

HYDROGEOCHEMICAL APPRAISAL OF FLUORIDE IN GROUNDWATER OF LANGTANG AREA, PLATEAU STATE, NIGERIA

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ABSTRACT

Consumption of high fluoride in groundwater of Langtang area, manifest in the inhabitants of the area in form of dental fluorosis and skeletal fluorosis in older group. The aim of this study was to appraise the hydrogeochemistry of fluoride in the groundwaters of Langtang area. Thirty seven surface and groundwater samples and nine rock samples were collected in Langtang area for geochemical analysis. The Inductively Coupled Plasma Emission Spectrometry (ICPOES) was used to detect cations. The anions (Cl^- , SO_4^{2-} and Br^-) were determined by Ion Chromatography method. Fluoride was determined by the Specific Ion Electrode and bicarbonate was determined by titration. Major oxides, trace elements and rare earth elements for the rock samples were determined by the XRF method and fluorine by the Fusion method. Polished thin sections for rocks were prepared and studied. Geochemical results from analysis of the samples (rock and water) show that four major rock units make up the geology of the area; coarse porphyritic biotite granite, migmatite, rhyolite and riebeckite granites, the minor ones are pegmatite, trachyte, aplite and fine to medium grained biotite granites. The rhyolite, the riebeckite granites and trachyte have the highest level of fluorine content in the area (1,470, 1000, 900 and 800 ppm) respectively. The fluorine mineral (Fluorite) crystallized in the late stage of the magma as replacement of Fe/Mg mineral probably hornblende or biotite. Fluorine is leached into the groundwater from the rhyolite under the slightly alkaline (Ca-Mg-HCO_3 evolving Na-HCO_3) water in the area. The two major groundwater types (Ca-Mg-HCO_3 and Na-HCO_3) in the area have good relationship with content of fluoride in water. Although, the riebeckite granites have high fluorine content, contribution of fluoride from them is towards the southern portion of the map, owing to the groundwater flow direction. The different water sources in the area do not show variation in content of fluoride in water. However, groundwater barriers (dykes) may be responsible for some area having low fluoride (<1.5 mg/l) content. The consumption of high content of fluoride in the area has resulted in severe dental fluorosis in both children and youths and bowing of legs (*Genu Valgum*) in children with no discrimination between the sexes.

KEYWORDS: Fluoride, Fluorite, Fluorine, Fluorosis, Riebeckite Granite, Groundwater

INTRODUCTION

In most rural communities in northern Nigeria, the supply of water for drinking and other purposes is solely from surface (ponds, streams and rivers) and groundwater. Very often the qualities of such waters destined for human consumption are not known. Fluoride levels in water is of concern because of its harmful effect to man. Fluoride levels of < 1.5 mg/l in water may cause dental caries and higher values of > 1.5 mg/l fluoride content may result in the development of dental fluorosis and values of 4 mg/l may cause skeletal fluorosis (WHO, 2004). Other harmful effects associated with fluoride in drinking water are: reduced IQ, neurological disorder, hip fracture in women, endocrine effect (Dissanayake, 1991). Fluoride enters the human body mainly through drinking water (Dissanayake, 1991). Other sources may be from certain foods, dust, and industrial exposure. Sources of

fluoride in ground water are fluoride bearing minerals from rocks, such as fluorite, Fluor-apatite, cryolite, hydroxylapatite, biotite, hornblende among others. Concentrations of fluoride are generally localized in their geological occurrence. Highest concentrations are found in acid igneous rocks, mineralized veins and sedimentary formations where biogeochemical reactions have taken place (Smedley et al, 2004). On weathering fluorine tends to be released preferentially from minerals. Where biotite and amphiboles are abundant as in granites major sources of fluoride in water bodies is formed. In sedimentary rocks apatite may be an accessory mineral contributing fluoride to water while fluorite may be cementing materials in sandstones. Consumption of fluoride in groundwater commonly manifest in the inhabitants of Langtang area as dental caries and genu valgum (Dibal et al, 2008, Wongdem et al, 2002). The aim of this work is to geochemically appraise fluoride in the groundwater of Langtang area,

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Plateau State Nigeria with a view to understanding its sources and mobility pathways in water.

DESCRIPTION OF THE STUDY AREA

The study area is defined by latitudes $9^{\circ} 00''$ and $9^{\circ} 11''$ N and longitudes $9^{\circ} 45''$ and $9^{\circ} 54''$ (Fig 1). It is part of the Crystalline Hydrogeological Province of Nigeria. Over 60% of the area is entirely underlain by coarse to porphyritic granite intruded by rhyolites on the western part, fine grained biotite granites and intrusions of aplitic, pegmatitic and microgranites with xenoliths of the coarse to porphyritic granite are common so are small volcanic hills (trachytes). Apart from the large body of the rhyolite on the western portion of the mapped area, several minor flows of the rhyolite occur as boulder on the porphyritic biotite granite and the migmatite are common within fractures of these rocks. The southern portion of the map is underlain by migmatites with large intrusion of non orogenic granite, which probably belong

to the Younger Granite series of the Benue Trough of Nigeria. Pegmatite dykes have also intruded the migmatite. Large scale fault was formed as a result of the rhyolite intrusion trending in an almost N – S direction. The study area is drained by the River Bapkwai which takes its source from the hills on the western side and flow towards the south east direction. Several other small streams which flow in the same direction drain the area.

Hydrogeologically, groundwater is found in three different aquifers; recently deposited alluvium found along river and stream channels (Soft Overburden Aquifer), Weathered Overburden and Fractured Crystalline Aquifer. Groundwater is encountered in the alluvium at depths of between 4 – 5m, 10 – 15 m in the Weathered Overburden Aquifer and between 30 – 35 m in the Fractured Crystalline Aquifer. In the dry season, most of the hand dug wells dry up and water is obtained from scooped water holes in streams and river sands.

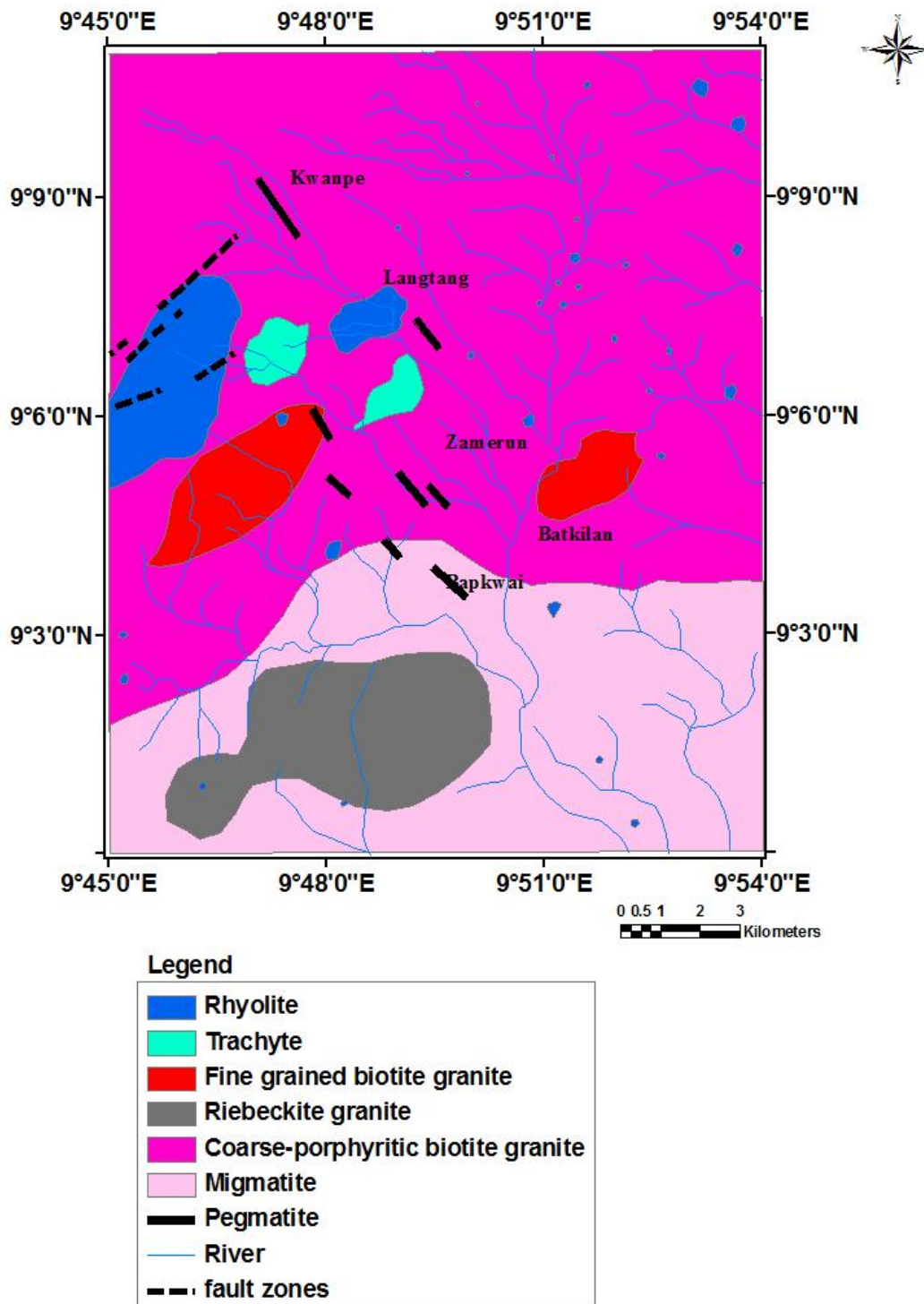


Figure 1: Geological Mp of Langtang

METHODOLOGY

Water samples were collected to determine their fluoride contents and other parameters in hand dug wells, boreholes, streams, dam, springs and a pond. Hydrogen exponent and temperature were determined in the field with an Oakton pH/Temp/ meter. Geological mapping of the area was carried out on a scale of 1: 20,000. Also, during the mapping exercise, rock samples were collected at several points from different rock units (trachyte, rhyolite, riebeckite granites, porphyritic biotite granite, migmatite, aplite and fine to

medim grained biotite granite and pegmatite) out of which representative samples were selected for thin sectioning and pulverization. On returning from the field, the water samples were filtered with United Nation International Children Educational Fund (UNICEF) standard filter to free the water from suspended particles. The water samples were transferred into 30 ml plastic bottles and transported to ACME Laboratory in Canada for geochemical analysis of the anions

LABORATORY ANALYSES OF WATER AND ROCK SAMPLES

Analysis of water samples for major (cations and anions) and trace elements was carried out in two laboratories Acme Laboratory in Canada and the Department of Geology, University of Jos Laboratory). At the Activation Laboratory, the Ion Chromatography was used to determine the anions, fluoride by Specific Ion Electrode and bicarbonate alkalinity was determined using titration method. At the Department of Geology University of Jos, the Inductively Coupled Plasma Optical Emission Spectrometry was used to determine the major and some trace elements. The rocks were crushed and pulverized at the Department of Geology, Ahmadu Bello University Zaria by Tungsten Carbide Ring Mill. The major oxide and elemental composition of these rocks were analysed by the XRF and the Inductively Coupled Plasma Mass Spectrometry Method at the ACME Laboratory in Canada. Fluorine in rocks were analysed by the fusion method. Three of the rock types (rhyolite and riebeckite granites) identified with high fluorine content were subjected to mineral analysis for the identification of fluorine mineral at the ACME Laboratory.

EQUILIBRIUM MODELING

Equilibrium modeling is a critical step in establishing the identity of chemical species likely to be present under given conditions particularly in aquatic system or in solutions. Numerous computer software programs are in used today to facilitate such modeling among which are MINTQA2 (USEPA) PHREEQC (Parkhurst and Appelo, 1999), The Geochemist's Workbench (Berthke, 2002) and WATEQ4F (Ball and Nordstrom, 2004).

Equilibrium modeling generally assumes that all reactions in a system have gone to completion and is thus not suited to evaluating kinetics. However, it can be very powerful in modeling equilibrium among dissolved adsorbed, solid and gas phases as a function of pH and ionic strength for many ionic species. Speciation refers to aspect of the chemical and physical form of an element: oxidation state, stoichiometry coordination (including the number of ligand) and physical state or association with other phases (Richard et al, 2006). These properties govern the chemical behavior of

elements, whether in the environmental settings or in human organ. The potential for dissolution or precipitation of a specific mineral in aqueous solution depends on the mineral's solubility and the composition of the aqueous solution (Burt, 1993) the potential is measured by the saturation index (SI) defined by (Langmuir, 1971) as

$$SI = \log (IAP/KT)$$

Or by the saturation percentage (SP)

$$SP = (IAP/KT) \times 100$$

Where IAP is the ion activity product in the aqueous solution of a given mineral and KT is the equilibrium constant at a given temperature. A value of zero (0) for the saturation index or (100 for the saturation percentage) indicate that an aqueous solution is in equilibrium with respect to the mineral. A negative value for SI or SP less than 100 indicates sub-saturation of the solution with respect to the mineral so that dissolution of the mineral is thermodynamically favoured. A positive value for SI or SP greater than 100 indicate super saturation of the solution with respect to the mineral indicating thermodynamically favoured condition for precipitation of the mineral. The ion activity products of the dissolved species are approximate due to thermodynamic uncertainties, for this reason saturation is assumed in the range 0 ± 0.5 .

RESULTS AND DISCUSSION

Petrography

Modal mineralogy from polished thin section of the rhyolite (Plate DH1) show that K-feldspar constitute 40%, occurring mainly as primary clasts and as matrix, quartz constitute 40% sericite – 5 -7%, plagioclase – 5%, chlorite – 5%, fluorite - 1, carbonate (dolomite) - 1, rutile - 1 and pyrite - < 1. Accessory rutile and local pyrite is concentrated in certain mafic/felsic lithic clasts respectively. Minor fluorite appears to be associated with thin carbonate veinlets. Fluorite is locally present as subhedra <1 mm. Generally this sample consists of about 30-40% recognizable felsic lithic clasts and 25-30% quartz/feldspar and sparse relict (chloritized) mafic crystal shards set in a finely comminuted matrix of K-feldspar-quartz sericite (Plate DH1).

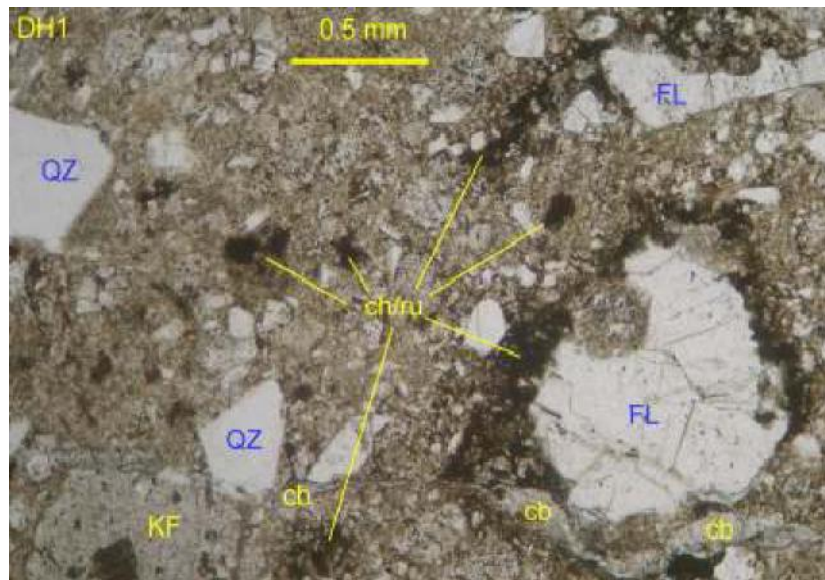


Plate 1: Fluorite (Fl) possibly replacing mafic crystal shards (note dark rim of chlorite-accessory rutile), associated with thin carbonate (cb) veinlets, cutting rhyolitic tuff containing shards of quartz (qz) and kspars (kf) in fine-grained matrix of k-feldspar-quartz-minor sericite. Transmitted plane light, field of view ~3 mm wide.

Modal mineralogy in polished thin section of the riebeckite granite (Plate 2, HDX1) is approximately: K-feldspar (mainly primary) 60%, Quartz (mainly primary) 30% , Biotite (partly chloritized) 3%, Hematite 2%, Sericite, clay 2%, Plagioclase 1% , Rutile, sphene (associated with relict mafic sites) ~1%, Sodic amphibole (dark blue, riebeckite?) <1%, Fluorite

(associated with relict mafic sites) <1%, Apatite (associated with relict mafic sites) <1%, Zircon/monazite, associated with mafic sites <1%, Carbonate (inclusions in fluorite; possibly dolomite) <<1%. Traces of carbonate <35µm in size may be included in the fluorite.

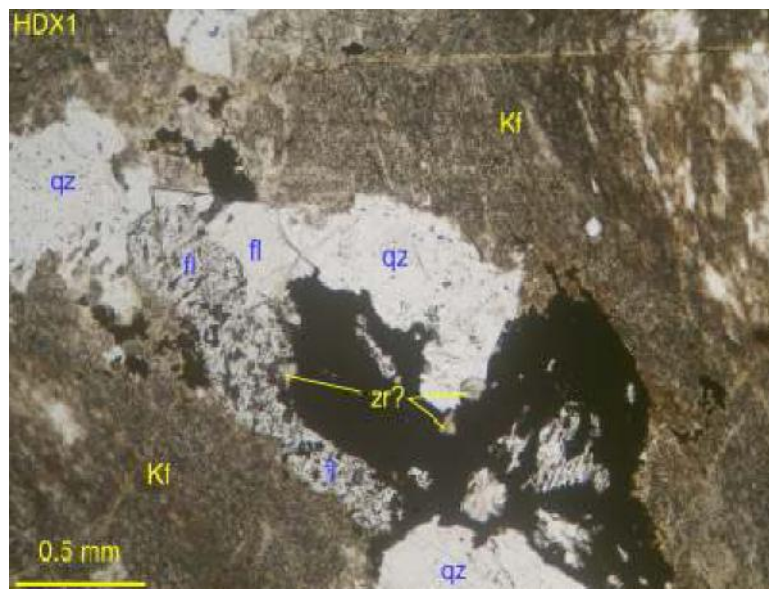


Plate 2: Riebeckite granite composed of coarse k-feldspar (kf, perthitic orthoclase) with interstitial quartz (qz), relict mafic site replaced by fluorite (fl, either clear or clouded by minute inclusions of carbonate) Transmitted plane light, field of view ~3 mm wide.

The riebeckite granite (Plate 3, HDX2) modal mineralogy in polished thin section is approximately: K-feldspar (mainly primary) 50%, Quartz (primary phenocrysts/groundmass, partly micrographic) - 30%, Plagioclase - 10%, Sodic amphibole (dark blue-green,

riebeckite) - 5% Hematite (after magnetite, some of which remains)- 2% Sericite, clay (after mafics, feldspars) - 1%, Rutile, sphene (associated with relict mafic sites) ~1% Limonite (goethite/hematite, after magnetite/hematite) ~1% and Apatite trace. (Plate 2).

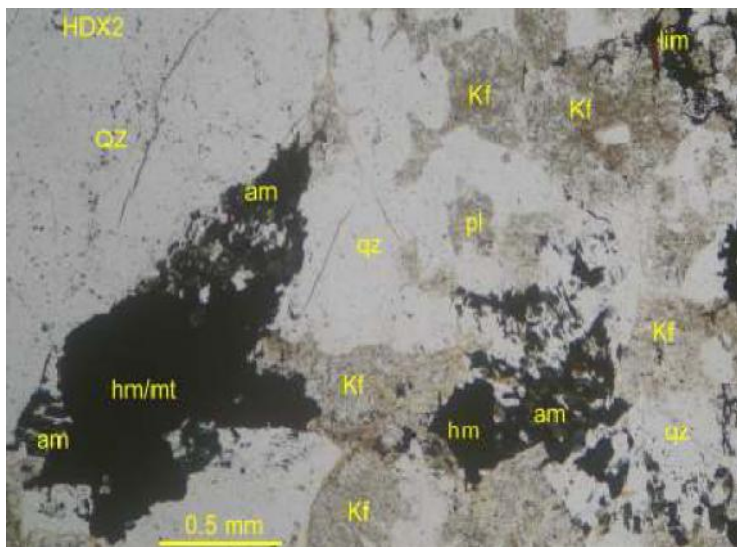


Plate 3: Margin of Quartz Phenocryst (Qz), Relict Mafic Crystals set in Phaneritic Groundmass of Quartz (Qz) and K-Feldspar (Kf) with local minor Plagioclase (overgrown by Quartz) in Granite/Rhyolite Porphyry). Transmitted Plane Light, Field of View ~3 mm wide.

No fluorite was observed in this section, but the presence of possible Fe-Na rich amphibole which is associated with fluorite in the previous sample, suggests it could be present in the sample.

Whole Rock Geochemistry

The bulk XRF analysis of rocks in the study area (oxide composition) is presented in Table 1. Plutonic rocks diagram classification of Na₂O +K₂O versus SiO₂ according to Middlemost 1996 is presented in (Fig 2). The TAS classification diagram for the volcanic rocks (Middlemost, 1994) is presented (Fig 3).

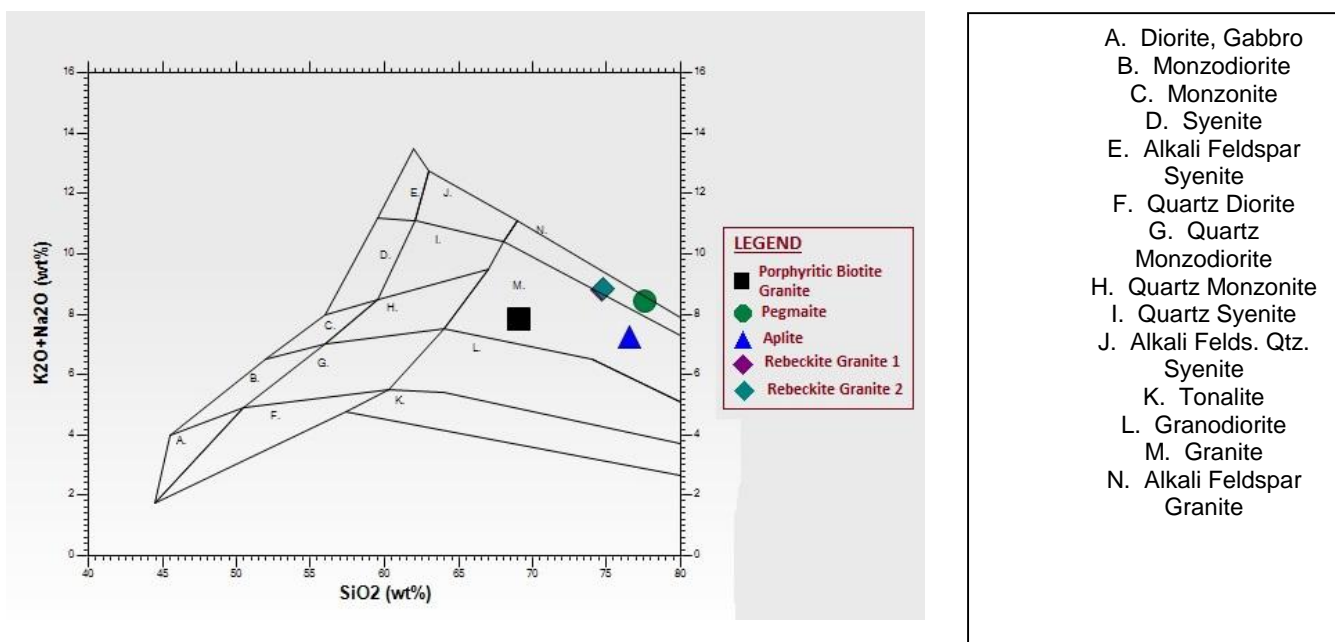


Figure 2: TAS discrimination diagram for plutonic rocks (Middlemost, 1996)

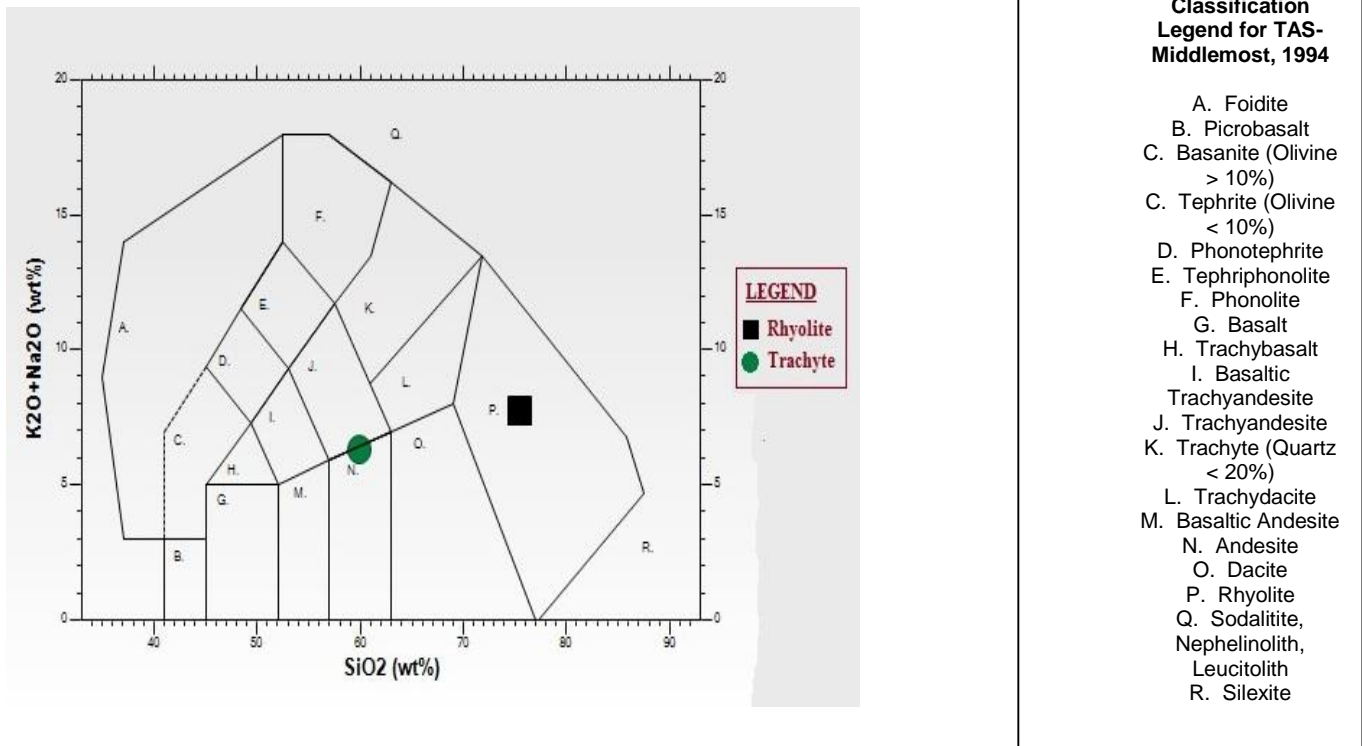


Figure 3: TAS discrimination diagram for volcanic rocks (Middlemost, 1994)

TABLE 1: MAJOR OXIDE COMPOSITION (Wt %) OF THE ROCKS DETERMINED BY XRF AND FLUORINE (PPM) ANALYSIS AT THE ACME LABORATORY, CANADA.

Oxides	Rhyolite	Porphyritic Biotite Granite	Pegmatite	Trachyte	Migmatite	Aplite	Fine grained Biotite Granite	Riebeckite Granite 1	Riebeckite Granite 2
SiO ₂	75.43	69.07	77.56	59.92	68.82	76.58	nd	74.67	74.78
Al ₂ O ₃	12.36	13.20	12.32	13.14	17.34	13.08	nd	11.73	11.43
Fe ₂ O ₃	2.18	5.97	0.56	9.24	0.09	0.62	nd	3.70	3.48
CaO	0.46	1.64	0.48	3.77	0.33	1.64	nd	0.28	0.37
MgO	0.24	0.63	0.07	0.86	<0.01	0.10	nd	<0.01	<0.01
Na ₂ O	2.93	3.09	3.26	3.39	3.98	3.84	nd	3.86	3.92
K ₂ O	4.85	4.76	5.19	2.96	9.12	3.41	nd	4.96	4.91
MnO	0.02	0.10	0.03	0.12	0.12	0.01	nd	0.09	0.09
TiO ₂	0.13	0.77	0.08	1.04	0.03	0.11	nd	0.18	0.19
P ₂ O ₅	0.02	0.26	<0.01	0.41	0.02	<0.01	nd	0.01	0.01
Cr ₂ O ₃	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	nd	0.143	0.142
Total	99.62	100.77	100.00	99.19	100.10	100.01	nd	100.06	100.33
F (ppm)	1,749	380	71	949	25	79	240	800	1000

Table 2: Trace and rare earth elements composition for rocks in the study area

Trace Elements	Rhyolite	Porphyritic Biotite Granite	Pegmatite	Trachyte	Migmatite	Aplite	Rebeckite Granite 1	Rebeckite Granite 2
Ba	152.0	1213.0	142.0	875.0	304.0	840.0	35	52
Co	50.9	125.7	161.1	74.8	92.9	136.0	5.7	5.4
Cs	1.6	2.5	0.9	0.4	2.3	5.7	0.5	0.8
Nb	127.1	30.9	4.3	55.2	1.3	5.8	237.2	159.6
Rb	272.0	172.5	159.5	73.5	365.3	102.4	171.6	150.0
Sr	38.8	200.2	64.6	261.5	106.9	487.8	11.3	14.3
Th	23.2	6.0	19.9	9.2	2.2	11.7	40.2	18.6
U	6.5	6.7	2.0	1.6	0.3	1.5	7.3	4.0
V	<8	19.0	<8.0	9.0	<8.0	9.0	<8	<8
Zr	301.6	670.7	54.8	651.7	16.7	54.1	1017.5	883.9
Y	110.6	41.7	1.6	57.6	4.2	8.8	154.1	106.6
Cu	9.6	9.2	5.7	2.6	0.4	1.9	22.3	22.6
Pb	15.2	10.8	14.9	7.2	5.0	6.6	3.3	9.3
Zn	739.0	132	14.0	160.0	3.0	11.0	169	424
Ni	0.5	1.9	2.3	<0.1	0.4	0.7	269.9	308.7
La	62.5	52.4	11.3	73.5	11.9	6.8	115.2	108.5
Ce	129.3	115.4	21.7	146.3	14.8	15.3	246.2	218.1
Pr	16.3	16.26	1.25	18.71	1.52	2.27	28.09	26.74
Nd	63.1	70.4	3.4	75.8	4.4	10.5	103.2	101.0
Sm	17.20	14.86	0.45	15.06	0.85	2.83	24.27	22.03
Eu	0.41	2.61	0.10	4.16	0.50	0.65	0.70	0.92
Gd	17.83	12.21	0.37	14.59	0.51	2.32	25.03	21.87
Tb	3.25	1.59	0.05	2.13	0.09	0.36	4.61	3.54
Dy	20.48	8.92	0.31	12.16	0.61	1.69	30.54	21.18
Ho	4.01	1.57	0.04	2.21	0.08	0.31	5.83	3.88
Er	11.68	4.15	0.13	5.63	0.39	0.89	16.70	10.56
Tm	1.71	0.58	0.03	0.83	0.07	0.12	2.43	1.51
Yb	10.24	3.50	0.18	4.96	0.47	0.71	14.50	9.52
Lu	1.38	0.53	0.03	0.73	0.06	0.12	2.06	1.37

Physico-chemical composition of the waters in langtang area

Table 3 shows the mean minimum and maximum values of the parameters in the waters of Langtang area. Temperature of the waters ranges from 26 – 27.90°C with a mean of 27.90°C as against the 26.5°C obtained in Crystalline Hydrogeological Province of Nigeria according to Schoeneich and Lawal, 2004. Hydrogen exponent ranges from 6.40 – 10.70 with a mean of 7.32, indicating waters in the study area to be slightly acidic to mildly alkaline. Total Dissolved Solids ranges from 51.81 – 784.05 with a mean of 268.27. Reasons for this high values cannot easily be explained, but probably it may be the result of residential pollution. Total Hardness ranges from 11.09 – 407.06 with a mean 120.11. According to Davies and Deweist, 1967, classification of water hardness, 22% of the water is classified as soft, 61% as moderately hard and the remaining 17% as hard. Calcium ranges from 5.91 – 117.10 mg/l with a mean of 30.31 mg/l. This mean value

is ten times more than the mean of 3.0 mg/l given by Schoeneich and Lawal, 2004 for calcium in Crystalline Hydrogeological Province of Nigeria. Dissolution of calcium bearing mineral alone cannot account for this high concentration of calcium in the Langtang waters. Magnesium ranges from 1.17 – 36.48 mg/l with a mean of 11.16 mg/l, Sodium ranges from 5.07 – 40.37 with a mean of 19.98 mg/l. Potassium ranges from 0.59 – 33.74 with a mean of 4.00. These values are all higher than those given by Schoeneich and Lawal, 2004 for waters in the Crystalline Hydrogeological Province of Nigeria. Bicarbonate in the waters ranges from 20.00 – 672.00 mg/l with a mean of 187.97 mg/l. sulphate ranges from 0.50 – 51.00 with a mean of 8.10 mg/l. A borehole at Bapkwai has this value of 51.00 mg/l. Chloride ranges from 0.50 – 75.00 mg/l with a mean of 11.90. Few of the water sources have been found to have elevated level of sulphate with corresponding elevated level of nitrate. Such water sources may have been contaminated.

Table 3: Maximum and mean values of physical and chemical parameters in Langtang area

Parameters	No	Minimum Mg/l	Maximum Mg/l	Mean mg/l	Crystalline Hydrogeol . Province Average	W.H.O Standards. 1984
Temperature °C	41	26.00	27.90	27.90	26.5°C	-
Ph	41	6.40	10.70	7.32	5.0 – 7.4	6.5-8.5
TDS	36	51.81	784.05	268.27	60 mg/l	500
TH	36	11.09	407.06	120.11	20 mg/l	500
Ca ²⁺	41	5.91	117.10	30.31	3.0 mg/l	75
Mg ²⁺	41	1.17	36.48	11.16	1.1 mg/l	150
Na ⁺	41	5.07	40.37	19.98	5.0 mg/l	200
K ⁺	41	0.59	33.74	4.00	1.5 mg/l	-
HCO ₃ ⁻	35	20.00	672.00	187.97	30 mg/l	-
Cl ⁻	36	0.50	75.00	11.59	0.6 mg/l	500
SO ₄ ⁼	36	0.50	51.00	8.10	1.3 mg/l	400
F ⁻	37	0.12	10.30	2.47	0.3 mg/l	1.5

Saturation index of some mineral in Langtang area.

Saturation indices of calcite and fluorite, the two minerals which have effect on the geochemistry of fluoride in groundwater are presented in (Fig 4).From the figures, 77% of the water is under-saturated with respect to fluorite and 22% are close to being at equilibrium with respect to fluorite, only 1% is supersaturated with respect to the water. With respect to calcite, 57% are under-saturated, 33% are close to being at equilibrium and 10% are oversaturated with

respect to calcite (Fig 5 and 6). Super-saturation with respect to calcite causes precipitation thereby removing Ca from the water. This makes the water more alkaline and enhances the dissolution of fluorite mineral (Handa, 1975, Gaciri and Davies, 1993). However, this is not the case in the Langtang area as the larger percentages of the water have been found to be under-saturated with respect to both minerals. Under-saturations with respect to calcite therefore have great implication on fluorite solubility in the area.

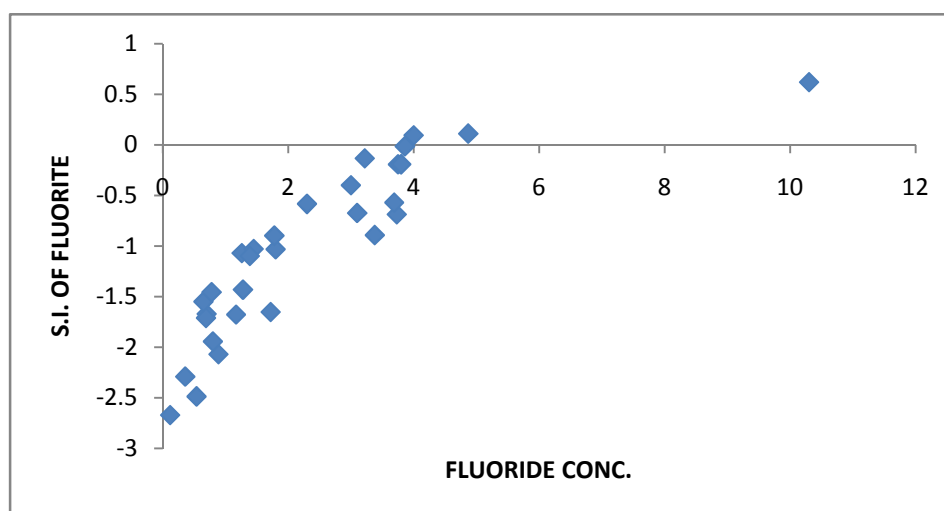


Figure 4: Saturation index of fluorite vs fluoride concentration

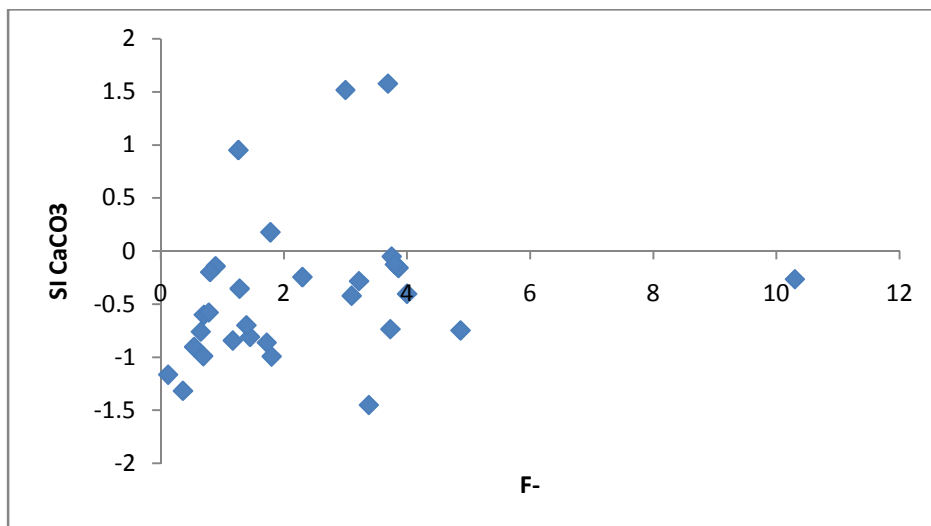


Figure 5: Saturation index of calcite vs fluoride concentration

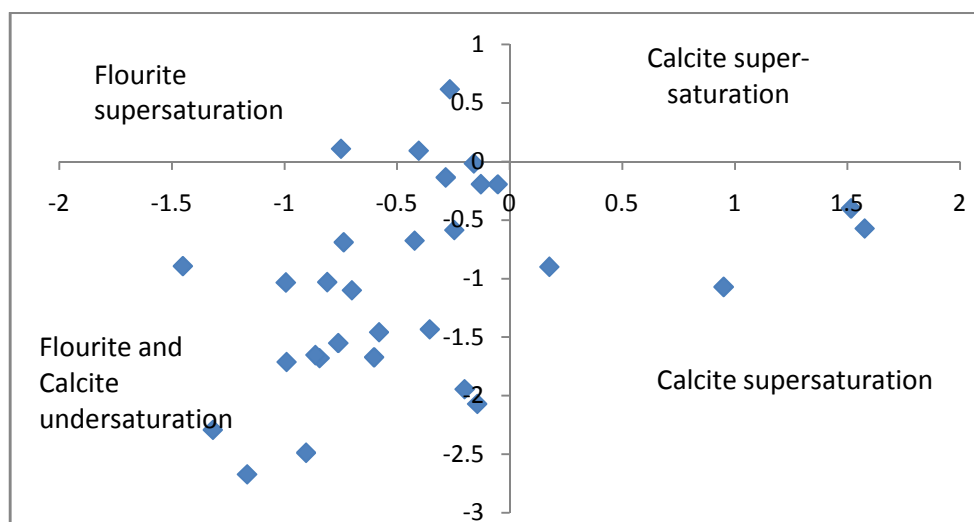


Figure 6: Fluorite and Calcite Saturation Indices

Sources of fluoride in waters of Langtang area

Fluorine occurrence in natural waters is closely related to its abundance in the local mineral rocks. Apatite and fluorite, besides the replacement of OH^- by F in mica, hornblende and soil consisting of clay minerals (Robinson and Edington, 1946; Hem, 1991) is the major contributor of fluorine in groundwater. Anthropogenic inputs from industries and the use of phosphate fertilizers in commercial agricultural farming activities are other sources where fluoride can be released into groundwater (Rao *et al.*, 2002). In the Langtang area, source of the fluoride is dominantly from the rock (rhyolite) with minor contribution from the other rocks. This rock type (rhyolite) has the highest level of fluorine content of 1,470 ppm. The fluorine mineral (fluorite) however, does not seem to be part of the original magma from which the rhyolite was formed, but probably a result of injection from metasomatic fluid and or derived from a melted host rock. The negative Eu anomaly in this rock indicates the removal of Eu from

early crystallization of plagioclase feldspar mineral. However, the enrichment of the incompatible elements (Rb, Cs, Ba, Pb, Nb, Y, Tl and the LREE) do not justify a fluorine mineral formed from well differentiated magma. The association of fluorine mineral to carbonate veinlets, dolomite and pyrites as revealed from the thin section studies further supports the formation of fluorine mineral from metasomatic fluid rich in carbon dioxide and sulphur. The formation of the fluorine mineral may probably be the result of the ion by ion replacement in minerals (Zharikov, 2006) (replacement of an iron/magnesium mineral which probably may be a hornblende or biotite by fluorite). The fluorine is leached into the groundwater from weathering of fluorite mineral (Fig 7). The association of fluoride and calcium in the waters indicate that fluoride is leached into the waters from the dissolution of the fluorite and probably little contribution from the chlorite and the sericite minerals in the rhyolite rocks under the influence of pH (Krainove *et al.*, 1969).

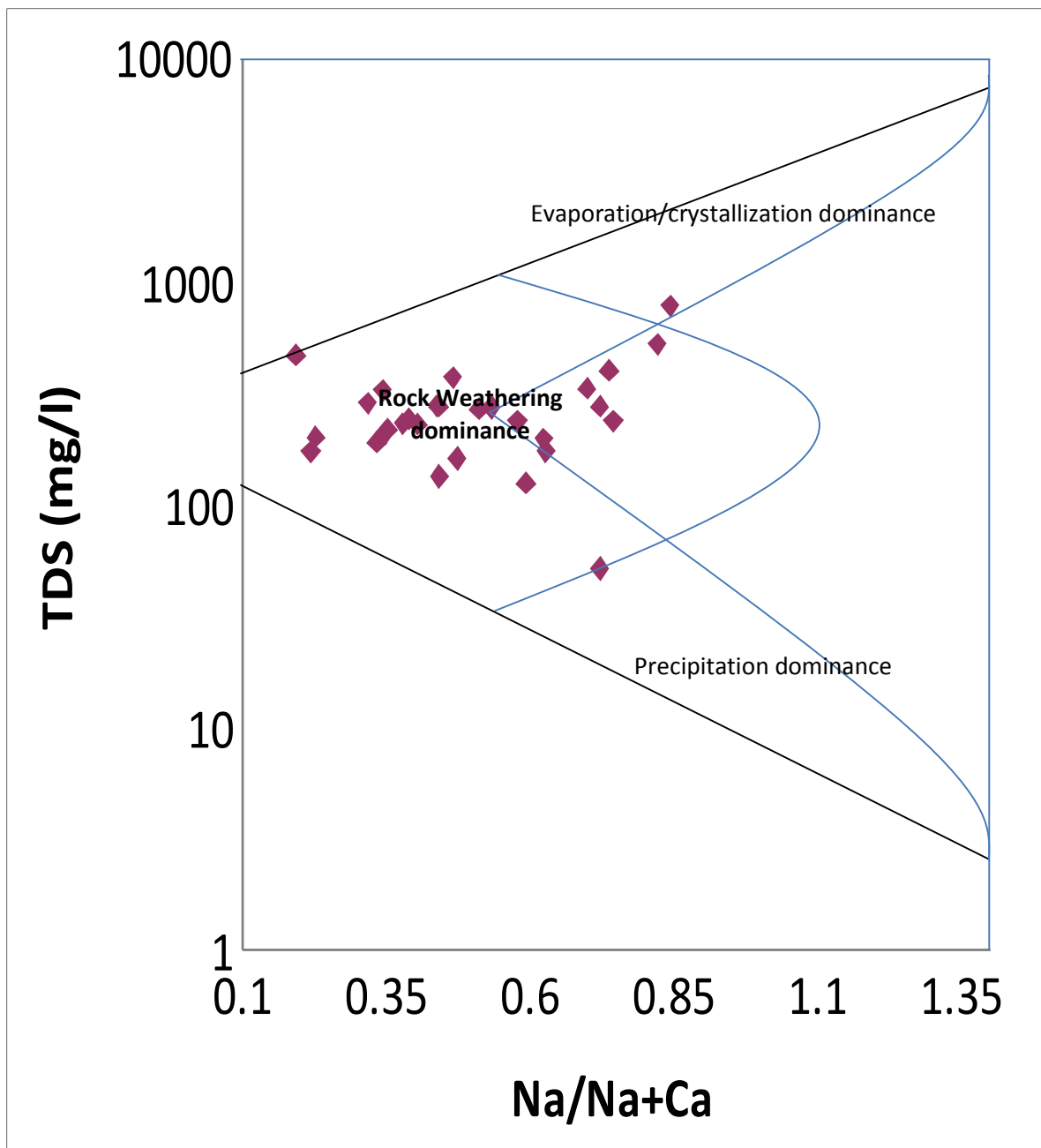


Figure 7: Gibbs diagram showing the predominant source of variation in the hydrochemistry of groundwater in the study

Distribution of fluoride in Langtang waters

Fluoride distribution symbol map of Langtang area is shown in (Fig 8). The intervals used for mapping fluoride concentrations are based on expected dose – response health outcomes given by the World Health Organisation. Fluoride concentrations higher than the WHO upper limit of 1.5 mg/l occupy a larger portion of the map (Fig 9). Fluoride concentration lower than these values, are found occupying a small portion in the northwest and some portion in the central and eastern sections of the map. No clear variation of fluoride concentration is seen in the different sources from which water was collected. Waters collected from scooped sands along stream channels have lower fluoride concentration as against those in hand dug wells and boreholes. Probably this is because waters in the streams are recently infiltrated water from immediate past rainfall and therefore did not have enough time to

interact with fluorine bearing minerals. Concentration of fluoride in hand dug wells and in boreholes are similar, indicating that depth of water sources in the Lantang area do not determine the concentration of fluoride. One of the water source (hand dug well at Kuyin) located in the western portion of the study area has the highest level of fluoride concentration of 10 mg/l. Groundwater flow direction plotted for the area (Dibal, 2012) also shows that, distribution of fluoride is not controlled by direction of groundwater flow as it is evidently seen in the concentration of fluoride in some parts of the central and the south eastern portion of the map located along the direction of groundwater flow. Probably the several intruded dykes of pegmatite and apalites in the host rock and clays which may hinder groundwater flow may be responsible for variations of fluoride distribution in the area. The flow direction of the groundwater shows how little or near absence of the contribution of the riebeckite

granite to concentration of fluoride in the study area despite their high level of fluorine content. Contribution

of fluoride from these into the groundwater may therefore be towards the southern areas.

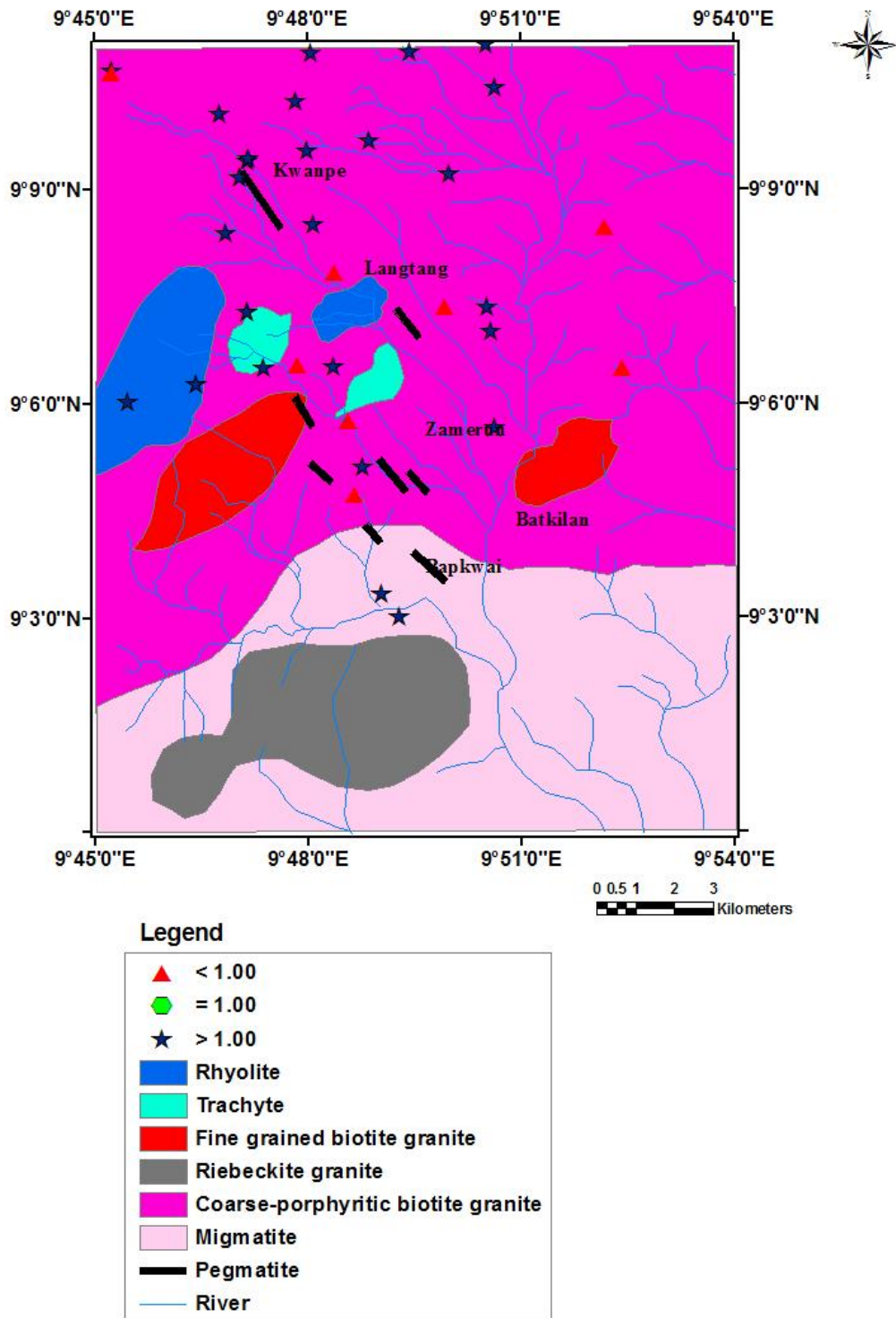


Figure 8: Concentration of fluoride symbol map of Langtang area

Fluoride and groundwater type in Langtang.

In Langtang, two major water types have been identified (Fig.9); Ca-Mg-HCO₃ constituting 68% with fluoride concentration ranging from 0.12 – 10.30 mg/l; the. Na-

HCO₃ water type constitute 17% with fluoride content in the range of 0.54 – 3.73 mg/l and the Ca-Mg-SO₄ 3% with fluoride content of 0.80 mg/l.

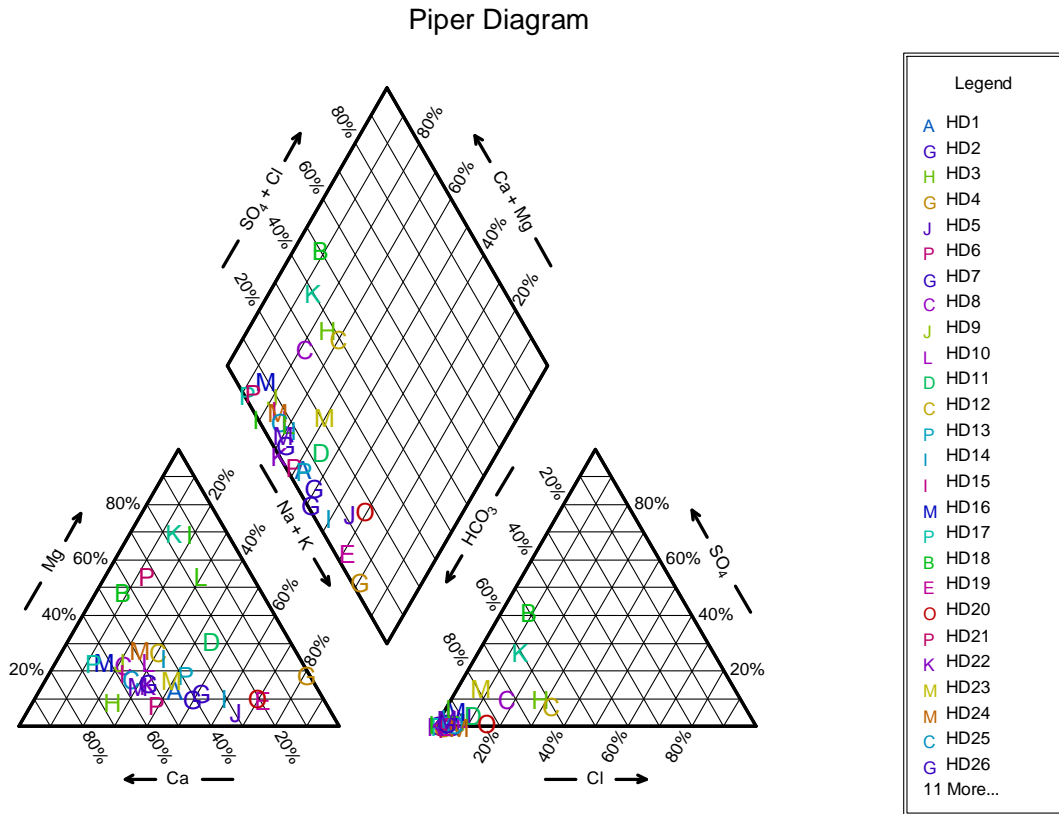


Figure 9: Piper Trilinear diagram showing water types in Langtang area

It can be seen from the figure that the waters are evolving from the Ca-HCO₃ to the Na-HCO₃ water type. However, the present study in the Langtang area differs slightly with other studies which gave the association of high fluoride groundwater to the Na-HCO₃ water type (Handa, 1975; Edmunds and Walton, 1983, Gaciri and Davies, 1993). The two major groundwater types obtained from the area have good relationship with content of fluoride. With over 60% of the waters in the area under-saturated with respect to both calcite and

fluorite, it means that both minerals are still dissolving and going the forward direction. It is obvious that base exchange is not taking place in the area (Fig 10) and hence the reason for the persistence of calcium in the water. This is however, of great importance in the Langtang water, because calcium in the waters is suppressing fluorite from dissolving which could have caused more fluoride to be leached into the water leading to elevated level of fluoride in the water.

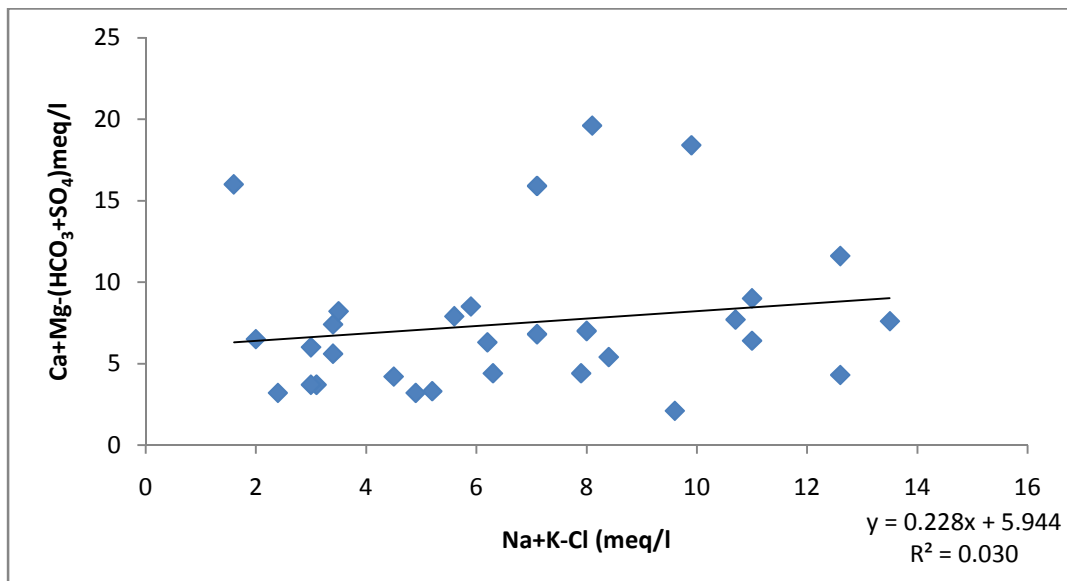


Figure 10: A plot suggesting the possibility of cation exchange in Langtang area

Water quality and health effects of fluoride in Langtang area

In the Langtang area only 13 (36%) out of the 36 (Fig 11) water sources analysed for fluoride content imbibe waters having fluoride within the WHO 2004 optimal level of 0.5 – 1.5 mg/l. 12% of the water sources have fluoride concentration lower than the 0.5

mg/l lower limit recommended for dental caries prevention. Population of inhabitants consuming water from these sources may therefore be at the risk of having dental caries. 52% of the water sources in the area have fluoride concentration greater than the 1.5 mg/l WHO upper limit.

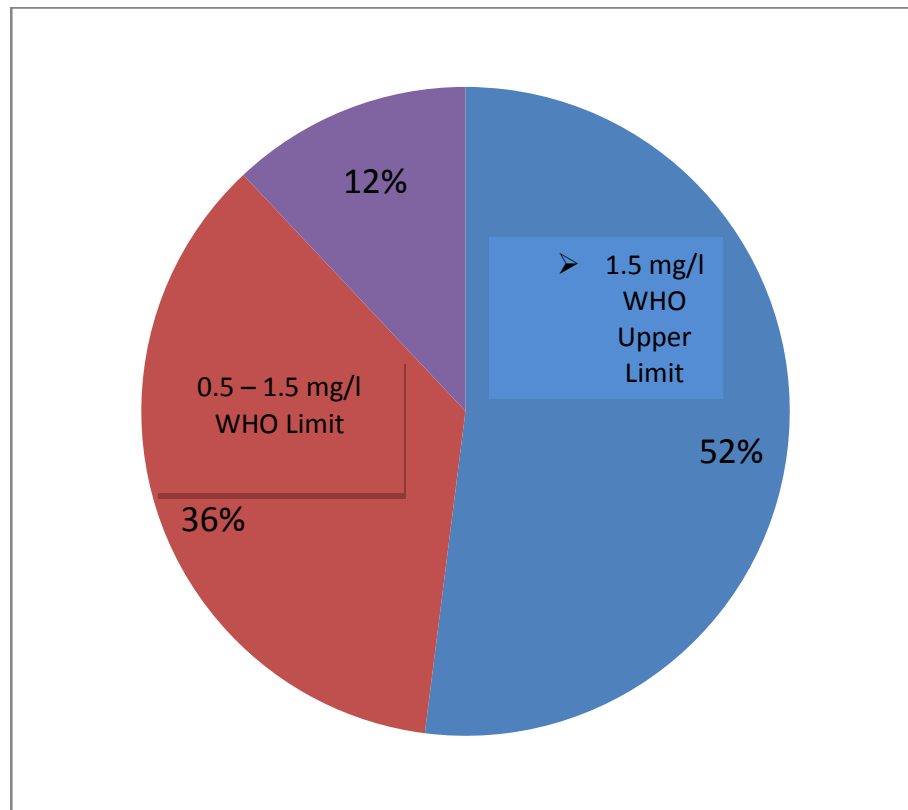


Figure 11: Pie diagram showing relative abundance of fluoride in the waters of Langtang area

Based on the WHO 2004 classification of chronic health effects of fluoride consumption in drinking water, population consuming water from 18 of the 30 water sources with fluoride value greater than 1.5 mg/l may have dental fluorosis. Inhabitants consuming water in the remaining 7 water sources with fluoride concentration from 4.0 mg/l and upwards may have chronic skeletal fluorosis. Demographic studies carried out earlier in the area (Wongdem *et al*, 2002) on

sampled population by age group (n=473) has established highest frequency of mottling 28.6% of the population aged 10 – 19 years (Table 4) with a uniform decrease towards the age group 70 – 79 years. There is however, no discrimination found between these age groups with respect to sex (Table 5). This study has also established cases of genu valgum (bowing of legs) in the lower ages of between 6 – 9 years (Wongdem *et al* in 2002).

Table 4: Demography of the sample population by age groups (n =473)

Age group	Frequency	Percentage (%)	Cummulative (%)
0 – 9	93	19.6	19.6
10 – 19	136	28.6	48.6
20 – 29	95	20.0	68.2
30 – 39	62	13.1	81.3
40 – 49	44	9.3	90.5
50 – 59	26	5.5	96
60 – 69	14	2.9	98.9
70 – 79	5	1.1	100
Total	475	100	

Source: Wongdem *et al*, 2002.

Chronic manifestation of dental fluorosis in school children (Dibal *et al*, 2007) with greater manifestation in school children aged between 7 – 11 years has also been established.

Table 5: Demography of sample population by age group and sex.

Age group	Male	Female	Total
0 – 9	42	51	93
10 – 19	67	69	136
20 – 29	41	54	95
30 – 39	31	31	62
40 – 49	16	28	44
50 – 59	11	15	26
60 – 69	10	4	14
70 – 79	4	1	5
Total	222	253	475

Source: Wongdem *et al*, 2002

CONCLUSION

Study on the geochemical appraisal of fluoride in the waters of langtang area show that, among the rocks of the study area, the rhyolites have the highest content of fluorine followed by the riebeckite granites and trachyte respectively (1,470, 1000, 800 and 900 ppm). Fluorine crystallized in the late stage of magma crystallization, as a replacement of Fe/Mg mineral which may probably be hornblende or biotite. The major source of fluoride in the Langtang groundwater is from the mineral fluorite hosted in the rhyolite which occurs as dykes in several places in the porphyritic hornblende - biotite granites and the migmatite gneiss.

Although the riebeckite granites have high fluorine content their contribution to groundwater is

towards the southern areas due to the direction of groundwater flow in the area. No clear variation in fluoride contents exist in the different sources. Groundwater barriers such as dykes may probably be responsible for sources which have low fluoride.

Under-saturation with respect to both calcite and fluorite in the area suggest that reaction is still going on in the forward direction for both minerals. Also under-saturation with respect to calcite and lack of base exchange in the area may also be responsible for the persistence of calcium in some of the water being Ca-Mg-HCO₃ type. Groundwater evolution from Ca-Mg-HCO₃ towards Na-HCO₃ water type results in the water being slightly alkaline and hence dissolves fluorite in the water. Inhabitants of Langtang area show manifestation of dental fluorosis in form of dental fluorosis in the age

groups 10 – 19 years and decreases uniformly towards the older ages and bowing of legs (*Genu Valgum*) in lower age groups 7 - 9 years manifest bowing of legs.

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