

Environmental Impact and Geochemistry of Rare Earth Elements in Shallow Groundwater from Oban Massif and Environs, Southeastern Nigeria

G. U. Sikakwe^{1*}, E. A. Amah¹, E. E. U. Ntekim¹ and B. E. Ephraim¹

¹*Department of Geology, University of Calabar, Calabar, Nigeria.*

Authors' contributions

This work was carried out in collaboration between all authors. Author GUS designed the study, wrote the protocol and wrote the first draft of the manuscript. Author EAA managed the literature searches; analyses of the study performed the spectroscopy analysis. Author EEUN managed the experimental process. Author BEE appraise data quality. All authors read and approved the final manuscript.

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ABSTRACT

The study of hydrogeochemical processes using rare earth elements was carried out using water samples from weathered basement aquifers in Oban Massif and environs. A total of only 29 as number water samples were collected from boreholes, streams, springs and river sources. Physical parameters (pH, Eh, Ec, TDS and turbidity) were measured insitu using standard equipments. Anions (NO_3^- , SO_4^{2-} , HCO_3^- , PO_4^{3-} , Cl^-) were measured in the laboratory using titration and chromatography, major cations (Mg^{2+} , Ca^{2+} , K^+ , Na^+) were analysed using inductively coupled plasma argon emission spectrometry while the rare earth elements were assayed using inductively coupled plasma mass spectrometry. Speciation modeling for solution complexation and saturation indices was done using the software VISUAL-MINTEQ3.1. Results showed that low to medium pH(5.61-7.20) range and Fluorine mean value 20.08 ppm is common in the area which are not within WHO (2006) recommended values of 6.5-85 and 1.5 respectively for potable water. Rare earth elements exhibited very low values with exception of Ce (0.98 ppb), Gd (0.13 ppb), La (0.56

*Corresponding author: Email: dielegba@yahoo.com;

ppb), Nd (0.66 ppb), Pr (0.15 ppb) and Sm (0.11 ppb) that recorded appreciable concentrations compared to Dy (0.09 ppb), Er (0.05 ppb), Eu (0.02 ppb), Ho (0.02 ppb), Lu (0.011 ppb), Tb (0.01 ppb), Tm (0.01 ppb) and Yb (0.04 ppb). Trilinear plot showed that the water type is dominantly Ca+Mg, Cl+SO₄. Rare earth elements concentrations are within permissible limits for potable water. Light rare earth elements had dominance over heavy rare earth elements. Rare earth elements were higher in groundwater than surface water. The dominant complexing ligand in groundwater is Carbonato complex ligand (LnCO₃)₃ while surface water is dominated by free ionic REE species. Oversaturated rare earth minerals at S>1 are dominantly light REE phosphates (PO₄³⁻). In surface water both light and heavy rare earth elements minerals of phosphate ligand were supersaturated. Normalized rare earth elements to granite of Honkong and PAAS showed more enrichment of HREE. Two water types classified as recharge (type1) and discharge (type 2) were identified in the area. Rare earth elements levels are not toxic and within permissible level for potable water. Minor treatment of water to reduce acidity should be expedient and a research on bioavailability of REE in humans within the area is important.

Keywords: Speciation; complexation; rare earth elements; bioavailability; Nigeria.

1. INTRODUCTION

When groundwater geochemistry is adequately characterized, interpreted and understood, the knowledge can be applied in the study of geochemical processes and integrated water flow. This helps to identify groundwater sources, improve prediction of contaminant fate and transport, repository performance assessment and safety analysis [1,2].

Rare earth elements (REE) have been used to trace many geological processes including crust evolution, weathering processes, paleoclimate change and water rock interaction [3]. In recent times, aqueous rare earth elements from rivers, seas and groundwater has attracted attention following the introduction of state of the art analytical instruments. Because of the complex nature of aquifers, rare earth elements in groundwater are predominantly governed by aquifer mineralogy, pH, redox condition, water type, organic or inorganic complexation and colloidal particulate transport [4,3]. Rare earth elements are potential tracers for studying groundwater aquifer rock interactions because of their generally coherent and predictable behavior [5].

Granitoid weathered crust has predominance of rare earth elements [3], and granitic rocks are common in the Oban Massif. However, knowledge of the distribution of rare earths in the basement rocks, chemical behavior in the natural terrestrial waters and groundwater in the Oban Massif is lacking. Preceding works anchored on heavy metals analysis include those of Ushie and Amadi [6], Ekwere [7], Ekwere and Edet [8].

In this study, REE concentration, aqueous REE speciation and PAAS-normalized patterns for rare earth elements in surface and groundwater from the Oban Massif in southeastern Nigeria are presented. On the basis of the presented data, factors controlling REE concentrations, fractionation patterns and rare earth elements bioavailability and toxicity are discussed. The impetus for the research is the need to advance the frontier of rare earth elements geochemistry in weathered basement aquifers.

2. STUDY AREA

2.1 Geographical Setting

The study area, Oban Massif and environs, is delimited by latitudes N05° 18' 57.7" to N05° 45' 26.8" and Longitudes E08° 34' 59.4" to E08° 05' 20.5", located within present-day Akamkpa and Biase Local government Areas of Cross River State of Nigeria (Fig. 1). The area encompasses the Oban Hills and forests, which have a common boundary with the Republic of Cameroon in the east. The western part is bounded by Ebonyi State along the Cross River Channels, while the southern and northern borders are with the Calabar Flank and the Mamfe Embayment respectively (Fig. 1).

The study region is characterized by tropical climate having distinct alternating dry and wet seasons. The area records an annual rainfall of about 2000 mm and warm temperature in the range of 28°C to 36°C. Total precipitation in the wet season range from 1800 to 2500 mm. The wet season lasts from April to October, while the dry season lasts from November to March.

The relative humidity in the area is 77 percent with evaporation of 3.85 mm/day [9]. The main occupation of the inhabitants is farming.

2.2 Geological and Hydrogeological Setting

The study area, Oban Massif and environs, comprises part of an extensive spur or inlier of Precambrian crystalline rocks, overlaid by Cretaceous - Tertiary and younger sediments of the Calabar Flank. With regards to the basement geology, the Oban massif can be divided in an

eastern and western sector. The western region exhibit imprints of at least three phases of deformation, with the maximum of metamorphic conditions being in the amphibolites facies. This condition is associated with copious intrusions of simple – composite granite – granodioritic plutons which are tectonically controlled by the Late Older Granite Orogeny. Rocks occurring in the region include but are not limited to: migmatitic and sheared gneisses, paraschists, phyllites, metaconglomerates, quartzites, amphibolites, metadiorite, pegmatite, aplite, pyroxenite and unmetamorphosed dolerites and microdiorites [10,11] (Fig. 2).

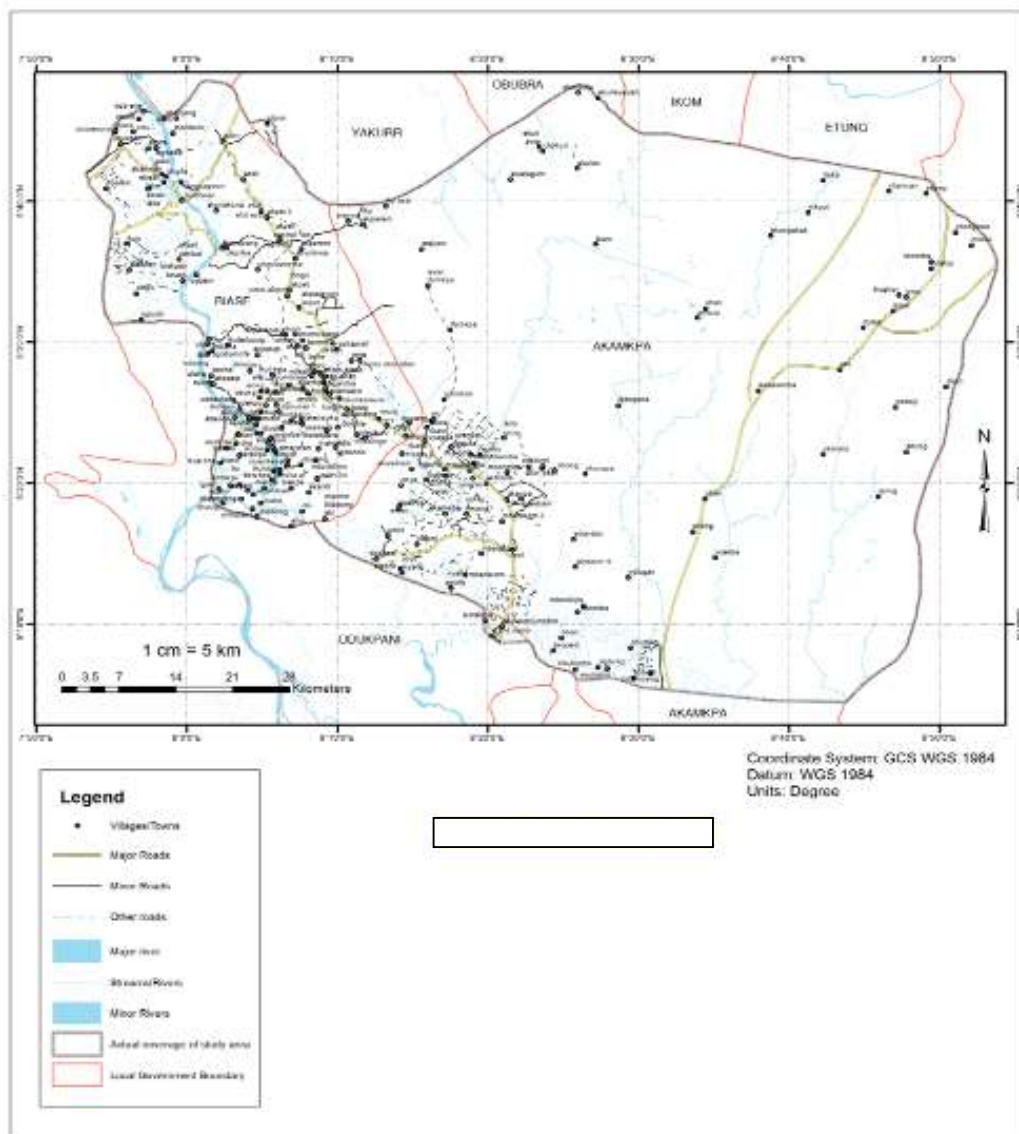


Fig. 1. Location map of the study area

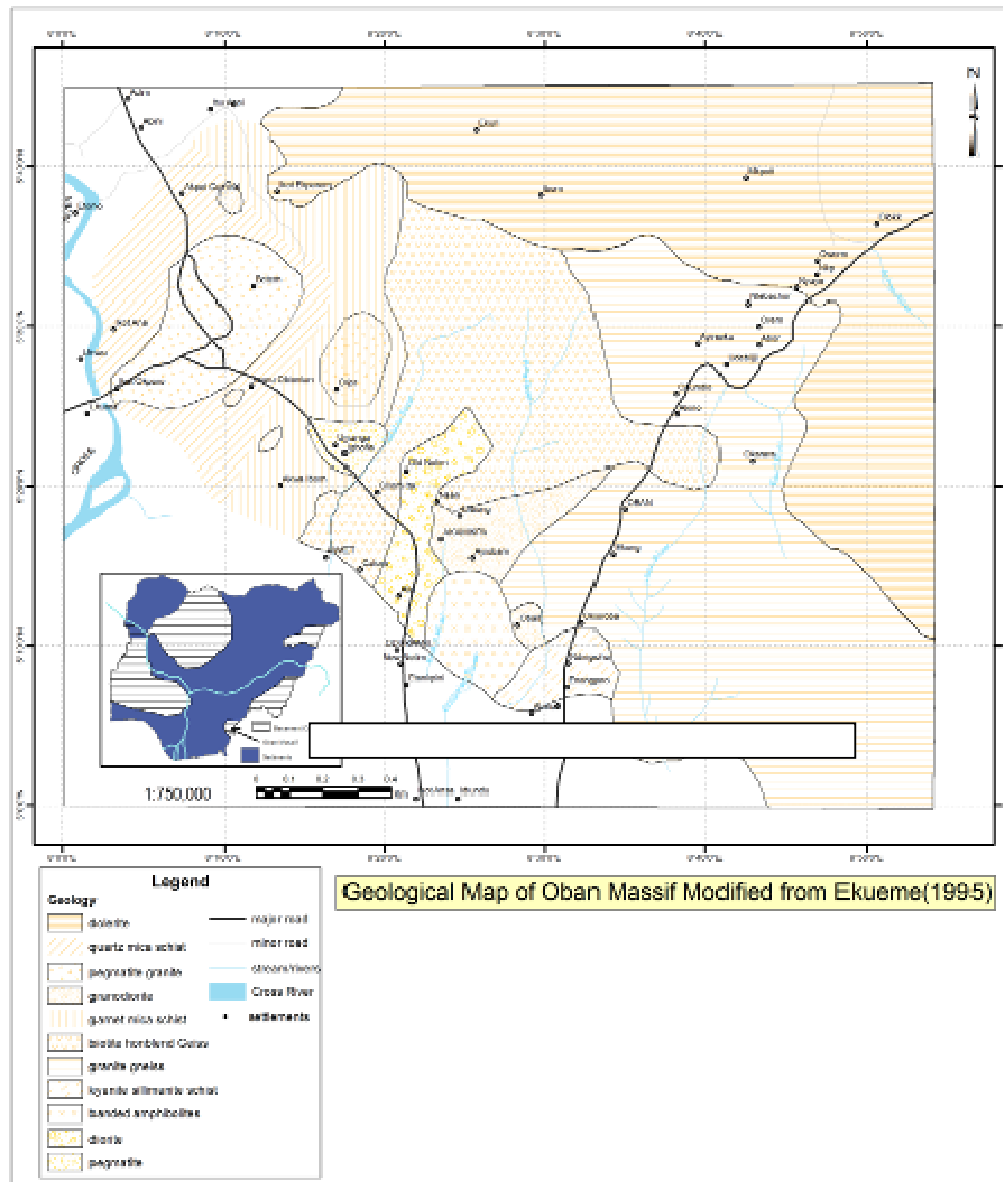


Fig. 2. Geological map of the study area

On the other hand, the geology of the eastern Oban Massif is dominated by quartzofeldspathic gneisses which have been intruded by acidic, intermediate and basic igneous rocks. Granites of various composition, pegmatite and charnockites constitute the acidic intrusions, while the intermediate intrusions include syenites and diorites [12] (Fig. 2). Dolerites and probably pyroxenites are the basic intrusive in the area. The quartzofeldspathic gneisses of the area also enclose mappable bodies of banded and homogeneous amphibolites.

In terms of hydrogeological setting, groundwater occurring within the area is present in the weathered overburden or along fractures/ fault systems. The aquifers are unconfined with an overburden thickness varying from 15 m to 70 m, and an estimated depth to water table of 3 m. Transmissivity values are in the range of 41065-725.88 m²/day [9]. Boreholes drilled to a depth of 24m with a yield of 1.9 l/s are common in the area. Generally, low values of aquifer parameters such as well yield, transmissivity and storativity are prevalent in the

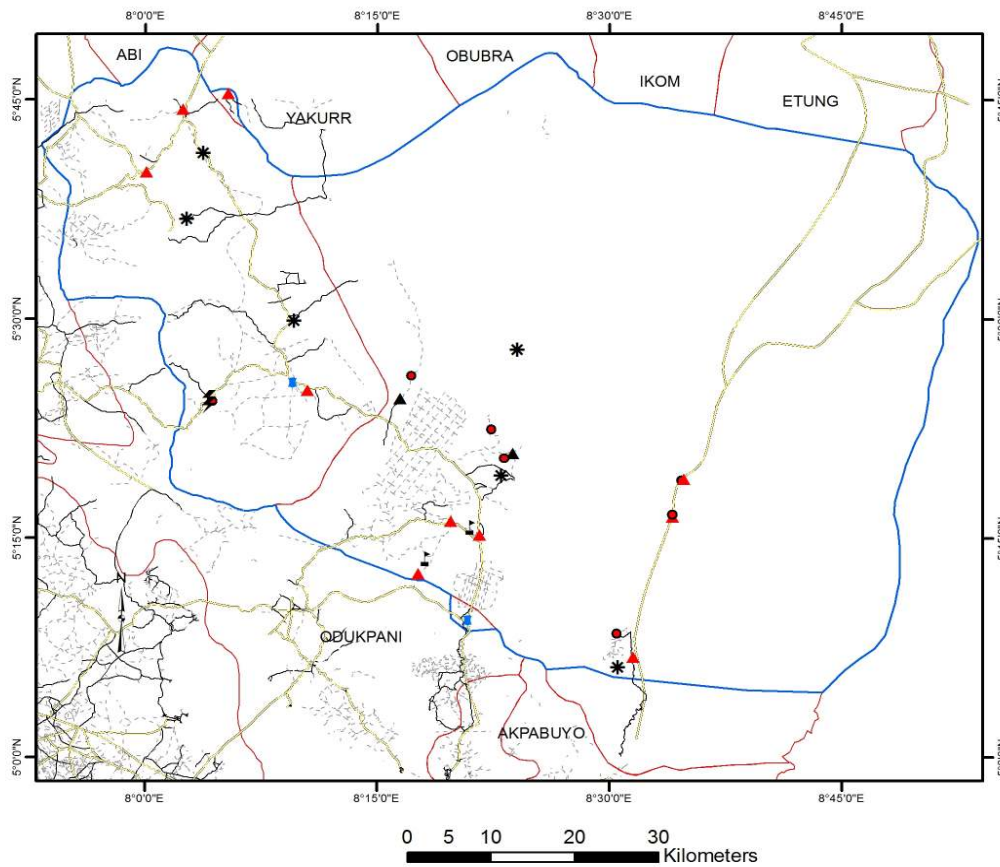


Fig. 3. Sample location map of the study area

area, and this is indicative of poor water storage potential in the basement complex area [13].

3. SAMPLING AND LABORATORY METHODS

Boreholes, wells and springs water sources occurring in various locations within the study area were sampled for the purpose of this study.

Altogether, a total of 29 water samples were collected for analysis (see above Fig. 3).

Physico-chemical parameters (pH, Eh, temperature and conductivity) were directly measured in the field. Eh was measured using a platinum combination electrode (Metler Pt 4805). Electrodes are inserted into a cell constructed to minimize diffusion of atmospheric oxygen into the

sample during measurement. Eh values are presented in mV relative to standard hydrogen electrode. Temperature was determined with the aid of Mercury – in – Glass Thermometer, while pH was measured with a digital mV Redox pH meter. The accuracy of the pH measurement is given as ± 0.05 pH unit. Conductivity was measured with a special conductivity meter (WA 3000), which gives Conductivity (σ) values in $\mu\text{S cm}^{-1}$. The same instrument was also used to measure the Total Dissolved Solids. Turbidity was measured with a Spectrophotometer (Dr 3000).

At each sample location, water samples were filtered through a $0.45 \mu\text{m}$ millipore filter *in-situ*, and stored into 50 ml HNO_3 -washed density polyethylene bottles. The samples for cation (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) and trace elements (Ba, Mn and Fe) determinations were preserved immediately after on-site acidification with ultra-pure HNO_3 , while anion samples (SO_4^{2-} , Cl^- , HCO_3^- , NO_3^- , F) were not acidified. Water samples for determination of total aqueous REE concentrations were filtered with identical filters and immediately acidified to $\text{pH} < 2$ with ultra-pure HNO_3 .

All procedures (sampling, filtration, storing and analysis) were carried out in order to minimize contamination. The polyethylene bottles used for sample storage were pre-washed with dilute trioxonitrate V acid (HNO_3) and rinsed with de-ionized water. At the point of storage of the water sample, each sample bottle was rinsed thrice with the water to be stored to condition the bottle before the actual water samples were stored.

The water samples for chemical analysis were stored in a refrigerator prior to expeditious transportation to the laboratory for analysis.

Major anions (SO_4^{2-} , Cl^- , HCO_3^- , NO_3^- , F) were determined using titration and ion chromatography techniques that permits uncertainty below $\pm 4\%$, while the cations (Mg^{2+} , Ca^{2+} , Na^+ , K^+) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Rare earth elements were analyzed using inductively coupled plasma mass spectrometry. The rare earth elements isotopes of ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{174}Yb , and ^{175}Lu were used to quantify REE in the water samples. All analyses were carried out at the

Acme Analytical Laboratories, Vancouver BC, Canada.

The aqueous speciation of the rare earth elements was calculated using the VISUAL-MINTEQ geochemical software because of its extensive database of mineral aqueous facies for interpretation purposes, unlike the PHREEQC method used by Ekwere [8].

4. RESULTS AND DISCUSSION

4.1 Physico-Chemical Composition and Hydrochemistry

Statistical summary of the concentrations of the measured physico-chemical parameters, major dissolved ions and selected trace elements composition of the groundwater samples are given in Table 1. As shown, the median temperature of the groundwater samples is 26°C (min. 25°C , max. 29.4°C), which is consistent with the ambient surface temperature of the catchment region. The pH values vary between 5.61 and 7.20 with a median value of 6.49, which reflects some level of acidity. The redox potential, Eh, ranged from 7 to 24 mV with the mean and standard deviation being 15.86mv and 5.41 respectively. The electrical conductivity documents the highest variability as it ranged between $0.01 \mu\text{S cm}^{-1}$ and $3429 \mu\text{S cm}^{-1}$, with a mean value of $548 \mu\text{S cm}^{-1}$. Turbidity values ranged between 0 and 42 FTU with a mean value of 4.11 FTU. A value of 500mg/L is the permissible limit of TDS in drinking water by (WHO 2006). However, in this study, the TDS values ranged between 27 – 1501 mg/L, with a mean and standard deviation of 325.75 ± 479.48 mg/L. The values are presented in Table 1.

The major dissolved ions composition of the groundwater includes cations, such as Ca (12.9 ± 23.7 mg/L), Mg (2.8 ± 4.3 mg/L), Na (12.3 ± 25.9 mg/L), K (6.5 ± 14.4 mg/L), and anions, notably: SO_4 (24.1 ± 46.6 mg/L), Cl (173.1 ± 333.9 mg/L), HCO_3 (17.4 ± 24 mg/L), NO_3 (3.3 ± 2.2), PO_4 (0.3 ± 0.9 mg/L) (Table 1). In uncontaminated groundwater systems, the principal origin of Ca and Mg ions is carbonate minerals and their dissolution and depositional processes. Weathering of silicate minerals can also contribute towards the enrichment of these minerals. However, in the study area, the predominance of silicate basement rocks with relatively less abundance of carbonate minerals suggests that the major origin of Ca and Mg is silicate weathering. Na ions in groundwater are

often largely controlled by saline intrusions, evaporites and silicate minerals. However, in the study area, Na and K are most likely sourced through weathering of hard rocks, i.e. silicate weathering. Among the anions, Cl occurs in higher concentrations. Chloride ion is generally used in delineating saline intrusions. The high concentration can be explained by the fact that this ion has high mobility and hardly undergoes sorption.

Next in abundance are the Bicarbonate ions. Apart from the dissolution of carbonate minerals, the major origin of bicarbonates is the sewage systems. However there is no prescribed permissible limit for this ion (Table 1). Sulphate (SO₄) and phosphate (PO₄) constitute the least in terms of abundance of anions. The major origin of sulphate is the dissolution of Gypsum, oxidation of sulfides minerals (pyrite, galena, and chalcopyrite) and/or anthropogenic activities.

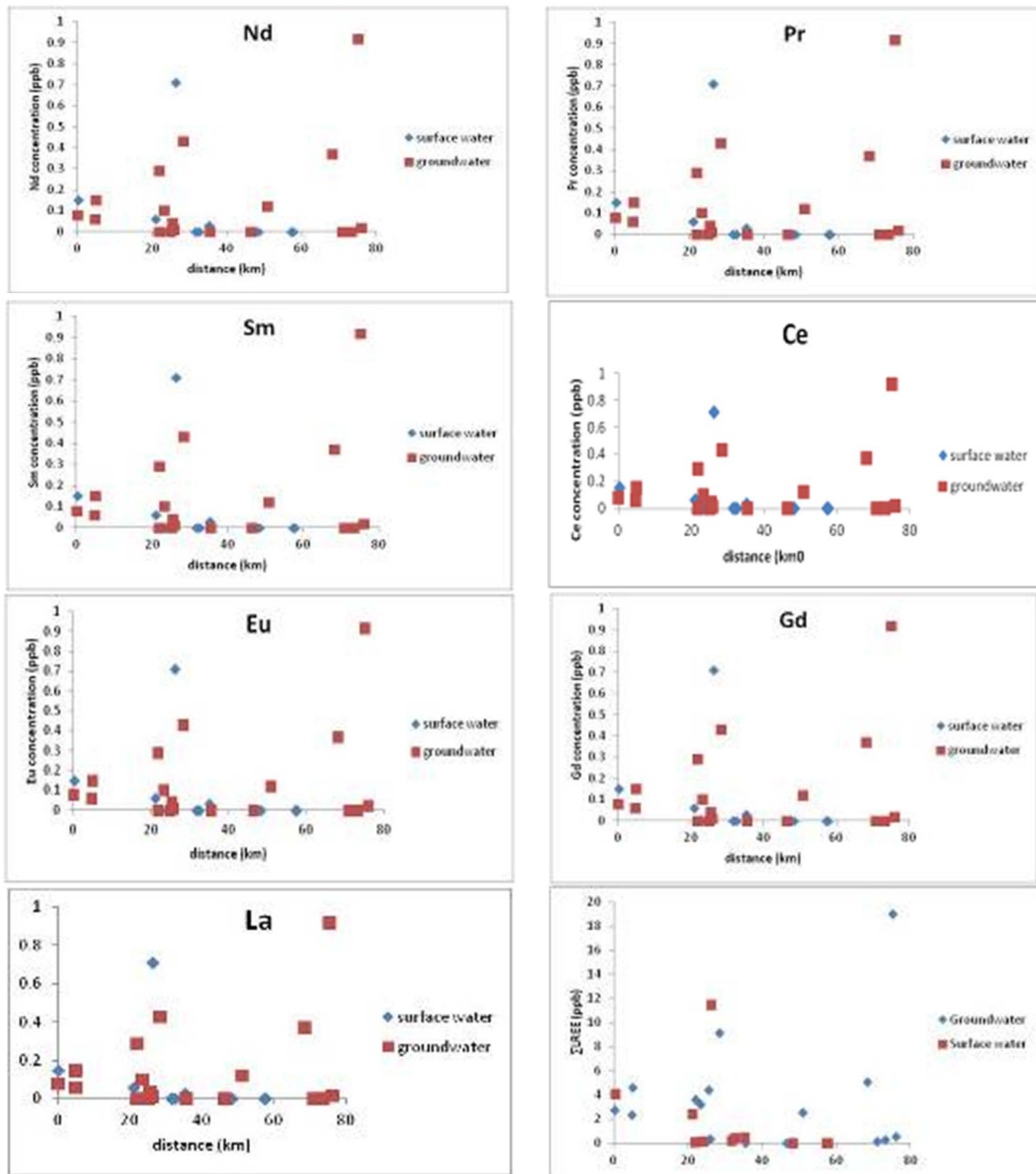


Fig. 4. Light rare earth elements variation with distance across the study area from basement in Oban Massif to sedimentary area in the Mamfe Embayment

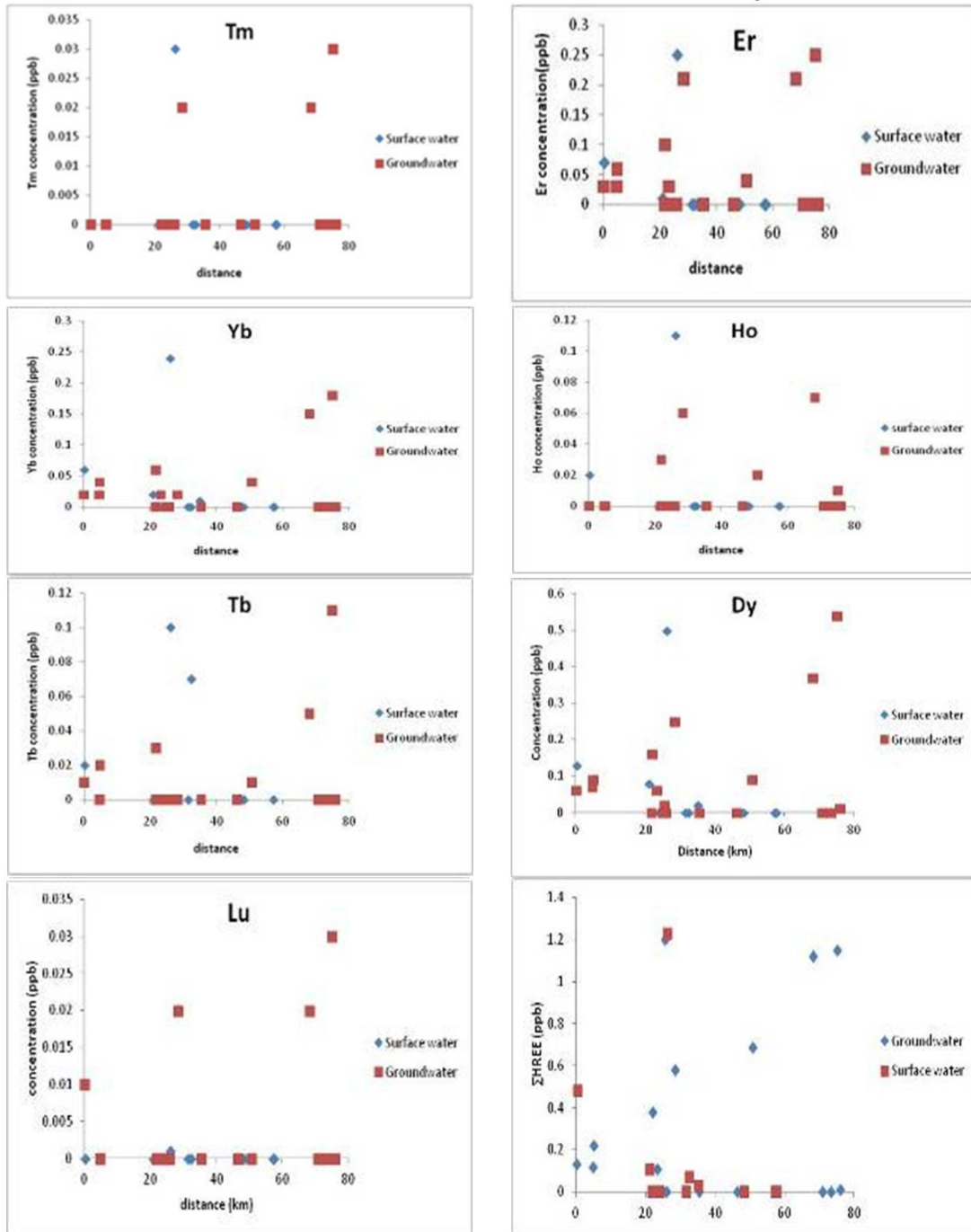


Fig. 5. Heavy rare earth elements concentrations variation with distance across the study area from e Oban Massif in the basement to sedimentary area in the Mamfe Mbayment

The SO_4 in the studied waters are mostly sourced through addition of sulphate fertilizers known as anthropogenic contaminations.

Other dissolved components in the water include F (20.1 ± 43.9 mg/L) and Br (10.5 ± 12.0 mg/L). It is

worthy to note that fluoride composition, which varied from 0 to 220 mg/L is predominantly higher than the 1.5 mg/L value stipulated by WHO[14] for potable drinking water.

Al, Fe, Mn and Ba are included as selected trace elements (Table 1). The mean levels of these selected trace elements are given as 177.41, 405.73, 92.5 and 44.71 ppm for Al, Fe, Mn, and Ba respectively. The mean values recorded for Al, Fe, Mn and Ba do not only exceed the WHO [14] recommended values of 0.05 - 0.2 ppm, 0.2 ppm, 2 ppm, and 0.4 ppm for potable drinking water respectively, but are very high in comparison with the Nigerian standard for Drinking water quality (Table 1). Moreover, the measured Fe values are anomalous, compared to what obtains in uncontaminated groundwater [14].

The concentrations of the major dissolved ions were plotted onto the Piper's trilinear diagram (Fig. 3). The results indicated that the water type vary from Ca+Mg-Cl+SO₄, Cl+SO₄-Na+K, Ca+Mg-HCO₃ to HCO₃-Ca+Mg. however, the waters are predominantly Ca+Mg,-Cl+SO₄ type.

4.2 Rare Earth Elements (REE) Abundance in the Groundwater

The REE data measured in the groundwater, together with \sum REE and fractionation index (La/Yb)_n are given in Table 2. As shown in Table 2, the total REE concentrations (\sum REE) vary from 0.15 to 20.19 ppb with an average of 2.87 ppb. Also, the elements, La, Ce, and Nd are more abundant than other REE elements, and Ce is the most abundant element of the REEs (Table 2). So, it seems that the abundance of REE decreases with increasing atomic number, resulting in the concentration of LREEs being higher than that of the HREEs in the groundwater (Table 2); with the exception of Gadolinium (Gd),

Dysprosium and Erbium (Er), which display mean values that are close to those recorded for the LREE.

Among the light rare-earth elements (LREE) with relatively higher concentrations are Ce (0.98±1.51 ppb), Nd (0.66±1.08 ppb) and La (0.56±0.96 ppb). The high relative abundance of Ce may be due to dissolution of Ce under reducing conditions and the presence of cerium-bearing minerals such as Allanite and Monazite [15]. Also it is proven that the most abundant rare earth element in the earth crust is Cerium and Ytterium (Y) while Thulium (Tm) is considered the rarest of all the rare earth elements [16]. The concentration of Neodymium (Nd) vary between <0.01 and 4.66 ppb with a median value of 0.11ppb. Lanthanum (La) content ranged from <0.01 to 4.5 ppb with a median value of 0.08 ppb. Elevated Lanthanum content may be attributed to the fractionation of Lanthanum containing minerals such as Monazite and rock – water interactions [17]. Praseodymium (Pr) show concentration that vary between <0.01 and 1.02 ppb with a mean and standard deviation of 0.15±0.23 ppb Samarium (Sm) displays a mean and standard deviation of 0.14±0.23 with a median value of 0.02 ppb. Europium (Eu) concentration ranges from <0.01 to 0.15 ppb with mean and standard deviation being 0.02±0.033 ppb.

Among the Heavy Rare Earth Elements (HREE), Gadolinium (Gd) (0.13±0.22 ppb), Dysprosium (Dy) (0.09±0.15 ppb), and Erbium (Er) (0.05±0.08 ppb) have relatively higher concentrations. The next, in terms of abundance, is Yb (0.04±0.06 ppb), while other HREE have mean composition of between 1 and 2 ppb.

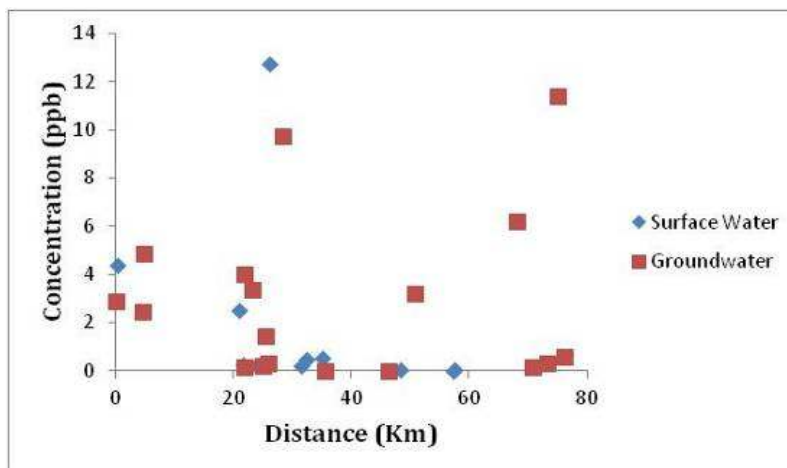


Fig. 6. Total REE variation with distance across the study area

Table 1. Summary of concentration (mg/l) physicochemical parameters in water

Parameter	Count	Min	Median	Max	Mean	ST. DEV	Groundwater (Rose et al., 1979)	Max permitted (Nigerian standard for drinking water quality, 2007)	WHO (2006)
TEMP °C	29	25	26	29.4	26.69	1.48	-	-	-
pH	29	5.61	6.49	7.2	6.42	0.54	-	6.5-8.5	6.5-8.5
Eh (mv)	29	7	16	24	15.86	5.41	-	-	-
EC ($\mu\text{S cm}^{-1}$)	29	0.01	181	3429	547.88	977.55	-	1000	1400
Turbidity (FTU)	29	0	2	42	4.11	7.64	-	-	5
TDS (mg/l)	29	27	122	1501	325.75	479.48	-	500	500
SO ₄ "	29	0.51	5.64	1.49	24.05	46.63	-	100	250
Cl "	29	1.1	40.23	1060	173.14	333.93	20,000	250	250
HCO ₃ "	29	1	6.81	89.1	17.37	23.96	-	-	-
NO ₃ "	29	<0.02	4.42	5.03	3.28	2.22	-	50	50
PO ₄ "	29	<0.05	0.002	4.5	0.32	0.9	-	-	1
F "	29	0	0.007	220	20.08	43.91	-	1.5	1.5
Br "	29	<5	7	43	10.53	11.97	20	-	-
Ca "	29	0.71	4.17	28.54	12.94	23.69	50,000	-	12
Mg "	29	0.48	1.16	23	2.82	4.3	7,000	0.2	30-150
Na "	29	1.3	4.82	144	12.31	25.89	30,000	200	12
K "	29	0.87	2.12	79.07	6.51	14.41	3,000	-	-
Al ppm	29	<0.05	75	1328	177.41	289.95	-	0.2	0.05-0.2
Fe "	29	<0.05	88	2008	405.73	956.18	100	0.3	0.2
Mn "	29	<0.05	27.09	188.2	44.71	53.12	15	0.2	0.4
Ba "	29	15.1	44..31	39.3	92.50	108.45	-	0.7	2

Table 2. Summary Rare Earth Elements (REE) concentration (ppb) in water

Parameter	Mean	Std	Mean	Minimum	Maximum
Ce	0.98	1.49	0.25	<0.01	6.81
Dy	0.090	0.14	0.02	<0.01	0.54
Er	0.050	0.075	0.01	<0.01	0.25
Eu	0.021	0.033	0.01	<0.01	0.15
Gd	0.13	0.22	0.02	<0.01	0.92
Ho	0.019	0.022	0.01	<0.01	0.11
La	0.56	0.94	0.08	<0.01	4.5
Lu	0.011	0.005	0.01	<0.01	0.03
Nd	0.66	01.062	0.11	<0.01	4.66
Pr	0.15	0.23	0.03	<0.01	1.02
Sm	0.14	0.22	0.02	<0.02	0.98
Tb	0.021	0.026	0.01	<0.01	0.11
Tm	0.012	0.005	0.01	<0.01	0.03
Yb	0.036	0.055	0.01	<0.01	0.18

Table 3. Speciation and solution complexation of rare earth elements in springs and streams

component	% of total component concentration	Species name	component	% of total component concentration	Species name	component	% of component concentration	Species name
Ce ³⁺	92.164	C ³⁺	Ho ³⁺	0.22	GdHPO ₄ ⁺	Tb ³⁺	2.81	SmF ²⁺
	0.931	CeOH ²⁺		0.148	GdCO ₃ ⁺		4.625	SmSO ₄ ⁺
	1.666	CeF ²⁺		0.011	GdHCO ₃ ²⁺		0.027	SmNO ₃ ²⁺
	0.458	CeCl ²⁺		5.169	Ho ³⁺		0.01	SMHCO ₃ ²⁺
	0.022	CeNO ³⁺		5.169	HoOH ²⁺		0.178	SmCO ₃ ⁺
	0.227	CePO ₄ (aq)		5.974	HoF ³⁺		86.224	Tb ³⁺
	0.073	CeCO ₃ ³⁺		3.653	HoSO ₄ ⁺		4.363	TbOH ²⁺
	Dy ³⁺	85.674		Dy ³⁺	La ³⁺		0.013	HoCO ₃ ²⁺
4.864		DyOH ²⁺	0.208	HoCO ₃ ⁺		4.159	TbSO ₄ ⁺	
5.369		DyF ²⁺	93.88	La ³⁺		0.024	TbNO ₃ ²⁺	
3.856		DySO ₄ ⁺	0.321	LaOH ²⁺		0.013	TbHCO ₃ ⁺	
0.014		DyHC ₃ ⁺	0.776	LaF ²⁺		0.171	TbCO ₃ ⁺	
0.214		DYCO ₃ ⁺	0.426	LaCl ²⁺		82.102	Tm ³⁺	

component	% of total component concentration	Species name	component	% of total component concentration	Species name	component	% of component concentration	Species name
Er ³⁺	84.289	Er ³⁺	Nd ³⁺	4.528	LaSO ₄ ⁺	Yb ³⁺	7.388	TmOH ²⁺
	5.622	ErOH ²⁺		0.018	LaNO ₃ ⁺		6.329	TmF ²⁺
	6.223	ErSO ₄ ⁺		0.011	LaHCO ₃ ²⁺		0.356	TmCl ²⁺
	0.014	ErHCO ₃ ²⁺		0.035	LaCO ₃ ⁺		3.529	TmSO ₄ ⁺
	0.237	ErCO ₃ ⁺		91.338	Nd ³⁺		0.014	TmHCO ₃ ²⁺
Eu ³⁺	88.18	Eu ³⁺	Pr ³⁺	1.333	NdOH ²⁺	Yb ³⁺	0.271	TmCO ₃ ⁺
	3.385	EuOH ²⁺		2.557	NdF ²⁺		77.23	Yb ³⁺
	3.18	EuF ²⁺		4.613	NdSO ₄ ⁺		9.816	YbOH ²⁺
	0.439	EuCl ²⁺		0.027	NdCO ₃ ²⁺		6.234	YbF ²⁺
	4.557	EuSO ₄ ⁺		0.12	NdCO ₃ ⁺		0.266	YbCl ²⁺
	0.053	EuNO ₃ ²⁺		91.863	Pr ³⁺		3.028	YbSO ₄ ⁺
	0.014	EuHCO ₃ ²⁺		0.971	PrOH ²⁺		2.817	YbSO ₄ ⁺
	0.184	EuCO ₃ ³⁺		2.139	PrF ²⁺			
Gd ³⁺	87.724	Gd ³⁺	Sm ³⁺	0.457	PrCl ²⁺			
	2.866	GdOH ²⁺		4.431	PrSO ₄ ⁺			
	3.716	GdF ²⁺		0.022	PrNO ₃ ²⁺			
	4.43	GdCl ²⁺		0.108	PrCO ₃ ⁺			
	0.013	GdNO ₃ ⁺		89.489	Sm ³⁺			
	0.624	GdPO ₄ (aq)		2.857	SmOH ²⁺			

Table 4. Speciation and solution complexation of rare earth elements modeled from borehole water samples

Component	% of total component	Species name	Component	% of total component	Species name	Component	% of total component	Species name
Ce ³⁺	41.909	Ce ³⁺	Nd ³⁺	1.152	GdOH ²⁺	Nd ³⁺	5.703	LuSO ₄ ⁺
	0.508	CeOH ²⁺		0.034	GdF ²⁺		2.489	LuHCO ₃ ²⁺
	0.021	CeF ²⁺		0.088	GdCl ²⁻		4.314	Lu(CO ₃) ⁺
	0.233	CeCl ²⁺		0.102	Gd(SO ₄) ²⁻		67.962	LuCO ₃ ⁺
	0.116	Ce(SO ₄) ⁻		13.622	GdSO ₄ ⁺		33.915	Nd ³⁺
	18.564	CeSO ₄ ⁺		0.103	GdPO ₄ (aq)		0.594	NdOH ²⁺
Dy ³⁺	23.211	Dy ³⁺		0.962	GdHPO ₄ ⁺		0.026	NdF ²⁺
	1.538	DyOH ²⁺		51.336	GdCO ₃ ⁺		0.094	Nd(SO ₄) ²⁻
	0.04	DF ²⁺		3.193	GdHCO ₃ ²⁺		15.731	NdSO ₄ ⁺

Component	% of total component	Species name	Component	% of total component	Species name	Component	% of total component	Species name
	0.032	Dy(SO ₄) ²⁻	Ho ³⁺	23.565	Ho ³⁺		0.012	NdNO ₃ ²⁺
	9.595	DySO ₄ ⁺		1.722	HoOH ²⁺		3.067	NdHCO ₃ ²⁺
	3.843	Dy(CO ₃) ²⁺		0.045	HoF ²⁺		0.544	Nd(CO ₃) ²⁺
	2.046	Dy(CO ₃) ₂ ⁻		0.041	Ho(SO ₄) ²⁻		46.017	NdCO ₃ ⁺
Er ³⁺	21.412	Er ³⁺		9.303	HoSO ₄ ⁺	Pr ³⁺	36.093	Pr ³⁺
	1.715	ErOH ²⁺		3.225	HoHCO ₃ ²⁺		0.548	PrOH ²⁺
	0.043	ErF ²⁺		2.555	Ho(CO ₃) ₂ ⁻		0.023	PrF ²⁺
	0.059	Er(SO ₄) ²⁻		59.54	HoCO ₃ ⁺		0.201	PrCl ²⁺
	8.453	ErSO ₄ ⁺	La ³⁺	51.404	La ³⁺		0.063	Pr(SO ₄) ²⁻
	3.14	ErHCO ₃ ²⁺		0.211	LaOH ²⁺		15.987	PrSO ₄ ⁺
	3.061	Er(CO ₃) ²⁻		0.012	LaF ²⁺		0.01	PrNO ₃ ⁺
	62.114	ErCO ₃ ⁺		0.261	LaCl ²⁺		3.046	PrHCO ₃ ²⁺
Eu ³⁺	25.838	Eu ³⁺		0.226	La(SO ₄) ²⁻		0.471	Pr(CO ₃) ²⁻
	1.191	EuOH ²⁺		22.769	LaSO ₄ ⁺		43.647	PrCO ₃ ⁺
	0.025	EuF ²⁺		0.011	LaNO ₃ ²⁺	Sm ³⁺	26.946	Sm ³⁺
	0.144	EuCl ²⁺		5.337	LaHCO ₃ ²⁺		1.033	SmOH ²⁺
	0.143	Eu(SO ₄) ²⁻		0.111	La(CO ₃) ²⁻		0.033	SmF ²⁺
	12.263	EuSO ₄ ⁺		19.657	LaCO ₃ ⁺		0.075	Sm(SO ₄) ²⁻
	0.019	EuNO ₃ ²⁺	Lu ³⁺	16.972	Lu ³⁺		12.789	SmSO ₄
	3.619	EuHCO ₃ ²⁺		2.418	LuOH ²⁺		2.798	SmHCO ₃ ²⁻
	1.195	Eu(CO ₃) ²⁻		0.04	LuF ²⁺		0.99	Sm(CO ₃) ²⁻
Gd ³⁺	55.563	EuCO ₃ ⁺		0.059	Lu(SO ₄) ²⁻		55.337	SmCO ₃ ⁺
Yb ³⁺	26.565	Tb ³⁺	Tm ³⁺	18.94	Tm ³⁺			
	1.614	TbH ³⁺		2.04	TmOH ²⁺			
	0.042	TbF ²⁺		0.04	TmF ²⁺			
	0.074	Tb(SO ₄) ²⁺		0.092	TmCl ²⁺			
	11.767	TbSO ₄ ⁺		0.053	Tm(SO ₄) ²⁻			
	3.636	TmHCO ₃ ²⁺		7.477	TmSO ₄ ⁺			
	1.736	TmHCO ₃ ²⁺		2.976	TmHCO ₃ ²⁺			
	55.557	TbCO ₃ ⁺		3.824	Tm(CO ₃) ₂ ⁻			
				64.55	TmCO ₃ ⁺			
				27.267				

Tang and Johansson [4] observed that the dissolved rare earth elements are influenced mostly by geochemical reactions due to distribution and concentrations of complexing ligands, characteristics of surface absorption sites and pH. Also, rare earth elements solubility depends on the solution and this relates to the differences in the stability of soluble complexes of elements [18]. Light rare earth elements exhibited higher concentrations than heavy rare earth elements, because reductive dissolution of Fe Oxyhydroxide would result to a release of preferentially scavenged rare earth elements into groundwater [5]. The relative higher light rare earth elements concentration in this study can be attributed to the presence of monazite, which preferentially contains light rare earth elements. On the other hand, lack of zenotime may explain why heavy rare earth elements have lower concentrations in the groundwater studied. Very low concentration of Lutetium (Lu) and Holmium (Ho), which are heavy rare earth elements, may be explained by the presence of the mineral called basnasite, which contains very low rare earth elements [19] found in igneous rocks such as carbonatites, granites, and pegmatites which are common in the study area. More enrichment of light rare earth elements over heavy rare earth elements can also be ascribed to differences in solution complexation behavior across the rare earth elements suit. The presence of light rare earth elements more than heavy rare earth elements in the groundwater could be due to preferential release of the light rare earth elements to groundwater while reabsorption of the heavy rare earth elements at sediment particle surface occurs.

4.3 Bioavailability and Toxicity of Rare Earth Elements

Organic compounds of rare earth elements are better absorbed compared to the inorganic compounds. Furthermore, water soluble rare earth elements compounds present slightly higher absorption rates [20]. Bioavailability is not a characteristic property of a specific source of any mineral element; it merely defines an absorbed fraction of a consumed nutrient from a particular source that reaches the body system circulation than being available to animal metabolism [21].

Rare earth elements toxicity increases in the order $Nd > Ce > Pr > La$ [22]. Nguyet [23] recommended an indicated admissible

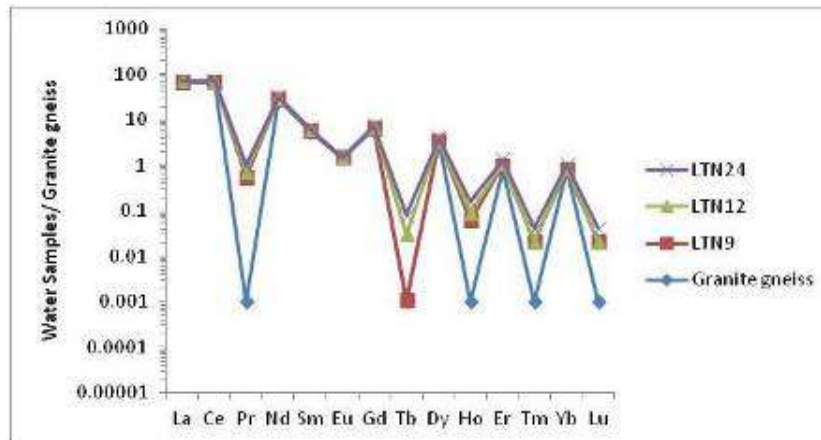
concentration for the rare earth elements Pr, Nd, Sm, Eu, Dy, Ho, Er and Lu to be 1500 ppb and the rare earth elements Gd and Tm were given drinking water indicator admissible concentration of 10.5 ppb. Elements such as La, Ce, Tb, Yb, Sc and Y were assigned drinking water admissible concentration of 2 ppb. Going by these standards a few locations in this study had concentrations of La, Ce, Sc, and Y that exceeded 2 ppb. Most of the locations had concentrations below this standard. Water in the area is therefore certified fit for drinking purposes with respect to rare earth elements concentration. De Boer [24] recommended levels of 2 $\mu\text{g/L}$ of REE for safe drinking water purposes. Most values of REE recorded in this study were also below this standard, it can be concluded that the water in the study area is suitable for safe drinking water.

Continuous exposure to rare earth elements is reported to cause emphysema, pneumonitis, bronchitis, and pulmonary fibrosis and excessive intake of REE causes symptoms such as writhing ataxia, labored respiration, walking on toes with arch back and sedation [25]. No study so far has associated rare earth elements with carcinogenicity. Notwithstanding, some older research traced the formation of tumours in the lung tissue, liver, stomach and intestinal tract due to REE [25].

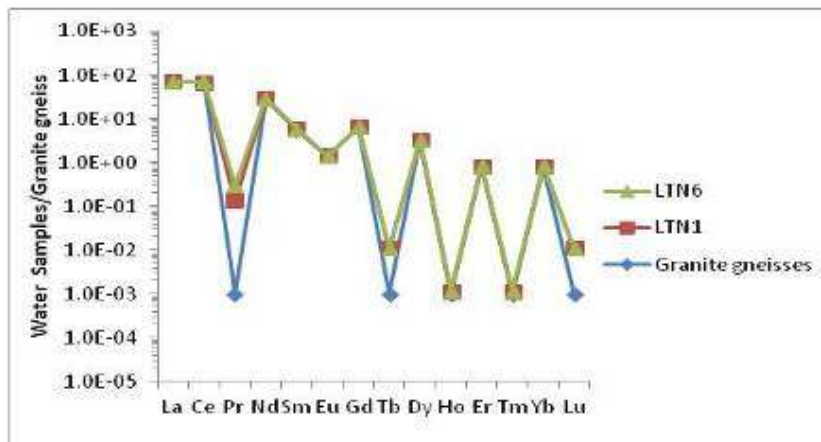
4.3.1 Post Achaean Australian Shales (PAAS) normalized rare earth elements patterns

The Post Achaean Average Shales (PAAS) is used to normalize the REE concentrations in groundwater and granitic rocks. It has been extensively used in groundwater studies. In order to best evaluate the geochemical processes responsible for the fractionation of rare earth elements in natural waters. It is most appropriate to normalize the waters to the rocks which the waters reacts with.

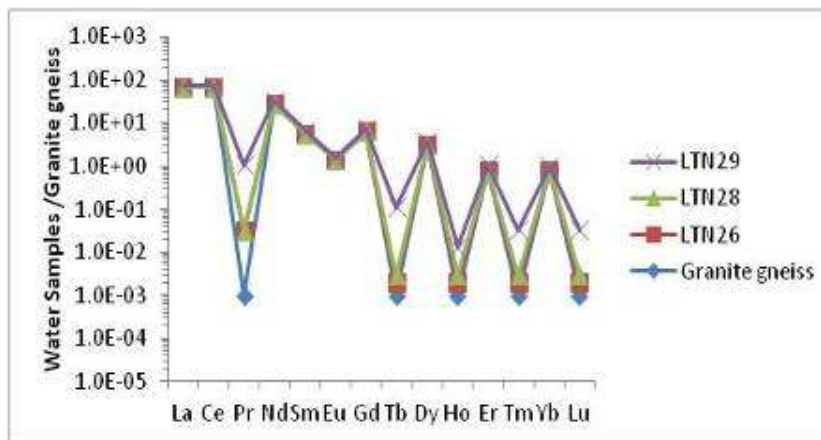
Granitic gneiss normalized rare earth elements pattern from the Oban Massif are presented in Fig. 7. Granite gneiss of Hong kong by Jayaran [26] is plotted as a reference. Groundwater in the study area is normalized to granitic gneiss because the aquifer rocks in the study area are predominantly weathered granite gneiss and also normalized to Post Achaean Australian Shale (PAAS) because part of the study area is composed of shale, clays and sandstones.



(a)



(b)



(c)

Fig. 7. Normalized rare earth elements in granitic gneiss [27]

Normalized rare earth elements show enrichment of Pr, Ho, Tm and Lu in the basement at Mbarakom (9) Fig. 7, Oban (1) and Mfamosing

(4) Fig. 7. There was more fractionation of the elements Pr, Tb and Lu in the study area. At Abini and Adim, which are locations 26 and 28

respectively there was only fractionation of Pr. At Agwagune in location 29 the rare earth elements Pr, Tb Ho, Tm and Lu indicated high enrichment.

4.4 Rare Earth Elements Speciation and Solution Complexation Modeling

Speciation modeling of aqueous rare earth elements in Oban Massif aquifers was performed to assess the importance of Carbonate $\text{LnH}(\text{CO}_3)$, $\text{Ln}(\text{CO}_3^+)$ and $\text{Ln}(\text{CO}_3)$. Phosphate complexes are $\text{LnH}_2(\text{PO}_4^{3-})^{2+}$, $\text{LnH}(\text{PO}_4)_2^-$, $\text{Ln}(\text{PO}_4)^0$ and sulphate complexes $\text{Ln}(\text{SO}_4)$, $\text{Ln}(\text{SO}_4)^+$ and free ionic species Ln^{3+} where Ln stand for the rare earth element. Aqueous speciation of REE was calculated using the

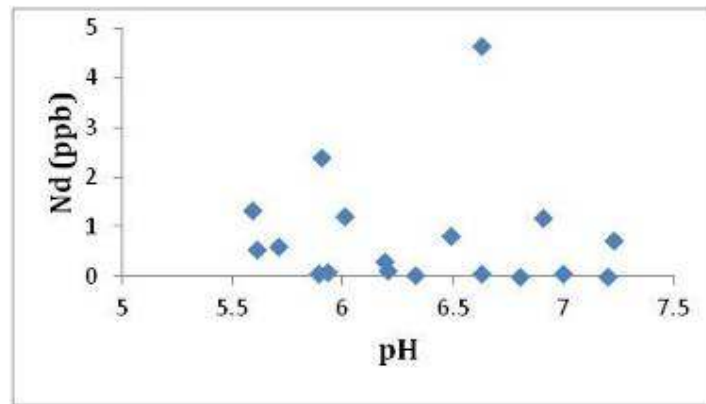
hydrogeochemical code VISUAL-MINTEQ. The result demonstrated that the dominant complexing ligand in boreholes is Carbonate Complex (LnCO_3^+). This is evident that rare earth elements are dissolved or leached in form of Carbonate Ligand. The predominant carbonate ligand (LnCO_3^+) had a percentage range from 19-67%. Dicarbonate complex ligand ($\text{Ln}(\text{CO}_3)_2^{2+}$) ranged from 0-3% and free metal ionic species ranged from 21-57%. This is evident that rare earth elements in boreholes are dissolved as carbonate complex (LnCO_3^+) and free metal ionic species (Ln^{3+}) through rock water interaction. Sulphate (LnSO_4) and Phosphate (LnPO_4) rare earth element ligands were negligible in borehole water samples.

Table 5. Saturation indices of rare earth elements in borehole water samples

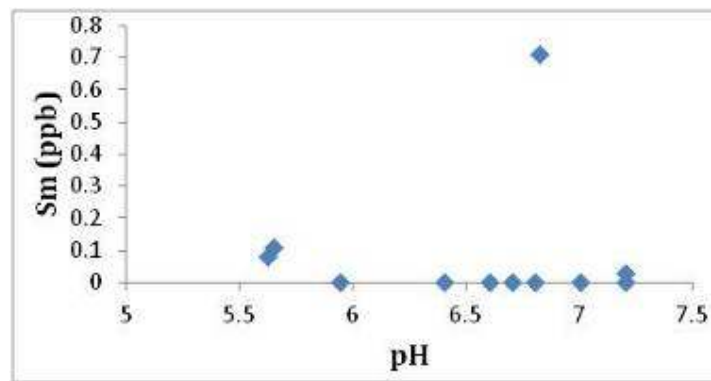
Mineral	logIAP	Saturation index	Mineral	logIAP	Saturation index
CePO ₄	-22.39	3.963	TbPO ₄	-25.659	-0.859
DyPO ₄	-23.758	1.44	TmPO ₄	-25.596	-0.859
EuPO ₄	-24.14	1.721	La ₂ (CO ₃) ₃	-37.718	0.596
GdPO ₄	-23.741	1.859	Ho(OH) ₃	9.151	-3.313
LaPO ₄	-22.907	2.843	Sm(OH) ₃	10.094	-6.539
NdPO ₄	-23.147	3.053	TmF ₃	-32.443	-6.296
SmPO ₄	-24.07	2.12	TbF ₃	-32.269	-15.353
ErPO ₄	-24.07	2.12	SmF ₃	-30.917	-14.279
GdPO ₄ *H ₂ O	-23.741	0.559	ErF ₃	-30.987	-11.727
LuPO ₄	-25.659	0.859	PrPO ₄	-23.719	-12.987

Table 6. Saturation indices of rare earth elements minerals in surface water samples

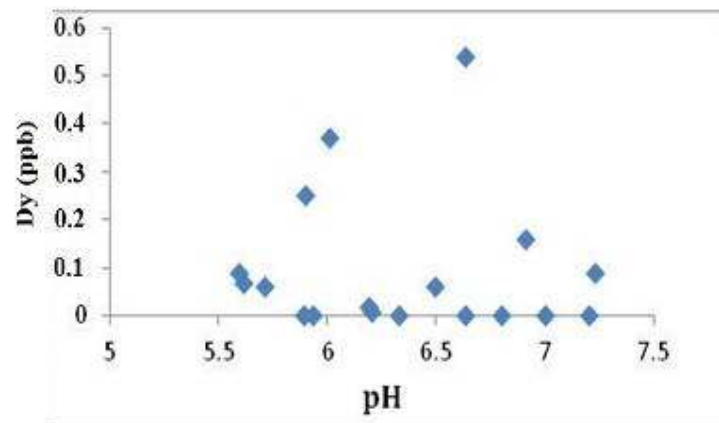
Mineral	Log IAP	Saturation index	mineral	Log IAP	Saturation index
CePO ₄	-21.9	4.4	DyF ₃	-27.02	-9.43
ErPO ₄	-23.236	1.864	Eu(OH) ₃	9.948	-5.542
NdPO ₄	-22.53	3.647	Eu ₂ (CO ₃) ₃	-48.76	-16.66
EuPO ₄	-23.728	2.32	EuF ₃	-26.133	-4.233
GdPO ₄	-22.739	2.861	Gd ₂ (OH) ₃	10.937	-4.153
GdPO ₄ *H ₂ O(s)	-22.739	1.561	HoF ₃	-25.989	-8.899
HoPO ₄	-23.583	1.519	La ₂ (CO ₃) ₃	-46.324	-11.924
SmPO ₄	-23.659	2.531	NdF ₃	-24.958	--4.647
TbPO ₄	-23.602	1.788	Pr(OH) ₃	10.96	-8.531
LaPO ₄	-22.41	3.34	PrF ₃	-25.122	-4.932
DyPO ₄	-24.615	0.583	Sm(OH) ₃	-10.017	-6.322
TmPO ₄	-24.173	0.827	Sm ₂ (CO ₃) ₃	-48.822	-16.322
YbPO ₄	-23.307	1.593	SmF ₃	-26.064	-6.874
YbPO ₄ *H ₂ O	-23.307	0.793	TbF ₃	-26.008	-8.018
Ce(OH) ₃	11.777	-8.113	TmF ₃	-26.578	-9.488
Dy(OH) ₃	9.061	-7.027	Yb ₂ (CO ₃) ₃	-48.118	17.018
Dy(CO ₃) ₃	-50.734	19.234	YbF ₃	-25.712	-9.422
La(OH) ₃	11.266	-9.025	YbF ₃ *H ₂ O(s)	-25.712	-9.712
LaF ₃	-24.815	-6.115			



(a)



(b)



(c)

Fig. 8. Showing concentration of Nd, Sm and Dy versus pH

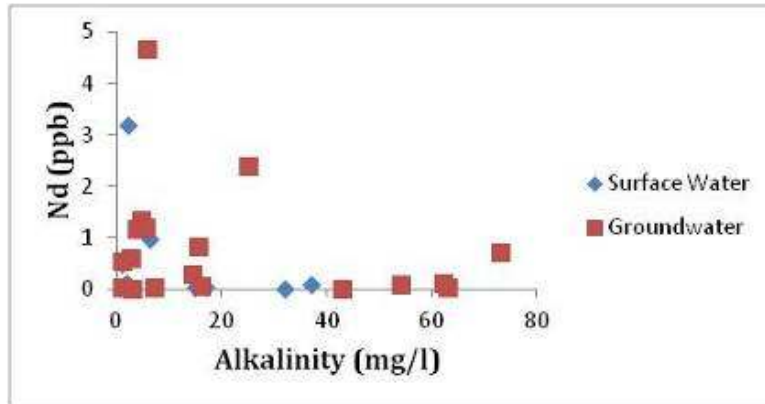
Free metal ionic species dominantly dissolved rare earth elements in springs, streams and rivers in the study area accounting for 77-97% of dissolved rare earth elements next to Sulphate ligand (LnSO_4^+) ranging between 3-4% of rare earth elements fractionation in surface values. It was discovered that the ligands LnCl_3^+ , LnNO_3^+

and LnPO_4 were negligible complexing ligands in surface waters. This demonstrates that rare earth elements are dissolved principally as free metal species and LnSO_4^+ ligand in surface water in the study area. Significant CO_3 complexing is possible at $\text{pH} < 6$ [28] and the study area is characterized by this pH range.

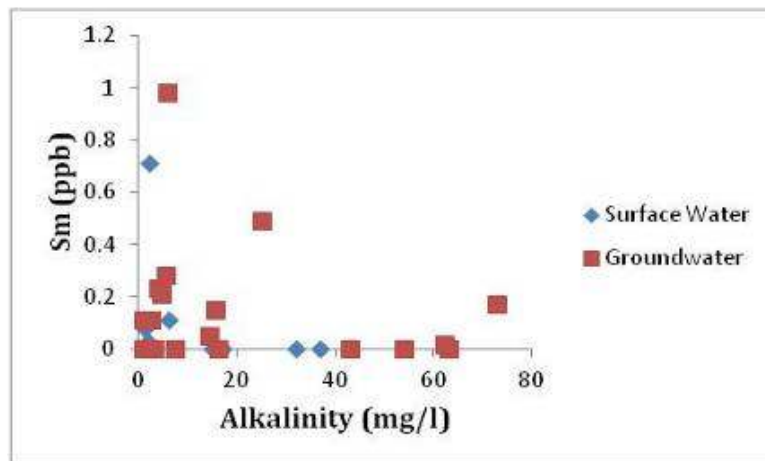
Rare earth elements speciation findings in this study square with those obtained by [29,28] that rare earth elements carbonate complex dominate rare earth elements speciation in natural waters of neutral to high pH.

4.4.1 Rare earth elements mineral saturation indices

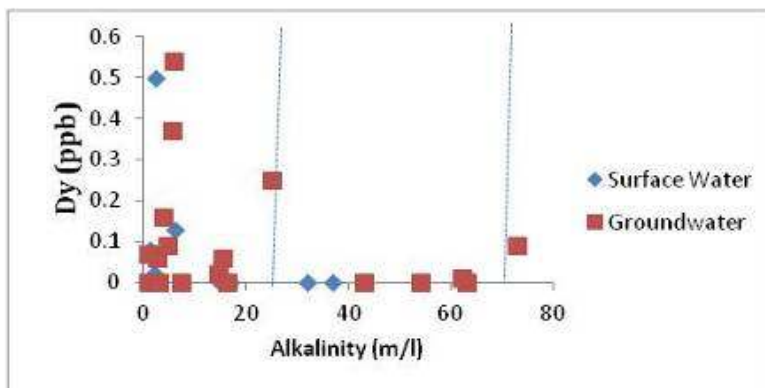
Mineral saturation indices are used to indicate what minerals might be dissolving or precipitating into groundwater or from the standpoint



(a)



(b)



(c)

Fig. 9. Showing concentration of Nd, Dy, Sm versus alkalinity

of controlling groundwater composition [8]. Calculation of saturation indices in this study using VISUAL-MINTEQ demonstrated that in borehole water samples, oversaturated minerals at $S>1$ are Ce Dy Gd La Nd Pr Sm (PO_4). Equilibrium saturated minerals ($S=0$) were Er Ho Lu Tb Tm(PO_4) and $\text{GdPO}_4 \times \text{H}_2\text{O}$ while at under saturated mineral ($S>1$) phase it was with respect to Ho Sm Lu Gd Er Dy Ce (OH_3), La Gd (CO_3), and Sm Er Eu Ce Tm Tb (F_3). This may be due to co precipitation. In streams, springs and river sources, modeling unfolded that rare earth elements minerals were over saturated with respect to Ce Er Nd Gd Ho Sm Tb La (PO_4)₃ and $\text{GdPO}_4 \times \text{H}_2\text{O(s)}$. Equilibrium or near equilibrium saturation minerals ($S=0$) were with respect to Dy Tm (PO_4) and $\text{YbPO}_4 \times \text{H}_2\text{O}$. under saturated ($S<0$) minerals were with respect to Ce Dy Eu Gd Pr Sm (OH_3), Dy Eu Gd La Sm Yb (CO_3)₃, Pr Sm Tb Nd La Eu Ho Dy (F_3) and Gd Yb ($\text{F}_3 \times \text{H}_2\text{O(s)}$).

Oversaturated and equilibrium rare earth elements minerals species in surface and groundwaters are dominantly phosphate (PO_4) complex ligands which shows that such minerals are mobile under the prevailing condition of pH and Eh regime. Under saturated mineral species were dominantly (CO_3)₃ and F ligands. The oversaturated rare earth elements were dominantly light rare earth elements minerals (Ce Eu Gd Nd Pr La (PO_4)). There may be basnasite mineral which contains abundant LREE found in carbonatites, granites, and pegmatite which are common rocks in the study area. Near equilibrium saturation minerals were mostly heavy rare earth elements (Er Ho Lu (PO_4), Tb TmSO_4). This may be zentotime rare earth elements mineral, because it contains abundant heavy rare earth elements and typified by phosphate radical. The under saturated rare earth elements mineral constituted of both light and heavy rare earth elements [19] in surface water the oversaturated rare earth minerals were in the same proportion of light to heavy rare earth elements.

4.5 The Behavior of Rare Earth Elements in Water

Rare earth elements have proved to be powerful tools as hydrogeochemical tracers. Figs. 8 and 9 are plots of pH and alkalinity versus Neodymium (Nd), Samarium (Sm) and Dysprosium (Dy) concentrations for the groundwater samples. The plots revealed an inverse relationship with alkalinity. High rare earth elements

concentrations are recorded in the regions of lower alkalinity groundwater. At higher alkalinity values lower concentration of Nd, Sm and Dy were observed. Water types in the area through this plot can be classified into type, which is recharge water that recorded the highest level of REE. The water type with the lowest concentration of rare earth elements is classified as groundwater type 2. Starzinski [15] made a similar discovery to this study. They plotted REE versus pH and alkalinity separately and obtained similar relationships. Plots of the Oban Massif aquifer groundwater data exhibited disparate water groups described in the foregoing. It has been noted that the distinction between low pH and higher rare earth elements are not clear-cut as obtained in rare earth elements versus alkalinity plots (Figs. 8 and 9).

5. CONCLUSION

Water source in the study area has low to medium pH range and the water type is dominantly of the hydrochemical facies Ca+Mg, $\text{Cl}+\text{SO}_4^{2-}$ in both basement sedimentary regions. The abundant rare earth elements in the study area are Ce, La, Gd, Nd, Sm and Pr. The rare earth elements with the highest concentration are Cerium (Ce) and Lanthanum (La) and REE with the least concentration are Lutetium (Lu) and Holmium (Ho). Results indicated that the provenance of rare earth elements in the area is granitic rocks. The dominant complexing ligand in aqueous speciation of groundwater in the area is carbonato complex (LnCO_3^+), but free ionic species dominate in surface water. The parameters pH and alkalinity are the major factors controlling that control aqueous speciation of rare earth elements in the area. The water types in the area have been discriminated into recharge (type 1) and discharge (type 2) using pH, and alkalinity plots. At low pH REE are mobilized and decrease at high pH values. At low alkalinity high REE are mobilized while at high alkalinity low REE are mobilized. Light rare earth elements are more fractionated than heavy rare earth elements. On the contrary REE normalized to PAAS show more fractionation of heavy rare earth elements than light rare earth elements in the study area. Oversaturated and equilibrium mineral species are dominantly phosphate complex ligands (LnPO_4) in both surface and groundwater. The under saturated mineral species were predominantly Carbonate ligands (LnCO_3)₃, F) minerals. The oversaturated rare earth elements were Ce Eu, Gd, Nd, Pr La (PO_4). Rare earth elements are more bioavailable as

organic compounds than inorganic compounds. Rare earth elements concentration in water samples in the study area are within acceptable limits for potable water.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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