been reported that the same uranium belt is shared by Zambia, Malawi and Tanzania, it can be expected that the concentrations of the valuable elements in uranium deposits found in Zambia, Malawi and Tanzania are similar (Bowden and Shaw 2007). Therefore, both Malawi and Tanzania will enjoy huge benefits if they will adopt the Zambia uranium mining strategy.

Previous studies conducted at Mkuju river project (Mohammed and Mazunga 2013 and Banzi et al. 2015) analysed elemental composition and radioactivity level of the surface soil to shallow depth soil (0 - 30) cm, water and plants grown in the area. These studies focused on the environmental effect of the radioactivity and heavy metals to the population living near the uranium deposit. Also, the data obtained were used for establishment of baseline but did not investigate the presence of rare earth and valuable elements. Unlike those studies, the aimed present study to analyse the concentration of rare earth and valuable elements found in uranium deposit, for the purpose of optimising the uranium extraction process to improve the economy of the whole project.

## Materials and Methods Study area

Mkuju River Project is a uranium development project located within the Selous Sedimentary Basin in Southern part of Tanzania between latitudes 9º 45' to 10º 30' S and longitudes  $36^{\circ}$  30' to  $37^{\circ}$  00' E in Namtumbo district, Ruvuma region as shown in Figure 1. Mkuju uranium project has licensed area of  $\sim 3000 \text{ km}^2$  deposit and its uranium is hosted in sandstone deposit and its subtype deposit is tabular (Banzi et al, 2015, Boytsov et al. 2014). The characteristics of Mkuju cross section demonstrates the shallow depth of mineralization within 26 - 56 m and depth of underground water is at 21.8 - 24 m. Mkuju deposit has planned to use open pit mine and for the ore body which are either too deep, too low grade or too small in-situ leaching will be used (Boytsov et al. 2014).



#### Figure 1: Mkuju uranium deposit (Boytsov et al. 2014).

#### Sample collection

The selection of sampling points considered the characteristics of Mkuju cross section on the depth of drilled boreholes, colour of soil and their distance apart. This approach enabled 20 samples of uranium cores to be collected to determine the concentration and variation of REE and valuable elements for recovery. 200 g of cores at each borehole was collected and packed in plastic bags. These plastics bags were labeled as S1 to S20 with their specific depth interval in meter (m) as follows; S1(0 - 1) m, S2(9 - 10) m, S3(10 - 10)11) m, S4(18 - 19) m, S5(20 - 21) m, S6(21 -22) m, S7(27 -28) m, S8(32 -33) m, S9(34 – 35) m, S10(35 – 36) m, S11(36 – 37) m, S12(37 – 38) m, S13(38 – 39) m, S14(38 – 39) m, S15(50 – 51) m, S16(77 – 78) m, S17(83 - 84) m, S18(89 - 90) m, S19(90 -91) m and S20(140 - 141) m. The sample was then sent to Tanzania Atomic Energy Commission (TAEC) laboratory in Arusha for elemental composition analysis.

#### Sample preparation

The samples were put into an oven to dry at 60°C for 24 hours and then grinded into fine powder using pestle and mortar. The powder was then sieved by plastic sieve to increases penetration depth of X-rays. Afterwards, 4 g of a sieved powder sample was mixed well with 0.9 g of binder to enhance binding and then pulverised at speed of 180 rpm for 10 minutes in order to make the sample homogenous. The homogenised mixture was then poured into the die and pressed with 15 tons to make a pellet with 32 mm diameter. Three pellets were made from each sample and placed in sample holders in EDXRF machine for elemental analysis. Each pellet sample was irradiated for 15 minutes where 5 minutes was for each of three secondary targets present within EDXRF for modification of spectrum (a) HOPG target, excites Na - V, (b) Mo-secondary target, excites Cr - Y and Pr - U and (c) Barkla  $Al_2O_3$  target, excites Zr - Ce.

## Concentration of the Elements in the Sample

The Spectro EDXRF system incorporated with X-Lab Pro<sup>TM</sup> software with Turboquant algorithm for (Tq9232) matrix effect correction was used to calculate the concentration of elements in a given sample. The software corrected the matrix effects and the interference effects base on fundamental parameter methodology. Also corrected for the background effect on spectral line intensity, given as counts per second (cps). Then the software converted measured net intensities into concentrations of the element using Equation 1 (Rousseau 2013).

$$C_i = K_i \bullet I_i \bullet M_{is} \tag{1}$$

Where:  $C_i$  concentration of the  $i^{th}$  element in the sample,  $K_i$  calibration factor,  $I_i$  measured net intensity of  $i^{th}$  element,  $M_{is}$  factor correcting the effect of the specimen matrix composition on the intensity of  $i^{th}$  element.

### Limit of Detection (LOD)

In this study the turboquant method incorporated in the X-Lab  $\text{Pro}^{\text{TM}}$  software package using Equation 2 (Rousseau and Bouchard 2005) was used to calculate LOD of elements in Table 1, by distinguishing the peak intensity ( $I_p$ ) from the fluctuations of the background intensity ( $I_b$ ) due to counting statistics or background noise ( $T_b$ ). The system had lowest LOD (< 3 µg/g) for Ag and U unlike other elements. This is due to having high atomic number which produce desired peak compared to elements with lower atomic number (Rousseau 2001).

$$LOD = \frac{3 \times C_i}{I_p - I_b} \sqrt{\frac{I_b}{T_b}} \qquad (2)$$

Where:  $C_i$  minimum concentration level of the analyte,  $I_p$  peak intensity,  $I_b$  background intensity and  $T_b$  counting statistics or background noise.

### **Quality Control**

The value of  $C_i$  obtained from equation 1 may not be the actual concentration of the given element this is because experimental value can deviate from actual value due to contamination during sample preparation and/or instruments error. The precision and accuracy of the EDXRF result was checked with standard reference, IAEA-Soil 7 and 2711a Montana Soil. The accuracy between measured and certified elemental concentration values displays good agreement as shown in Table 1. The trueness for each element was obtained using Equation 3 and 4 interchangeably depending on value for measured and certified (Olujimi et al. 2014). The accuracy value of the EDXRF system for each element was characterized as excellent below 10%, good between 10% and 25%, fair between 25% and 50% and poor above 50%.

$$Bias = \frac{measured - certified}{certified} \qquad When$$

certified > measured (3)

$$Bias = \frac{measured - certified}{measured}$$
 When  
measured > certified (4)

Table 1:	Elemental concentr	rations of certifie	ed and measured reference	ce materials for IAEA-
	Soil 7 and 2711a	Montana soil an	d LOD by EDXRF	

		IAEA-Soi	17		2711a Mo	ntana soil	
Elements	LOD	Certified	Measured	Accuracy	Certified	Measured	Accuracy
Al	20.00	47000	49995.58	5.99	67200	62177.47	-7.47
Р	6.48	460	530.34	13.26	842	1077.71	21.87
K	10.00	12100	11504.71	-4.92	25300	23735.74	-6.18
Ti	5.00	3000	3727.24	19.51	-	-	-
V	37.05	66	92.20	28.42	80.7	20.17	-75.01
Mn	14.41	631	770.52	18.11	675	658.10	-2.5
Fe	5.00	25700	27990.03	8.18	28200	28863.18	2.3
Y	7.00	21	23.89	12.1	-	-	-
Mo	11.38	2.5	0	-100	-	-	-
Ag	2.01	-	-	-	-	-	-
Ва	37.15	159	155.10	-2.45	730	674.39	-7.62
La	44.50	28 (BDL)	28.23(BDL)	BDL	38(BDL)	43.86(BDL)	BDL
Ce	62.19	61	67.19	9.21	-	-	-
U	2.61	2.6	1.90	-26.92	3.01	7.13	57.78

Accuracy with negative sign means that certified value is greater than measured value and (-) means not reported

### **Results and Discussion**

### Elemental Concentrations in Mkuju Deposit

The mean concentration results for 20 samples (S1 - S20) of uranium cores are

presented in Table 2. Rare Earth Elements (Y, La and Ce) were detected unlike to Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc which were below LOD of the system used. The selected valuable elements

were Al, P, K, Ti, V, Mn, Fe, Mo, Ag, Ba and U.

Table 2:	Weighted	mean resul	ts of ele	mental	composition	ı of uranium	cores	samples	from	20
boreholes	s at Mkuju	uranium de	posit (µĮ	$g/g \pm S$	EM)					

_	Z	Symbol	Element	Weighted mean results
	13	Al	Aluminum	$96445.79 \pm 2638.05$
	15	Р	Phosphorus	$547.19 \pm 116.68$
	19	Κ	Potassium	$25296.88 \pm 1475.67$
	22	Ti	Titanium	$5926.33 \pm 441.93$
	23	V	Vanadium	$116.26 \pm 9.92$
	25	Mn	Manganese	$455.02 \pm 55.02$
	26	Fe	Iron	$32274.26 \pm 2788.70$
	39	Y	Yttrium	$60.10 \pm 4.43$
	42	Мо	Molybdenum	$142.34 \pm 9.72$
	47	Ag	Silver	$15.80\pm0.45$
	56	Ba	Barium	$493.98 \pm 39.99$
	57	La	Lanthanum	$67.53 \pm 7.49$
	58	Ce	Cerium	$118.68 \pm 10.92$
	92	U	Uranium	$128.37 \pm 28.71$

In Table 2, Valuable elements whose concentrations were above 1000 ppm included Al, K, Ti, and Fe. Whereas Fe shows higher concentration in Mkuju deposit due to being in the same basin with Liganga iron ore deposit at southern Tanzania (Maboko 2001). While, REEs (Y, La and Ce), and valuable element (P, V, Mn, Mo, Ag, Ba and U) showed concentrations below 1000 ppm.

# Crustal Abundance (CA) and Enrichment Factor (EF)

Crustal abundance is an average abundance of an element in the earth crust while enrichment factor is the extent to which an element must be enriched by geological processes for it to be mined at a profit. The enrichment factor of Mkuju uranium cores was calculated by Equation 5 as given by (Earle 2015, Barbieri 2016) in order to asses geological deposition of selected element. The mean concentrations of elements in this study were higher than their crustal abundance by a factor shown as enrichment factor in Table 3, 4 and 5 except for Fe, Mn, V and P which were below their abundance in earth crust.

$$EF = \frac{C_{soil}}{CA}$$
(5)

Where, EF is enrichment factor,  $C_{soil}$  is concentration of element in soil and CA is average crustal abundance.

In Table 3, 4 and 5, the values of  $0.5 \le EF \le$ 1.5 implies elements concentration come from natural weathering processes while EF >1.5 implies elements concentration was delivered by other sources like geological process (Barbieri 2016). This shows that selected elements at Mkuju deposit which includes Al, P, K, Ti, V, Mn, Fe and Ba occurred from natural weathering process while rare earth elements (Y, La and Ce), Mo, Ag and U occurred from rock through geological process and can be mined at a profit.

# Variation of Rare Earth Elements and Valuable Elements at Different Depth

This was determined by splitting (S1 - S20) samples into different depth intervals of 0 -

28 m (S1 - S7) had 7 samples, 29 - 57 m (S8)- S15) had 8 samples, 58 - 86 m (S16 & S17) had 2 samples, 87 - 115 m (S18 & S19) had 2 samples and 116 - 141 m (S20) had 1 sample. 0 - 28 m and 29 - 57 m depth intervals were selected to provide a near surface elemental composition, within ore body elemental composition and below underground water elemental deposition for open pit extraction respectively. 58 - 86 m, 87 - 115 m and 116 - 141 m were selected to provide elemental composition for depth in which in-situ leaching will be used. The mean concentration and weighted mean concentration values in µg/g at different depth interval for selected element were calculated as shown in Table 3. 4 and 5.

### Variation of Rare Earth Elements at **Different Depth**

Y, La and Ce in Mkuju deposit showed high concentration at lower depth interval below Mkuju mineralisation depth (0 - 28) m which will use open pit extraction as shown in Table 3.

Element	Depth (m)	Mid-point depth (m)	Mean Concentration $(\mu g/g \pm SEM)$	Weighted Mean Concentration (µg/g)	CA (µg/g)	EF
	0-28	14	$57.99 \pm 7.10$	(0.10	22	1 00
	29 - 57	43	$53.14 \pm 7.30$	60.10	33	1.82
V	58 - 86	72	$75.24 \pm 11.76$			
Ŷ	87 – 115	101	$83.89 \pm 1.17$			
	116 - 141	129	$52.72\pm0.53$			
	0 - 28	14	$49.66 \pm 5.20$	67 53	30	1 73
	29 - 57	43	$77.47 \pm 15.85$	07.55	39	1.75
T	58 - 86	72	$70.32\pm23.74$			
La	87 – 115	101	$66.32 \pm 6.15$			
	116 - 141	129	$109.96\pm11.79$			
	0 - 28	14	$92.35 \pm 10.14$	119 69	66 5	1 79
	29 - 57	43	$119.78\pm22.59$	110.08	00.5	1.70
C	58 - 86	72	$150.86\pm2.42$			
Ce	87 – 115	101	$156.19\pm26.31$			
	116 – 141	129	$154.76\pm16.62$	_		

Table 3: Mean concentrations in $\mu g/g$ at different depth of rare earth e	elements
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In Table 3, Ce showed high average concentration in all depth intervals with mean concentration of 118.68 µg/g compared to La showed mean Y which high and concentration at depth interval of 116 - 141 m and 87 - 115 m respectively. This is because Ce is enriched more than La and Y in weathering process but also Ce has high crustal abundance followed by La and Y. Furthermore, Ce and La are in same subgroup of light rare earth elements which increase their deposition in ore due to being mobile during weathering process unlike Y which is in sub-group of heavy rare earth elements (Jordens et al. 2013).



Figure 2: Mean concentration of rare earth elements at different depth in Mkuju deposit

In figure 2, Ce showed high concentration in all depth intervals compared to La and Y. Whereas, La and Y showed high mean concentration at depth interval of 116 - 141m and 87 - 115 m respectively.

# Variation of Valuable Elements at Different Depth

Valuable elements V, Fe, Ba and U had high mean concentration in depth of mineralisation of Mkuju ore body which started at depth of 26 m. Whereas; Al, P, Mn, K, Ti, Mo and Ag showed high mean concentration in lower depth of mineralisation due to presence of underground water table at depth of 21.8 - 24 m which facilitate downwards migration of mobile elements which cause their deposition at those depth as shown in Table 4 and 5.

In Table 4, valuable elements whose concentrations were above 1000 ppm in Mkuju deposit. Al showed higher mean concentration in all depth interval compared to other valuable elements followed by Fe which showed low mean concentration at 87 - 115 m and 116 - 141 m compared to K. K and Ti showed high mean concentration at depth interval of 87 - 115 m also showed again low mean concentration at depth interval of 0 - 28 m due to being mobile and depleted at near soil. Al had higher concentration than other valuable elements due to its high crustal abundance of 82300 ppm where weathering process enrich its concentration in ore body. Furthermore, all valuable elements above 1000 ppm at Mkuju deposit occurs from natural weathering process as explained by Equation 5 results.

In figure 3, Al showed higher mean concentration in all depth interval compared to other valuable elements followed by Fe except at 87 - 115 m showed low mean concentration compared to K. Ti displayed low mean concentration in all depth interval compared to other valuable elements.

Table 4: Mean concentrations (above 1000 µg/g) at different depth of valuable elements

			Weighted	CA	EF
		Mean	Mean	$(\mu g/g)$	
	Depth	Concentration	Concentration		
Element	(m)	$(\mu g/g \pm SEM)$	(µg/g)		
Al	0 - 28	95069.56 ± 6155.93			

	29 - 57	$98696.71 \pm 3340.30$	96445.79	82300	1.17
	58 - 86	$97325.26 \pm 1485.46$			
	87 – 115	$89025.48 \pm 10864.14$			
	116 - 141	$101153.72 \pm 521.13$			
	0 - 28	$23560.26 \pm 2554.22$	25206 88	20000	1.01
	29 - 57	$25090.94 \pm 2728.64$	23290.88	20900	1.21
Κ	58 - 86	$27339.68 \pm 1104.82$			
	87 – 115	$28944.16 \pm 5992.46$			
	116 - 141	$27720.62 \pm 81.29$			
	0 - 28	$5127.26 \pm 499.07$	502622	55(0)	1.07
	29 - 57	$5187.04 \pm 461.75$	5920.35	5500	1.07
Ti	58 - 86	$7885.99 \pm 1688.63$			
	87 – 115	$9574.57 \pm 1200.53$			
	116 - 141	$6218.30 \pm 15.76$			
	0 - 28	$38585.37 \pm 7030.23$	22274.26	5(200	0.57
	29 - 57	$28234.33 \pm 1986.93$	32274.20	36300	0.57
Fe	58 - 86	$36584.05 \pm 1064.61$			
	87 – 115	$27831.82 \pm 4221.06$			
	116 - 141	$20681.20 \pm 105.78$			





Table 5: Mean concentrations (below 1000 µg	g/g) at different depth of valuable elements
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		Mean	Weighted Mean	CA	EF
	Depth	Concentration	Concentration	$(\mu g/g)$	
Element	(m)	$(\mu g/g \pm SEM)$	$(\mu g/g)$		

	0-28	628.65 ± 303.91	547 10	1050	0.52
	29 - 57	$386.22 \pm 109.30$	347.19	1050	0.52
Р	58 - 86	$824.56 \pm 160.34$			
	87 – 115	$19.04\pm94.98$			
	116 - 141	$296.14\pm3.27$			
	0 - 28	139.45 ± 22.29	116.26	120	0.07
	29 - 57	$116.75\pm8.48$	110.20	120	0.97
V	58 - 86	$86.59 \pm 21.69$			
	87 - 115	$64.23 \pm 16.97$			
	116 - 141	$113.42 \pm 10.42$			
	0 - 28	$436.96\pm62.92$	455.02	050	0.48
	29 - 57	$510.91 \pm 120.92$	455.02	930	
Mn	58 - 86	$1048.69 \pm 100.25$			
	87 - 115	$478.08\pm15.92$			
	116 - 141	$114.70\pm5.25$			
	0 - 28	$117.14\pm5.93$	142 34	12	118
	29 - 57	$122.23\pm3.97$	142.34	1.2	62
Mo	58 - 86	$217.40\pm22.98$			
	87 - 115	$221.69\pm8.39$			
	116 - 141	$170.72\pm2.30$			
	0 - 28	$14.76\pm0.75$	15.80	0.075	210. 67
	29 - 57	$16.56\pm0.73$	15.00	0.075	
Ag	58 - 86	$15.45 \pm 1.79$			
	87 - 115	$15.76\pm0.26$			
	116 - 141	$17.76\pm0.85$			
	0 - 28	$427.91\pm59.32$	103 08	125	1 16
	29 - 57	$604.50\pm70.80$	495.96	423	1.10
Ba	58 - 86	$397.25 \pm 70.27$			
	87 - 115	$388.82\pm2.38$			
	116 - 141	$476.16\pm28.88$			
	0 - 28	$163.56\pm30.66$	128 27	27	17 5
	29 - 57	$164.46\pm58.39$	120.37	2.1	4
U	58 - 86	$7.10\pm7.10$			
	87 – 115	-			
	116 – 141	$92.60 \pm 0.59$			

In Table 5, valuable elements whose concentrations were below 1000 ppm in Mkuju deposit. Mn and P showed high mean concentration at depth interval of 58 - 86 m of 1048.69 ppm and 824.56 ppm respectively when compared to other valuable elements in all depth intervals followed by Ba with 604.5 ppm at 29 - 57 m. This is because Mn, P and Ba has high crustal abundance where weathering process enrich its concentration in ore body unlike to Ag with crustal abundance of 0.075 ppm which is present in ore due to geological settings in addition to Mo and U. V showed high mean concentration at depth interval of 0 - 28 m due to being immobile on top soil.

Mo and Ag showed high mean concentration at depth interval of 87 - 115 m and 116 - 141m respectively because of being mobile and depleted at near soil. Ba and U displayed high mean concentration at depth interval of 29 -57 m because of mineralisation in Mkuju deposit begins at depth of 26 m. Ba and U revealed low mean concentration at depth interval of 87 - 115 m and 58 - 86 m respectively in which all these depths were below water table and ore body depth. For this reason, elements in Mkuju ore body can be recovered and processed unlike to poor ore bodies such as earth crust which needs to process large amount of ore leadings to environment contamination and loss of energy.



**Figure 4:** Mean concentration (below 1000 µg/g) of valuable elements at different depth in Mkuju deposit

In figure 4, Mn showed high mean concentration of 1048.69 ppm at depth interval of 58 - 86 m when compared to other valuable elements in all depth intervals followed by P with 824.56 ppm at same depth interval then Ba with 604.5 ppm at 29 - 57 m. Ag displayed low mean concentration in all depth interval with concentration between 14 ppm and 18 ppm except at depth interval of 58 - 86 m and 87 - 115 m where U

showed low mean concentration of less than 8 ppm.

## Comparison of Mean Concentrations of Rare Earth Elements in Mkuju Deposit with other Mineral Deposits

The presence of REEs is considered to be significance if they occur in significant concentration, but different mineral deposits have different concentration values of REEs. Table 6 shows the mean concentration of REEs in Mkuju uranium deposit compared to other deposits.

**Table 6:** Comparison of the mean concentrations of rare earth element in Mkuju deposit and in other mineral deposits.

	Average		elements	Deference
Deposit	concentration in µg/g			Kelefence
	Y	La	Ce	
Mkuju (Tanzania)	60.10	67.53	118.68	This study
Operating uranium	08	22	222	Keegan et al. 2008,
mines, Australia	90	23	223	IAEA 2009

Table 6 shows, Ce and Y showed higher mean concentrations values in operating uranium mines in Australia than the values obtained in Mkuju uranium deposit. La in Mkuju deposit has higher mean concentration value than the values reported in operating uranium mines in Australia. The different in values may be due to different geographical location and uranium host rock. Furthermore, REEs in Australia was averaged from different operating uranium deposits which are Beverly, Ranger and Olympic Dam.

### Comparison of Mean Concentrations of Valuable Elements in Mkuju Deposit and in other Mineral Deposits

Valuable elements at Mkuju uranium deposit were compared with other uranium deposits and their economic ore concentrations were presented in Table 7.

Table 7: Comparison of the mean concentrations in µg/g of valuable element in Mkuju deposi	t
and in other mineral deposits.	

	Country					
Element	Tanzania (Mkuju sandstone deposit)	Poland (Peribaltic deposit)	Australia uranium deposits	Tanzania (Manyoni deposit)	Ore Grade %	
Al	96445.79	-	1055	-	24 - 32	
Р	547.19	-	-	200	-	
Κ	25296.88	-	-	-	-	
Ti	5926.33	-	26	2900	21.5 - 86	
V	116.26	1886	60	120	-	
Mn	455.02	-	135	500	-	
Fe	32274.26	75000	31185	20000	34.8 - 40.6	
Mo	142.34	296	107	-	0.1	
Ag	15.80	-	2.2	-	0.008 - 0.1	
Ba	493.98	-	7	-	-	
U	128.37	1,316	340	454	0.1 - 0.4	
Reference	Present study	Gajda et	Keegan et	Ngulimi	Nelson 2012,	
		al. 2015	al. 2008,	and Ishiga	Dahlkamp	
			IAEA	2016	2013 and Earle	
			2009		2015	

Means not reported

Most of the elements in Mkuju uranium deposit have mean concentration values above the concentration values reported for Manyoni uranium deposit in Tanzania except for three elements; V, Mn and U as shown in Table 7. The mean concentration value of Mo, V, Ag, Ba, Al and Ti in Mkuju uranium deposit is higher by a factor of 1.33, 1.94, 7.18, 70.57, 91.42 and 227.94 respectively

compared to the mean concentration values of those elements reported in operating uranium deposit in Australia.

Fe in Mkuju uranium deposit showed low mean concentration value  $(32274.26 \ \mu g/g)$ compared to the concentration value reported in Poland (75000 µg/g) and Australia (31185 µg/g) deposits. In Mkuju uranium deposit V, U and Mn have concentration values less by factor of 1.03, 3.54 and 1.1 respectively compared to the values reported in Manyoni uranium deposit. V showed less mean concentration value by a factor of 6.62 compared with the mean concentration value reported in Poland deposits. However, all elements across the discussed deposits, particularly in Poland and Australia remain below the ore grade threshold for them to be extracted as targeted mineral rather a secondary product. This implies that Mkuju deposit is in good position for doing recovery of secondary elements along with uranium extraction.

## Comparison of Mean Elemental Concentrations in Mkuju Deposit with Estimate of Extractable Global Resources.

Geological studies on the basis of the distribution of known deposits of minerals estimated the extractable amount of all mineral resources to be between 0.01% (100 ppm) and 0.001% (10 ppm). This is due to proportionality of the total amount of enriched deposits to the crustal occurrence of the mineral. Furthermore, in the top 1 km of the earth's continental crust an estimate of the extractable global resources is 0.01% of the total amount of a mineral (Henckens et al. 2016). For this estimate most elements in Mkuju deposit are extractable since the characteristics of Mkuju cross section demonstrates the shallow depth of mineralisation within 26 - 56 m (Boytsov et al. 2014).

In addition, (Dahlkamp 2009) defined resources of deposits: large = >20000 tU; medium = 5000 - 20000 tU and small = <5000 tU whereas ore grades (given as average of deposit): high = >0.5% U, medium = 0.15 - 0.5% U and low = <0.15%(1500 ppm) U. This shows Mkuju deposit has large resources deposit of ~58466 tU and very low ore grade of ~243 ppm (0.0243%) U (Boytsov et al. 2014). For this reason, recovery of selected element might increase value of low ore grade.

The Mkuju deposit, like other uranium deposits, exhibits lower concentrations compared to currently economical viable concentration levels for selected element as indicated in Table 7. However, if the world faces depletion of these crucial elements, the scenario may change. This suggests that a reduction in the supply of essential elements from economically viable deposits could drive up the prices of scarce elements. potentially increasing the demand despite the low ore grade of the deposit. Various factors contributing to the economic viability of any deposit, such as ore grade, depth beneath the surface, and adherence to environmental regulations in the region, favor the Mkuju deposit. Thus, results from this study provide an insight into Mkuju deposit in considering accompanied elements at an early stage of uranium mine development for suitable selection of extraction method.

## Conclusion

This study analysed the concentration and variation of rare earth and valuable elements in uranium cores at different depth interval from 20 randomly selected boreholes at Mkuju deposit. 13 Selected elements accompanying uranium which are significant in terms of volume consumed and monetary value, including rare earth elements (Y, La, and Ce), along with Al, P, K, Ti, V, Mn, Fe, Mo, Ag, and Ba. Their concentrations were higher compared to that of Earth's crust except for P, V, and Mn but they remained economically viable within the ore body. Enrichment factor calculations suggested the potential profitability of recovering most elements, particularly rare earth elements, Mo, Ag, and U, while secondary extraction is feasible for elements like Al, P, K, Ti, V, Mn, Fe, and Ba.

The comparative assessments with other mineral deposits indicated that, the selected elements across different deposits exhibit lower mean concentrations causing them to be unsuitable for profitable extraction as targeted minerals, rather indicating their potential extraction as secondary products alongside with uranium. The findings of this research provided essential groundwork data for optimising the extraction of uranium, REEs and valuable elements at Mkuju uranium project. The study current recommended further studies to be done at Mkuju uranium deposits using sensitive technique with low limit of detection in order to enhance detection of all other available REEs.

### Acknowledgements

The authors acknowledge technical support from members of XRF laboratory at TAEC and Mantra<sup>TM</sup> Tanzania for permission to use samples at Mkuju uranium deposit.

### **Conflict of interest**

We declare no conflict of interest in this research and manuscript.

### References

Banzi FP Msaki PK and Mohammed NK 2015 Distribution of heavy metals in soils in the vicinity of the proposed Mkuju uranium mine in Tanzania. *Environ. Pollut.* 4(3):42-50.

http://dx.doi.org/10.5539/ep.v4n3p42

Barbieri M 2016 The importance of enrichment factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. *J. Geol. Geophys. 5*(237): 1-4. http://dx.doi.org/10.4172/2381-

8719.1000237

Bowden RA and Shaw RP 2007 TheKayelekera uranium deposit, Northern Malawi: past exploration activities, economic geology and decay series disequilibrium. *Appl. Earth Sci.* 116(2):55-67.

https://doi.org/10.1179/174327507X1670 82

Boytsov A Stander S and Martynenko V 2014 The outlook on potential uranium ISL Mining at Nyota (Mkuju) Deposit (Tanzania) Proceedings of the International Symposium on Uranium Raw Material for the Nuclear Fuel Cycle: Exploration, Mining, Production, Supply and Demand, Economics and Environmental Issues (URAM 2014) Vienna, 2014, IAEA Vienna.

- Chen M and Graedel TE 2015 The potential for mining trace elements from phosphate rock. J. Clean. Product. 91:337-346. <u>https://doi.org/10.1016/j.jclepro.2014.12.0</u> <u>42</u>
- Dahlkamp FJ 2009 Part I: Typology of Uranium Deposits. Uranium Deposits of the World: Asia.451-452.
- http://dx.doi.org/10.1007%2F978-3-540-78558-3\_18
- Dahlkamp FJ 2013Uranium ore deposits. Introduction Table 1.2. pg 9.
- Earle S 2015. Physical geology. Geological resource Table 20.1 pp 547 <u>https://openlibrary-</u> <u>repo.ecampusontario.ca/jspui/handle/1234</u> 56789/402
- Frąckiewicz K Kiegiel K Herdzik-Koniecko I Chajduk E Zakrzewska-Trznadel G Wołkowicz S Chwastowska J and Bartosiewicz I 2012 Extraction of uranium from low-grade Poland ores: dictyonemicshales and sandstones. *Nukleonika*.57(4): 451-459.
- Gajda D Kiegiel K Zakrzewska-Koltuniewicz G Chajduk E Bartosiewicz I and Wolkowicz S 2015 Mineralogy and uranium leaching of ores from Triassic Peribaltic sandstones. J. Radioanal. Nucl. Chem. 303: 521-529.

https://doi.org/10.1007/s10967-014-3362-0

- Henckens MLCM Van Ierland EC DriessenPPJ and Worrell E 2016 Mineral resources: Geological scarcity, market price trends, and future generations. *Resour. Policy.* 49: 102-111. <u>https://doi.org/10.1016/j.resourpol.2016.0</u> <u>4.012</u>
- https://en.wikipedia.org/wiki/Abundance\_of\_ elements in Earth%27s crust#cite\_note-6. 28/04/2024
- IAEA. 2009. World Distribution of Uranium Deposits (UDEPO) with Uranium Deposit Classification, TECDOC-1629, 117, Vienna, International Atomic Energy Agency.

Jordens A Cheng YP and Waters KE 2013 A review of the beneficiation of rare earth element bearing minerals. *Miner. Eng.*.41: 97-114.

https://doi.org/10.1016/j.mineng.2012.10.017

- Keegan E Richter S Kelly I Wong H Gadd P Kuehn H and Alonso-Munoz A 2008 The provenance of Australian uranium ore concentrates by elemental and isotopic analysis. *Appl. Geochem.* 23:765-777. <u>https://doi.org/10.1016/j.apgeochem.2007</u> <u>.12.004</u>
- Kinnaird JA and Nex PA 2016 Uranium in Africa. *Episode*. 39(2):335-359. <u>https://doi.org/10.18814/epiiugs/2016/v39</u> i2/95782
- Long KR Van Gosen BS Foley NK and Cordier D 2012 The principal rare earth elements deposits of the United States: a summary of domestic deposits and a global perspective. In *Non-Renewable Resource Issues*,Springer, Dordrecht, pp 131-155. <u>https://doi.org/10.1007/978-90-</u> 481-8679-2\_7
- Maboko MAH 2001 The emplacement age of gabbroic rocks and associated granitoids of the Liganga-Msanyo complex, southeastern Tanzania. *Tanz. J. Sci.* 27(2): 1-14.

https://doi.org/10.4314/tjs.v27i2.18342

Mohammed NK and Mazunga MS 2013 Natural radioactivity in soil and water from Likuyu village in the neighborhood of Mkuju uranium deposit. *Int. J. Anal. Chem.* 2013:1-4.

https://doi.org/10.1155/2013/501856

Nelson, S.A., 2012. EENS 1110 Physical Geology.

https://www2.tulane.edu/~sanelson/eens1 110/minresources.htm. 28/04/2024

Ngulimi MF and Ishiga H 2016 Geochemical Examination of Surficial Soil Overlying Uranium Deposit in Manyoni, Central Tanzania. *Earth Sci. Res.* 5(2):135-145. http://dx.doi.org/10.5539/esr.v5n2p135

Olujimi O Steiner O and Goessler W 2014 Pollution indexing and health risk assessments of trace elements in indoor dusts from classrooms, living rooms and offices in Ogun State, Nigeria. J. Afr. Earth Sci. 101:396-404. https://doi.org/10.1016/j.jafrearsci.2014.1 0.007

René M 2008 Anomalous rare earth element, yttrium and zirconium mobility associated with uranium mineralization. *Terra Nova*. 20(1):52-58. <u>https://doi.org/10.1111/j.1365-</u>

3121.2007.00786.x

- Rousseau R 2013 How to apply the fundamental parameters method to the quantitative X-ray fluorescence analysis of geological materials. *J. Geosci. Geomat.* 1(1): 1-7.
- Rousseau RM 2001 Detection limit and estimate of uncertainty of analytical XRF results *Rigaku J.* 18(2), 33-47.
- Rousseau RM and Bouchard M 2005 Fundamental algorithm between concentration and intensity in XRF analysis – 2, Practical Application, J. Analytical, X-ray Spectrom.13(3):121 – 125.
- Zakrzewska-Koltuniewicz G Herdzik-Koniecko I Cojocaru C and Chajduk E 2014 Experimental design and optimization of leaching process for recovery of valuable chemical elements (U, La, V, Mo, Yb and Th) from lowgrade uranium ore. *J. Hazard. Mater.* 275: 136-145.

https://doi.org/10.1016/j.jhazmat.2014.04. 066