Chemical speciation and complexation modeling of trace and rare earth elements in groundwater of Oban Massif and Mamfe Mbayment southeastern Nigeria

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ABSTRACT
Chemical speciation was carried out on trace and rare earth elements on trace and rare earth elements data on water samples in Oban Massif and Mamfe Mbayment southeastern Nigeria. Product moment correlation showed significant correlation at r>0.7 between REEs Pr and Nd, Pr and Lu, Sm and Nd, Sm and Pr, Tb and Nd, Tm and Tb, and Yb and Nd. Speciation modeling result showed that free metal ionic species dominated boreholes and spring water samples. The predominant trace metal complex is the OH- ligand. Trace elements mineral saturation indexes in boreholes at over-saturation (S>1) predicted more mineral species than equilibrium saturation (S=0). Rare earth elements mineral oversaturation (S>1) in boreholes predicted least mineral species. Undersaturation (S<1) predicted highest range of rare earth elements minerals. Springs and streams at S>1, predicted more mineral range than equilibrium (S=O) while mineral prediction at S<1 were the highest. Rare earth elements are precipitated at undersaturated condition in the study area.

1. Introduction
There is considerable interest in using trace and rare earth elements as tracers of geochemical processes. Rare earth elements in solution primarily exist as complexes with halides, sulphate, phosphate, hydroxides, carbonates, DOC or as free ions. Chemical species of elements or group of elements have a direct bearing on their environmental chemistry and reflects their mobility, bioavailability to living organism as well as their potential toxicity. Chemical speciation shows the distribution of a chemical element between different molecular ionic forms in water [1,2,3 and 4]. For surficial conditions there is considerable interest in using trace and rare earth elements patterns of minerals and natural waters to decipher water-rock interactions in streams, soils, and aquifer [2].

The geochemistry and bioavailability of trace metals are strongly influenced by speciation. Trace metals exhibit a variety of aqueous and particulate species. In aqueous environment metals can associate with a range of ligands such as OH−, Cl−, SO4−, HCO3−, and F− to form complexes [5]. Rare earth elements species model can be used to predict their predominant complexation with organic and inorganic ligands [6]. Rare earth elements are commonly used as geochemical tracers in groundwater flow systems owing to their commonly reported similarities between their inputs normalized REE patterns and those of the aquifer rocks/sediments through which they flow and react [7]. It is revealed that groundwater inherit rock like REE fractionation patterns near the end of the flow paths prior to discharge [7]. One most important factor affecting rare earth elements and other heavy metals in natural water is complexation with dissolved inorganic and organic ligands. Complexation reactions exert important controls on the mobility, effective solubility, reactivity and toxicity of trace metals in the environment [8].

Unfortunately, solution complexation involving naturally occurring organic and inorganic ligands is poorly understood for most trace metals including REE in natural waters in the study area. However, Ekwere and Edet [4], examined speciation of selected heavy metals (Fe, Mn, Ni, Pb, Cd and Cr in groundwater of Oban Area, but a detailed chemical speciation of heavy and rare earth elements in the study area is nonexistent. The ultimate goal of this study is to model chemical speciation of an array of heavy metals and REE to predict mineral solubility and precipitation in the area. Also to ascertain the percentage total concentration and distribution of trace and rare earth elements mineral species and their saturation indices in the study area.

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1.1 Study area description

The study area Oban Massif and parts of Mamfe Embayment lies between the coordinates of latitude 05° 18.57.7 N to 05° 05 26.8 and longitudes 08° 34.39.4 to 08° 05 20.5 E (Figure 1). The area lies at a high elevation of 460 m in Oban area north east of the study area and a lowest elevation of 33 m in the southern part of the study in the sedimentary Mamfe Embayment characterized by sandstones in the central Cross River. There are isolated hills found in the eastern area of the massif. The area is characterized by two major relief features; viz highland and the flanking lowlands. The crystalline basement complex lies at an average height of about 150 m rising gradually from south to northwards and falls away towards the north. The high lands have elevations in excess of 400 m above sea level. By contrast, the lowlands have elevations with an average of 350 m. The western Oban Massif has a subdued topography with settlement swamps along the banks of the extensive rivers crisscrossing the area. The drainage is controlled by weathering fractures and joints trends. Drainage in the Oban Massif flows southwards, seawards and northwards to join the upper course of the Cross River in the Ikom depression [9]. Vegetation in the area is of the tropical rainforest type. The area experience tropical climate with dry and wet seasons with an annual rainfall of about 2000 mm and temperature range from 28°C to 36°C. Relative humidity and evaporation are reported by CRBDA [10] to be 76.86% and 385 mm/day respectively.

Figure 1. Location map of the study area.
1.2. Geology and hydrogeology

Basement and sedimentary rocks characterize the study area. In Oban Massif, rocks such as biotite garnet hornblende gneiss, kyanite gneiss, migmatite gneiss, granite gneiss and biotite hornblende gneiss are common in the area [11]. Charnokitic rocks in the area exhibit granite facies metamorphism [12]. Syntectonic granitoid known as Uwet granodiorite are common in the western Oban Massif [13]. Green schist facies dominate the western Oban Massif and are the most ubiquitous in the field which contain zonoliths and enclaves of other rocks [14]. The Eze Aku Group in the Mamfe Embayment shows sandstone ridges. The sandstones are calcareous and are of Late Turonian (Figure 2).

Transmissivity values ranged from 41,065–725.88 m²/day [15]. Okereke et al [16–19], found out that the top layer is less than 5 m thick and a section of the overburden is the aquiferous unit in the study varying between 15 to 70 m but generally not

Figure 2. Geological map of the study area.
The depth to water table is estimated at 3 m of the observed depth. The groundwater is unconfined and the aquifer is recharged directly by precipitation. Well yield of 1.9 l/s is estimated at a depth of 24 m.

2 Materials and methods

2.1 Instruments

Physical parameters such as pH, temperature, electrical conductivity, turbidity and total dissolved solids were measured in situ using standard field equipment such as Mercury – in – glass thermometer, digital mv Redox pH meter, conductivity meter, WA 3000, and spectrophotometer Dr 3000 respectively. All instruments were used in Calabar Nigeria. Major anions and cations were analysed using titration, chromatography and flame test respectively. Domestic RO purifier manufactured by Aquapuro Equipment Private Limited in Chunnabhatti Mumbai was used in filtering the water samples.

Trace and rare earth elements were analysed using inductively coupled argon mass spectrometer. The operating conditions of inductively coupled plasma argon mass spectrometer include sample uptake rate 1 ml/min, auxiliary argon flow rate 0.61 L/min, coolant argon flow rates 16.11 L/min, Spray chamber-ESI PC3 quartz, Nebulizer argon flow rate 0.88 L/min, torch quartz thermos fisher, RF power coil 1250 W, Nebulizer Teflon 100 μl, cones-nickel, radial and axial view, plasma, grating, entrance and exit slits and detectors. All analysis were done at ACME analytical Laboratories Ltd Vancouver Canada. The samples were transported from Nigeria to Canada through an affiliate Laboratory in Ibadan known as Oyeoshin Petroc Services Ibadan.

2.2 Sample preparation

Water samples were collected using prewashed polyethylene bottles. Prior to sample collections, all sample bottles were rigorously cleaned using trace elements free sample containers. The bottles were first tripled washed with distilled deionized water and then placed in a 10–20%v/v reagent grade nitric acid bath for 7 to 10 days. Water samples from boreholes, streams springs and river were collected from various sample locations from eastern to western parts of Oban Massif (Figure 3). Each sample bottle was rinsed three times with the water being sampled. Water samples for trace and rare earth elements analysis were immediately acidified to pH < 2 with ultrapure nitric acid with concentration of 15.8 M HNO₃ and 70% w/w of 63 mL manufactured by Adash chemicals Chennai India. Samples for major solutes were collected identically, only a drop of pure nitric acid was used to preserve the cations. Samples collected for anions analysis were not acidified at all.

2.3 Method of analysis

Anions such as nitrate (NO₃⁻), Chloride (Cl⁻), Bicarbonate (HCO₃⁻) sulphate (SO₄²⁻) and Phosphate (PO₄³⁻) were analyzed as follows: Nitrate was determined using PD303UV spectrophotometer. A known volume of 50 mL of sample was pipette into porcelain dish and evaporated to dryness in a hot water bath. 2 mL of phenol disulphonic acid was added to dissolve the residue by constant stirring with a glass rod. Concentrated solution of sodium hydroxide and distilled water was added with stirring to make it alkaline. This was filtered into Nessler’s tube and made up to 50 mL with distilled water. The absorbance was read at 410 nm a spectrophotometer after the development of a red color. The value of nitrate was found by comparing absorbance of sample with the standard curve and expressed in mg/L. For chloride determination, 100 mL of the clear sample was pipette into an Erlenmeyer flask and the pH adjusted to 7–10 m with either H₂SO₄ or NaOH solution. The level of K₂Cr₂O₇ was titrated and a reagent blank established. A blank of 0.2–0.3 mL is usual for the method. In determining sulphate a 250 cm³ of the water was evaporated to dryness on a dish. The residue was moistened with few drops concentrated HCl and 30 cm³ distilled water added. This was boiled and filtered. The filtered paper was washed with several portions of distilled water and both filtered titrate and washings added together. This was heated to boiling and then 10 cm³ of 10% BaCl₂ solution was added drop by drop with constant stirring. The mixture was digested for about 30 m filtered and the filter paper washed with warm distilled water. It was then ignited cooled and weighed in an already weighed crucible. Similar procedure was adopted for other anions.

Inductively coupled mass spectrometer works under the principle of atomic excitation for analyzing cations. A solution is aspirated into a thermal environment, creating a cloud of completely atomized elements that are excited through collision process which release electrons to an excited state. As atoms decay back to the ground state, characteristic radiation is released in the form of light energy. The characteristic resonance lines are then detected by a spectrometer. The ICP creates a thermal environment through the interaction of ionized argon gas and radio frequency field to form argon plasma. The temperature of the atoms ranges between 400–800°C and is sufficient to atomize almost all the elements in a sample. Further, the argon plasma is close to an ideal plasma.
thermal source, providing a high degree of excitation and multiplicity of resonance lines from which to quantify elemental concentrations.

2.4 Geochemical modeling

Geochemical modeling is used to predict chemical reactions among solutions, minerals, gases and inorganic and organic matter in aqueous systems. The fundamental behind geochemical modeling is that the analysis of water samples reflects the chemistry of groundwater sampled. Modeling in this study was to assess water quality issues. The geochemical code VISUAL MINTEQ was used in this study to examine which mineral dissolve or precipitate and prediction of water quality. Geochemical speciation modeling provides information on qualitative assessment of saturation indices (SI) for mineral phases which may be reacting within the water-rock system. The rules for saturation indices are as follows: (1) If SI< 0 and a specified mineral is present, the mineral could be dissolving but cannot precipitate; (2) SI> 0, the mineral could precipitate but cannot dissolve (3) if SI = 0, the mineral could be precipitating or dissolving to maintain equilibrium.

VISUAL MINTEQ can be used as an initial solution speciation code to calculate saturation indices, and total concentration of or total element valence concentration. Speciation modeling of REEs in Oban Massif aquifer groundwater were primarily to evaluate the importance of Carbonate (LnHCO$_3^-$, LnCO$_3^-$ and Ln (CO$_3$) and phosphate (LnH$_2$PO$_4^{2-}$, LnHPO$_4^{3-}$, Ln (HPO$_4$)$_2$ and LnPO$_4^{-}$) complexes, where Ln stands for trace or rare earth elements. For detail description of the model used in this study see Johanesson and Lyons, (17)

**Figure 3.** Sample location map of the study area.
VISUAL MINTEQ version 2.3 was developed by the department of Land and water Resources Engineering of the Royal Institute of Technology in Stockholm and is a window version of MINTEQA2 version 4 released by US EPA in 1992. MINTEQA2 is an equilibrium speciation model that can be used to calculate equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems (18). Visual MINTEQ 2.3 is useful in calculating (a) concentrations and activities of inorganic species (mol/L). (b) Molar percentage distribution among dissolved and adsorbed species of every component added. (c) Saturation indices of minerals for each solid, the saturation index (SI) and the stoichiometry and mineral components given. Amount of finite solids (mol/L) calculated of non-dissolved finite and possible solids that remains after equilibrium and (e) Equilibrium mass distribution among dissolved species, adsorbed species and multiple solid phases.

The calibrated parameters measured are Volta metric peak currents (IP) in a sample aliquot over a range of total metal concentration (M) sufficient to titrate inorganic ligands. A plot of IP on a linear graph and estimated slope S^IC at high (M) T.

In calibrating once titration is completed, typically a set of model parameters, including sensitivity S and one or more sets of Ki-(L)T pairs is filtered by performing a series of data analysis/modeling steps. As first step the measured peak current IP for each aliquot is plotted against the total concentration (M) T and a line fitted through the high (M) T part of the curve.

When the weakest ligands in the sample are completely titrated the slope of this line S^IC is equal to sensitivity S, the methods true sensitivity to the measured species. Deriving S from the slope of the IP-(M) T plot in this fashion is termed internal calibration (19). Values of titration data used are as follows MT (1,3.1,8,2,4, 3.3, 4.4, 5.9, 7.9, 11, 14, 14, 19, 26, 34, 46, 62, 83, 112, 150, 202 and 271) and IP (0.014, 0.024,0.033, 0.046, 0.048, 0.073, 0.10, 0.16, 0.21, 0.33, 0.54, 1.0, 2.8, 8.8, 20, 37, 60, 91 and 132).

### 3 Results and discussion

#### 3.1 Statistical summary of physicochemical parameters, trace and rare earth elements

Statistical summary of physicochemical parameters, trace and rare earth elements are presented in Tables 1 and 2 respectively. Certified reference materials compared with the present study are presented in Table 3. In Table 1 pH ranged from 5.61–7.20 with a mean of 6.41, exhibiting acidic condition this may be due to weathering of feldspars and dissolution of CO₂ from the atmosphere. Levels of EC had a mean of 547 µs/cm. carbonate dissolution contributes to EC level. Total dissolved solids had a mean of 325.75 mg/L and ranged from 27–1501 mg/L; this may be due to dissolution of sulphates, calcium carbonates and bicarbonates. Turbidity recorded a mean value of 4.11 NTU and ranged from 0–42 FTU. High turbidity values could be due to suspended

| Element | Mean | Standard deviation | Median | Minimum | Maximum |
|---------|------|--------------------|--------|---------|---------|
| pH      | 6.42 | 0.54               | 6.49   | 5.61    | 7.20    |
| Ec (µs/cm) | 547.88 | 977.55             | 181    | 0.01    | 3429    |
| eh (mv) | 15.86 | 5.41               | 16     | 7       | 24      |
| Turbidity (FTU) | 4.11 | 7.64               | 2      | 0       | 41      |
| Temperature °C | 26.69 | 1.48               | 26     | 25      | 29.4    |
| TDS (mg/L) | 325.75 | 479.48             | 122    | 27      | 1501    |
| F^−  | 20.08 | 43.91              | 0.007  | 0.0     | 220     |
| Br^−  | 10.53 | 11.97              | 7      | <5      | 43      |
| Cl^−  | 173.14 | 333.93             | 40.23  | 1.1     | 1060    |
| P^5−  | 41.23 | 36.26              | 32     | <10     | 110     |
| S^6+  | 4.52  | 8.60               | 1      | <1      | 36      |
| B^3+  | 14.93 | 30.04              | 5      | <5      | 157     |
| NO₃^−  | 3.28  | 2.22               | 4.42   | <0.02   | 5.03    |
| SO₄²− | 24.05 | 46.63              | 5.64   | 0.51    | 1.49    |
| PO₄³−  | 0.32  | 0.90               | 0.002  | <0.05   | 4.5     |
| HCO₃^-  | 17.37 | 23.96              | 6.81   | 1       | 89.1    |
| Mg²⁺  | 2.82  | 4.30               | 1.16   | 0.48    | 23      |
| Na⁺   | 12.31 | 25.89              | 4.82   | 1.30    | 144     |
| Ca²⁺  | 12.94 | 23.69              | 4.17   | 0.71    | 28.54   |
| K⁺    | 6.51  | 14.41              | 2.12   | 0.87    | 79.07   |
| Al³⁺  | 177.41 | 289.95             | 75     | <0.05   | 1328    |
| Fe²⁺  | 0.407 | 0.972              | 3.8    | <0.05   | 4.964   |
| Cu²⁺  | 1.078 | 1.101              | 0.74   | <0.05   | 4.60    |
| Zn²⁺  | 0.52  | 0.74               | 0.29   | <0.02   | 1.66    |
| Ni²⁺  | 2.81  | 5.63               | 1.5    | <0.05   | 5.4     |
| Cr³⁺  | 17.61 | 23.89              | 9.4    | <0.05   | 113.7   |
| Mo⁶⁺  | 44.71 | 5.12               | 27.09  | <0.05   | 188.2   |
| Mo⁵⁺  | 0.29  | 0.42               | 0.1    | <0.1    | 1.8     |
| Pb²⁺  | 3.97  | 3.49               | 3.8    | <0.1    | 11.2    |
| Zn²⁺  | 5.20  | 5.78               | 4      | <0.1    | 22.92   |
| Zn²⁺  | 31.42 | 31.31              | 28.2   | <0.05   | 128     |
Table 2. Summary rare earth elements (REE) concentration (µg/L) in water.

| Parameter | Mean | Std  | Median | Minimum | Maximum |
|-----------|------|------|--------|---------|---------|
| Ce        | 0.98 | 1.49 | 0.23   | < 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 | 0.06 | 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. Comparison of certified reference material values with present study.

| Element | Reference compiled CASS (mg/kg) | This study (µg/L) | Element | Reference compiled MX014 Australia waters | This study (µg/L) |
|---------|--------------------------------|------------------|---------|------------------------------------------|-----------------|
| La      | 9.37 ± 0.38                    | 0.56 ± 0.94      | Fe      | 22.43 ± 0.34                             | 40.73 ± 9.18    |
| Ce      | 4.69 ± 0.92                    | 0.98 ± 1.49      | Cd      | 1.363 ± 0.036                            | 1.078 ± 1.101   |
| Pr      | 1.33 ± 0.06                    | 0.15 ± 0.23      | Co      | 2.961 ± 0.070                            | 0.52 ± 0.74     |
| Nd      | 5.39 ± 0.06                    | 0.66 ± 0.06      | Cr      | 2.701 ± 0.077                            | 2.81 ± 5.63     |
| Sm      | 5.55 ± 0.17                    | 0.14 ± 0.22      | Cu      | 2.99 ± 0.27                              | 17.61 ± 23.89   |
| Eu      | 0.23 ± 0.03                    | 0.21 ± 0.03      | Mn      | 1.53 ± 0.16                              | 4.475 ± 5.20    |
| Gd      | 1.29 ± 0.1                      | 0.13 ± 0.22      | Mo      | -                                        | 0.29 ± 0.42     |
| Tb      | 0.20 ± 0.03                    | 0.02 ± 0.03      | Ni      | 3.78 ± 0.12                              | 3.97 ± 3.49     |
| Dy      | 1.41 ± 0.08                    | 0.09 ± 0.04      | Pb      | 2.55 ± 0.69                              | 5.20 ± 5.76     |
| Ho      | 0.38 ± 0.05                    | 0.019 ± 0.022    | Zn      | -                                        | 31.42 ± 3.31    |
| Er      | 1.20 ± 0.01                    | < 0.05 ± 0.75    | -       | -                                        | -               |
| Tm      | 0.23 ± 0.07                    | 0.02 ± 0.026     | -       | -                                        | -               |
| Yb      | 1.21 ± 0.14                    | 0.04 ± 0.05      | -       | -                                        | -               |
| Lu      | 0.20 ± 0.03                    | 0.01 ± 0.005     | -       | -                                        | -               |

(After Lawrence et al (39); Bayon et al (40))
3.2 Normalised aqueous trace elements pattern

The geochemical processes influencing the fractionation of heavy metals in groundwater systems due to rock water interaction can also be better appreciated when normalised to the waters in which the water reacts with. Figure 4 shows the normalized heavy metals plots with Post Archaen Australian Shales (PAAS) in the eastern and western flanks of the Oban Massif. The normalized heavy metals at locations 26, 28 and 29 in the western flank of the Oban Massif showed enrichment of Sr, Cu, Zn and Ba which are common in the sedimentary terrain. Normalised heavy elements in locations 1, 9, 6 and 12 in the eastern flank of the Oban Massif which is in a basement geologic setting show a depletion of Rb, Sr, Ba, Pb, Cu and Zn. Normalised trace element pattern (Figure 4) show enrichment of Rb, Sr, Ba, Cu, and Zn. This is evidence of rock–water interaction in producing the geochemistry of this water. These metals are commonly found in sedimentary areas indicating the presence of carbonate rock aquifer confirming that the locations are found in sedimentary environment.

In the basement the normalized trace elements show that Rb, Sr, Ba, Pb, Cu and Zn have low enrichment because it is a different geologic environment. This shows that as the groundwater migrate downgradient to the sedimentary area there was enrichment in transition metals, alkaline and alkaline earth metals. The transition metals patterns remain constant as groundwater flows from recharge to discharge areas. Throughout the length from the recharge to the discharge zone to about 80 km point of flow the metals patterns remain constant along the flow path. The elements Rb, Ba and Pb are likely from feldspars while Ca and Sr are from carbonates. Metal fractionation patterns at the basement areas were basically constant. This may be due to adsorption, coprecipitation and mobility. Samples from different boreholes show excellent reproducibility.

Rare earth elements concentration (Table 2). Rare earth elements are classified into light rare earth elements (LREE) (Cerium, Europium, Erbium, lanthanum, Neodymium, Samarium, and Praseodymium) and heavy rare earth elements (HREE) (Dysprosium,
Lutetium, Thulium, ytterbium, Harmonium, and Yb. Lanthanum (La) ranged from < 0.01 to 4.5 ppb with a mean of 0.5 ± 0.94 ppb. Lutetium (Lu) portrayed a range from < 0.01 to 0.3 ppb with a mean of 0.011 ± 0.005. Neodymium (Nd) possessed a mean of 0.66 ± 1.06. Praseodymium (Pr) showed a concentration range from < 0.01 to 1.02 ppb with a mean of 0.15 ± 0.23. The REE Samarium (Sm) recorded a mean of 0.14 ± 0.22 and ranged from < 0.02 to 0.98 ppb. Terbium (Tb) concentration varied from < 0.01 to 0.11 ppb with a mean of 0.02 ± 0.026. The mean level of Thulium (Tm) ranged from < 0.01 to 0.03 ppb and had a mean of 0.012 ± 0.005 ppb. Ytterbium (Yb) concentrations ranged from < 0.01 to 0.18 ppb with a mean of 0.036 ± 0.05 ppb.

Rare earth elements recorded lower concentrations in water samples than trace elements. This may be due to leaching, pH, redox conditions, co-precipitation and aqueous complexation of rare earth elements in water [25,26]. Also rare earth elements solubility depends on the solution and relates to the differences in the stability of soluble complexes of elements [27]. It has been established that reductive dissolution of Fe-Oxyhydroxide would result to a preferentially scavenged light rare earth elements into groundwater [28,29]. The relatively high concentration of light rare earth elements in this study may be due to the presence of monazite which principally contains light rare earth elements [30], while lack of the mineral xenotime may explain why heavy rare earth elements have lower concentration in the study. Cerium contains relatively higher concentrations than other rare earth elements in this study. This may be due to dissolution of Cerium under reducing conditions and the presence of the mineral allanite and monazite which are cerium containing minerals [31].

It is proven that the most plentiful rare earth element in the earth crust are Cerium (Ce) and Ytterbium (Y) and the rarest of all the REE is Thulium(Tm) [32]. Elevated concentrations of lanthanum (La) may be due to enrichment of La containing minerals such a monazite during rare earth elements fractionation [33]. Very low concentration of HREE (Lu and Ho may be explained by the presence of basnaesite which contains very low heavy REE [30]. Common igneous rocks such as carbonatite, granite, and pegmatite are common in the area. Levels of LREE superseded the HREE probably due to solution complexation behavior which contributes to preferential discharge of the light REE to groundwater and reabsorption of the HREE at sediment surface [34]. Heavy REE elements are mobile at high pH [35]. The overall rare earth elements levels in this study are low and broadly similar to other circumneutral pH groundwater [36 and 28]. The lowest REE level in the study is that of Europium (Eu) a light REE and its source is plagioclase feldspars. This may be due to scavenging, co precipitation, insolubility and complexation [28]. Nguyet [37], posited that the principal factors that control REE release is from weathering phases, pH and redox status, adsorption complexing ligands in groundwater and hydrogeological conditions.

### Table 4: Correlation matrix of rare earth elements in water samples from the study area.

| Alk  | pH  | Ce  | Dy  | Er  | Eu  | Gd  | Ho  | La  | Nd  | Pr  | Sm  | Tb  | Tm  | Yb  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1    |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Alk  | 0.204 | 0.204 | 0.017 | 0.017 | 1   |     |     |     |     |     |     |     |     |     |
| pH   | 0.050 | 0.110 | 0.070 | 0.070 | 0.260 | 0.310 | 0.210 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 |
| Ce   | 0.118 | 0.050 | 0.330 | 0.120 | 0.130 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 |
| Dy   | 0.010 | 0.310 | 0.090 | 0.110 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 |
| Er   | 0.100 | 0.330 | 0.110 | 0.100 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 | 0.910 | 0.090 | 0.307 |
| Eu   | 0.210 | 0.310 | 0.120 | 0.130 | 0.140 | 0.130 | 0.100 | 0.100 | 0.130 | 0.100 | 0.100 | 0.130 | 0.100 | 0.100 | 0.130 |
| Gd   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Ho   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| La   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Nd   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Pr   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Sm   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Tb   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Tm   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |
| Yb   | 0.110 | 0.307 | 0.910 | 0.910 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 | 0.940 |

3.3 Correlation analysis

A quantitative measure of the strength or degree of relationships between rare earths elements was computed using the computer statistica software and the result of the correlation of all parameters in water are presented in Table 4.

Generally, some parameters had very high correlation coefficient implying that their concentrations in the water and sediments were highly related. However, high correlation does not necessarily denote that there are relationships between variables, because of the interplay of other existing factors [38,39]. The type of correlation used in this study is
the product moment correlation which assesses the relationship between variables.

Product moment correlation was used to assess the relationship between variables. Variables exhibiting significant correlation at $r > 0.7$ are strongly correlated, on the other hand, relationships at $r < 0.5$–0.7 are said to be moderately correlated. At significance of $r \leq 0.5$ are not significantly correlated. In Table 4 significant correlation is between rare earth elements: Pr and Nd ($r = 0.93$), Pr and Lu ($r = 0.980$), Sm and Nd ($r = 0.980$), Sm and Pr ($r = 0.950$) Tb and Pr ($r = 0.830$), Tm and Tb ($r = 0.940$), Yb and Nd ($r = 0.830$), at $p < 0.05$ Tb and Nd, Tm and Sm, Yb and Tb (Table 4). There was no much significant correlation between trace elements.

Negative correlation shows that as one parameter is decreasing the other is increasing and vice versa. The rare earth elements were more significantly correlated at $p \leq 0.01$ than those at $p \leq 0.05$ showing their high degree of relationship.

### 3.4 Chemical speciation modeling

Ground waters likely inherit their dissolved trace and rare earth elements signatures in part from the aquifer materials they react with [31,40], and also from sorption desorption process. It is crucial to understand the aquifer material chemistry and solution chemistry in order to determine controls and roles of both the rare earths and trace elements signatures of water systems [41]. The geochemical software VISUAL MINTEQ was used to calculate distributions of aqueous species and mineral saturation indices from the analysed groundwater concentrations. The geochemical software VISUAL-MINTEQ was used in this study due to its extensive database of mineral and aqueous species for interpretation purposes, relative to PHREEQC [4].

#### 3.4.1. Trace element speciation and complexation modeling

Speciation modeling of a few potentially toxic trace elements (Fe, Pb, Cd, Ni, Cr and Mn) in Oban area was conducted by Ekwere [9], and [4]. In this study, an extensive list of heavy metals was modeled to determine their mineral distribution, concentration, fractionation and complexation in groundwater.

Trace elements fractionation in boreholes in this study are predominated by free metal species ranging from 69–99% of Al, Ba, Cd, Co, Cr, Cs, Cu, Ga, Li, Mo, Sb, Ti, V and Zn. With exception of Aluminum, Chromium, Mo, Sb, U and V that their free metal species percentage is less than their complexes. This is in agreement with the findings of Ekwere and Edet [4], while the metal fractionation is mostly by free ion species. Free ion species are the most bioavailable and toxic form of trace elements that exist in natural water [4]. The predominant trace metal complexing ligands are the $T(OH)_n^-$, where $T$ stands for the trace metal. They have a percentage range from 41.76–99.96%. The complex $Al(OH)_4^-$ had a percentage of 41.76% and $Ga(OH)_4^-$ at 99.96%. The $OH_3^-$ complexes are $Al(OH)_3$ at 18.57%, $Sb(OH)3$ at 99.94%. Ba, Cd, Co, Cu, Ga, Li, Ni, Pb, Rb, Ti, Y, V and Zn occurred predominantly as free metal ionic species at a range of 47.99%. The carbonate complex $PbCO_3$ occurred mostly in $PbCO_3$, $PbHCO_3$, $NiCO_3$, $NIHCO_3$, $CuCO_3$, and $CoCO_3$ at percentages between 0.02–4.7 percent. Sulphate ($SO_4^-$) and nitrate ($NO_3^-$) complexes were very low and almost negligible.

In springs and streams, free metal ionic species had a dominant percentage $Ca^{2+}$ (99.13%), $Mg^{2+}$ (98.92%), $K^+$ (99.87%) and complexed with $OH_2^-$ to form $A(OH)_x$ at 49.7% as the dominant complex. $Al(OH)^2^+$-complexed at 15.94%, $Al(OH)_2^+$ at 1.18%. $Al(OH)CO_3^-$ at 3.77%. Other trace metals in springs and streams were reported not available. This may be due to leaching and co precipitation of these trace elements in the water sources.

#### 3.5 Rare earth elements complexation

The dominant rare earth elements complexing ligands in borehole water in this study is the carbonate ligand, showing that the rare earth elements are dissolved or leached in form of carbonate ligands. The predominant carbonate complex $LnCO_3^{2-}$ had a percentage of 19.67% of dissolved rare earth elements. Significant $CO_3^{2-}$ complexing is possible at pH < 6 [42], and the study area is characterized by this pH range. Most workers reported that rare earth elements carbonate complex dominate rare earth elements speciation in natural waters of neutral pH [43,44].

The complexing REE ligand $Ln(CO_3)_2^{2+}$ had a percentage range 0–3%. The $LnCO_3^{2-}$ complex accounted for 3–5% and free metal ionic species $Ln^{3+}$ accounted for 21–50% of dissolved rare earth elements. Where $Ln^{3+}$ represent rare earth element. Sulphate complex had a negligible percentage range from 0.0–0.1% while $LnSO_4^{2-}$ had a ranged from 5–22% sulphate complex with lanthanum (La) as $LaSO_4^{2-}$ had a percentage of 22.77% which is the highest in sulphate complexes. This may be due to its solubility or aquifer type. This complex is found in CePO$_4$, GdPO$_4$ and YbSO$_4$. The level of phosphorous is very low in Oban Massif. Phosphorous is extremely insoluble [45] hydroxide (OH) complex $LnOH$ accounted for less than 1% while LnF and LnCl$_2$ are negligible due to their immobility and insolubility.

In springs, metals species ($Ln^{3+}$) were dominant accounting for 77–92% of dissolved free species. Sulphate complex such as $LnSO_4^{2-}$ was between 3–4% of rare earth elements fractionation. This may be due to rare earth elements solubility in water and acidic metavolcanic rocks. The LNF had percentage between 0.6% while $LnOH^-$ had a percentage range
LnCO$_3^+$ complex was between 0.03%-0.3 percent which is lower than that in boreholes. This may be due to acidic crustal rocks such as pegmatite, basalt, granodiorites and lateritic overburden soils. In springs, LnHCO$_3^-$ complex ranged from 0.01-0.3%. This is blatant that rare earth elements are dissolved as free metals species predominantly in streams and springs followed by LnSO$_4^{2−}$ complex. Rare earth elements in strongly acidic waters are dissolved mainly as free ions or as sulphate ion pairs [34]. Negligible percentage of LnCl, LnNO$_3^−$, and LnPO$_4^−$ may be due to its mobility and insolubility. Inorganic ligands such as PO$_4^{3−}$, CO$_3^{2−}$, HCO$_3^−$ and Cl$^-$ tend to form more stable complexes with heavy rare earth elements due to their smaller ionic radii [27].

3.6 Mineral saturation indices

When saturation index is less than 1 (S < 1), it shows under saturation, at S = 0 the mineral is at equilibrium, while at S > 1 the mineral is oversaturated. In borehole water samples oversaturated (S > 0) mineral species predicted include an antlerite, barite, boehmite, brochonite, diasporite, gibbsite, hydromorosite, langite, malachite, sernanomite, tennorite, tsumebite, vanterolite and zincite. At equilibrium saturation (S = 0) mineral saturation in equilibrium in boreholes were with respect to cerussite, hydroxyl, pyromorphite, larnalate, smithsonite and otavite. At undersaturation (S < 1) the minerals species predicted were anglesite, azurite, branchite, chalcanthite, goethite, glauomite, H-anatanite, hindsdalite, litharge, malachite, morenise, retgersite, ruthefordine, zincozite and zincite.

In springs and streams at S > 1 the water samples were oversaturate with respected to the minerals: alunite, barite, bixbyte, bohemite, chloropyromorphite, diasporite, hercynite, lindsdalite, hydroxylpyromorphite, plumbmgnite and valeranter. At equilibrium saturation (S = 0) we have the minerals larnalite, bentokite, ninyoates and verianite. Minerals predicted at undersaturation (S < 1) were anglesite, anhydrite, aragonite, artinite, bionicate, brucite, cerrusite, dolomite, magnesite, malachite and metanlerite.

Rare earth elements mineral saturation in boreholes at oversaturation (S > 1) predicted the minerals: CePO$_4$, DyPO$_4$, GdPO$_4$, LaPO$_4$, NdPO$_4$, PrPO$_4$ and SmPO$_4$. At equilibrium (S = 0) rare earth elements minerals species precipitated were ErPO$_4$, GdPO$_4$ × H$_2$O, HoPO$_4$, LuPO$_4$, TbPO$_4$ and TmPO$_4$. At undersaturation (S < 1) we have precipitation of the minerals: La(CO$_3$)$_3$, Ho(OH)$_3$, Sm(OH)$_3$, Lu(OH)$_3$, Gd(OH)$_3$, Er(OH)$_3$, Tb(OH)$_3$, Ce(OH)$_3$, TmF$_3$, TbF$_3$, SmF$_3$, ErF$_3$, Gd(CO$_3$)$_3$, EuF, CeF$_3$ and Ce(OH)$_3$.

In springs and streams at S > 1 the minerals CePO$_4$, ErPO$_4$, NdPO$_4$, Gd (PO$_4$ × H$_2$O (s), HoPO$_4$, SmPO$_4$, TbPO$_4$ and LaPO$_4$ were predicted. At equilibrium (S = 0) the mineral species precipitated were DyPO$_4$, TmPO$_4$, YbPO$_4$ × H$_2$O. Under saturated minerals predicted were with respect to Ce(OH)$_3$, Dy(OH)$_3$, Dy(CO$_3$)$_3$, DyF$_3$, Eu(OH)$_3$, EuF$_3$, Gd(CO$_3$)$_3$, Gd(OH)$_3$, GdF$_3$, × H$_2$O(s), HoF$_3$, La(OH)$_3$, La$_2$(CO$_3$)$_3$, LaF$_3$, NdF$_3$, Pr(OH)$_3$, PrF$_3$, Sm(OH)$_3$, Sm$_2$(CO$_3$)$_3$, SmF$_3$, TbF$_3$, TmF$_3$ (CO$_3$)$_3$, YbF$_3$ and YbF$_3$ × H$_2$O(s).

Oversaturated and equilibrium prediction of rare earth elements mineral species in boreholes and surface waters were dominantly PO$_4^2−$ complex ligand, which shows that such minerals are mobile under the prevailing condition of pH and Eh regime [4]. Undersaturated mineral species were majorly CO$_3^{2−}$ and F ligands. The oversaturated rare earth elements minerals were dominantly light rare earth elements (Ce, Eu, Gd, Nd, Pr, La (PO$_4^−$) minerals such as ancylite, khanneshite, monazite, parasite, calicucite, bastinase minerals which usually contain abundant light rare earth elements [27]. These minerals are common in rocks such as cabonatite, granite and pegmatite [27 and 46]. Near equilibrium saturation minerals were heavy rare earth elements (Er, Ho, Lu (PO$_4^−$), Tb, Tm (PO$_4$). This may be zenotrone rare earth element mineral, because it contains abundant HREE and is typified by phosphate radical [27]. The undersaturated rare earth elements minerals constitute of both light and heavy rare earth elements. This may be the mineral monazite which contains both heavy and light rare earth elements, but a higher proportion of light rare earth elements [45]. In springs and streams, the oversaturated rare earth elements minerals were in the same proportion of light and heavy rare earth elements.

5 Conclusion

Trace elements have higher concentrations in water samples in the study area than rare earth elements. Trace elements had a concentration in the order Mn> Cr> Zn> Pb> Cu> Co> Ni> Fe> Mo. The trend of rare earth elements concentration was of the order Ce> Nd> La> Pr> Sm> Gd> Dy> Er> Yb> Eu> Tb> Ho> Lu> Tb. major anions were dominated by sulphate but phosphate had the least mean level. The order of anions and cations is SO$_4^{2−}$, HCO$_3^−$, NO$_3^−$, PO$_4^{3−}$, Ca$^+$, Na$^+$, K$^+$, Mg. Mean levels of pH and turbidity exceeded world standards by WHO(2006) for potable water. The light rare earth elements (Ce, Eu, La, Nd, Sm, Pr and Gd) had higher concentrations than heavy rare earth elements (Dy, Lu, Tb, Er, Ho, Yb and Tb).

There was significant correlation between the following rare earth elements: Pr and Nd, Pr and Lu, Sm and Nd, Sm and Pr, Yb and Pr, Tb and Yb, Yb and Nd. Speciation modeling established that trace elements
in boreholes were dominated by free metal ionic species. The predominant trace metal complex were $T(OH)^{+}$ ligands. Free metal ionic species also dominated in springs and stream water samples. Carbonate ligand ($LnCO_3^-$) in REE dominate in boreholes. In springs free metal species $Ln^{3+}$ of REE dominated followed by $LnSO_4^{2-}$.

Trace element mineral saturation indexes in boreholes at $S > 0$ predicted mineral species more than equilibrium saturation ($S = 0$). Mineral prediction at $S = 0$ in streams and springs was less than those predicted in under saturation ($S < 1$). The degree of mineral prediction indexes of trace elements in boreholes was equivalent to those predicted in springs and streams. Rare earth elements mineral species saturation indexes predicted in boreholes at $S > 1$ was higher than those predicted at $S = 0$ while those predicted at $S < 1$ were the highest. The over-saturated rare earth elements were dominantly light REE (Ce, Eu, Gd, Nd, Pr, La (PO$_4^-$)) minerals. The rocks containing those minerals are carbonatites and granites. Near equilibrium ($S = 0$) mineral saturation were heavy rare earth elements (Er, Ho, Lu (PO$_4^-$)), Tb, Tm (PO$_4$). The under saturated rare earth elements consist of both light and heavy rare earth elements, but a higher proportion of light rare earth elements. In streams and springs the proportion of light and heavy REE forming mineral species were equal. Further work on rare earth elements in other geochemical media: soil, stream sediments and rock samples in the study area is necessary to fully reveal the rare earth elements potential in the study area due to their economic importance.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**References**

[1] Sharifi R, Moore F, Keshavarzi B. Geochemical behavior and speciation modeling of rare earth elements in acid drainage at sarchesmeh porphyry copper deposit, Kerman Province Iran. Chemie De Erde Geochemistry. 2013;73:509–517.

[2] Piaseki W, Sverjensky DA. Speciation of adsorbed yttrium and rare earth elements on oxides surfaces. Geochimica Et Cosmochimica Acta. 2008;72:3964–3979.

[3] Turner DR, Clegg SI Chemical speciation modeling in seawater to meet 21st Century Needs SCOR. Working Group Proposal 2014 MARCHMIESPEC. 2004; 1–16.

[4] Ekwere AS, Edet AE. Distribution and chemical speciation of some elements in groundwaters of oban area southeastern Nigeria. Res J Environ Earth Sci. 2012;4(3):207–214.

[5] Driscoll CT, Otton JK, Iverfeldt A Rare metals speciation and cycling bk chp biogeochemistry of small catchment a tool for environmental research. Edited by. Moldam B, Cenny Published by John Wiley and Sons Ltd; 1994. USA, Chapter 6:23–26.

[6] Willis SS Trace elements geochemistry in groundwater flow system. PhD Dissertation University of Texas at Arlington. 2010; 170pp.

[7] Willis SS, Johanesson KH. Controls on the geochemistry of rare earth elements in sediments and groundwater of aquiva aquifers maryland USA. Chemical Geology. 2011;285:32–49.

[8] Johanesson KH, Tang J, Daniels JM. Rare earth elements concentration and speciation in organic rich black waters of the great Dismal swamp, Virginia USA. Chem Geol. 2004;209:271–294.

[9] Ekwere AS Hydrogeology and hydrochemical framework of Oban massif southeastern Nigeria PhD Thesis University of Calabar Nigeria. 2010; 34–40.

[10] Cross River Basin Development Authority. Detailed data collection, collation and ground truthing campaign of 500 boreholes in hydrogeologic area (vi) for the enrichment of hydrogeologic information for the hydrological mapping of Nigeria. Draft final report. Nigeria cross river state calabar. Ministry of water resources. 2008; 9–13.

[11] Ekwueme BN. The Precambrian geology and evolution of the southeastern nigeria basement complex calabar university of calabar press. 2003.

[12] Ekwueme BN. An easy approach to metarmorphic petrology. In: Calabar university of calabar Press. 1993.

[13] Oden MI, Akpama TA, Amah EA. Comparative analysis of fractures, lineaments in oban and obudu areas, southeastern Nigeria. Journal of Geography and Geology. 2012;4(2):36–44.

[14] Ekwueme BN The Precambrian geology of oban massif southeastern Nigeria. Geological excursion guidebook to Oban massif, Mamfe Embayment and Calabar Flank southeastern Nigeria 31th annual conference of the Nigerian Mining and geochemical Society Calabar March, 1995; 12–16.

[15] Edet AE, Okereke CS. Assessment of hydrogeological condition of basement aquifers of precambrian oban massif Southeastern Nigeria. J Appl Geophysics. 1997;36:195–204.

[16] Okereke CS, Esu EO, Edet AE. Determination of potential groundwater sites using geological and geophysical techniques in the cross river state Southeastern Nigeria. J Afr Earth Sci. 1996;27(1):149–163.

[17] Johanessson KH, Lyons WB. The rare earth elements geochemistry of mono lake water and the importance of carbonate complexing. Limnology and Oceanography. 1994;39:1141–1151.

[18] Allison JD, Brown DS, Novo-Gradac KJ. MinteqA2/PRODEFA2, a geochemical assessment model for environmental systems; version 3.0 user manual. Georgia: US Environmental Protection Agency Athens; 1991. (EPA/600/3-91/021).

[19] Miller LA, Bruland KW. Competitive equilibrium techniques for determining transition metal speciation in natural waters, evaluation using model data. Anal Chm Acta. 1997;343:161–181.

[20] Cherry J, Freeze A. Groundwater. New Jersey (NJ): Prentice Hall; 1979. p. 413.

[21] Edet A, Ekpo B. Hydrochemistry of fractured aquifers in the ogoja/obudu area of southeastern Nigeria. Appl Groundwater Stud Africa. 2013;12:91–399.

[22] Ushie FA, Amadi PA. Chemical characteristics of groundwater from parts of the basement complex
of oban massif southeastern Nigeria. Sci Africana. 2008;7(2):81–88.

[23] Deer WA, Howie RA, Russman J. An introduction to the rock forming minerals. In: Pearson United Kingdom. 2nd ed. London: Geological Society; 1992. p. 712pp.

[24] Levinson AA. Introduction to exploration geochemistry. Illinois: Applied publisher. 1974. p. 164.

[25] Sigel FR. Environmental Geochemistry. New York: Wiley and sons; 1974. p. 24–29.

[26] Anderson T Compositional variation of some rare earth minerals from the fan complex (Telemark, SE Norway). Implications for the mobility of rare earth in Carbonatite system. Mineralogical Magazine. 1986; 50: 503–509.

[27] Guo H, Zhang B, Wang G, et al. Geochemical controls on arsenic and rare earth elements approximately along a groundwater flow path in shallow aquifers of the hetao basin inn mongolia. Chem Geol. 2010;270:117–130.

[28] Johansson KH, Cortes A, Ramosleal JA, et al. Geochemistry of rare earth elements in groundwater from rhyolite aquifer central Mexico. Water Sci Technol. 2005;51:188–200.

[29] Long B, Boer L, Glatz R. Rare earth elements and ores. In: Reston US geological survey. minerals data base web minerals.com; 2010. p. 34–37.

[30] Starzynski MA. Trace elements geochemistry of the milk river aquifer groundwater Alberta Canada. Saskatoon Sakachewan: Unpublished MSc Thesis University of Saskatchewan; 1998. p. 56–60.

[31] Rambeck WN Rare earth elements in Agriculture inaugural Dissertation. 2006; 260, 276–301.

[32] Kerr A, Rafuse H. Rare earth elements geochemistry of strange Lake Deposit. Implication for Resource Estimation and Metallgenic Models. Geological Survey Report. Research Newfoundland and Labrador. 2012;12:339–340.

[33] Gammons LH, Wood SA, Jonas JP, et al. Geochemistry of the rare earth elements and uranium in the Berkeley pit lake, butte, montana. Chem Geol. 2003;198:269–288.

[34] Leybourne ML, Cousens BL. Rare earth elements and nd and sr isotopes in groundwater and suspended sediments from the bathurst mining camp newick: water rocks reactions and fractionation. Water Sci Technol. 2005;51:254–260.

[35] Tang J, Johannesson KH. Rare earth elements concentration, speciation and fractionation along groundwater flow paths. Carizo Sand (Texas Upper Florida Aquifers Rare Earth Elements Groundwater Flow System. 2005;2:223–251.

[36] Nguyen VTM Hydrogeological characterization and groundwater protection of tropical mountains karst areas nw vietnam unpublished dissertation Vrije, Universiteit Brussel. 2006; 30–50.

[37] Bayon G, Birot D, Bollinger C, et al. Determination of trace elements in natural water reference material ICP-Ms SEMs after Tm addition and iron coprecipitation. Geostand Geoanal. 2010;35:145–153.

[38] Isaaks EH, Srivastava RM. An introduction to applied geostatistics. New York: Oxford University Press Inc.; 1989;10016–4314.

[39] Smedley PL. The geochemistry of rare earth elements in groundwater from the camellia area southwest England. Geochemical Cosmochin Acta. 1991;55:2767–2779.

[40] Michard A, Beaularie C, Michard G. Uranium and REE in Co2 rich waters from vals- les-banes (France). Geochemica Et Cosmochemica Acta. 1987;51:901–909.

[41] Wood SA. The aqueous geochemistry of rare-earth elements and yttrium Review of Available Low Temperature Data for Inorganic Complexes and the Inorganic Rare Earth Elements Speciation of Natural Waters. Chemical Geology. 1990;4:159–167.

[42] Udom GJ, Esu EO, Ekwere SJ. Quality status of groundwater in Calabar municipality southeastern. Global Journal of Applied Science. 1996;2(2):4–5.

[43] Tucker RD, Belkin HE, Schulz KJ, et al. Rare earth elements mineralogy, geochemistry and preliminary resource assessment of the khanneshin carbonatite complex helmond province, Afghanistan. United States geological Survey. Science for Changing World Afghanistan project Product No 200 Open-file Report 2011; 2011–1207.

[44] Jayanada F, Moyen JF, Martins H, et al. Late archaean (2550–2520). Juvenile magmatism in eastern Dhawar southern India constraints in geochemistry. Precambrian Research. 2000;99(3–4):225–234.