University of Venda

SCHOOL OF ENVIRONMENTAL SCIENCES

GEOGENIC FLUORIDE SOURCE IN GROUNDWATER: A CASE STUDY OF SILOAM VILLAGE, LIMPOPO PROVINCE, SOUTH AFRICA

By

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DECLARATION

I, Onipe Tobiloba Ayodeji, hereby declare that this dissertation for Masters of Earth Science in Hydrology and Water Resources at the University of Venda, hereby submitted by me, has not been previously submitted for a degree at this or any other institution. This is my work in design and execution, all reference materials contained herein have been duly acknowledged**.**

Signature ____________________ Date: ________________

DEDICATION

This work is dedicated to God who is the beginning and the end, and to my future wife. I love you in advance.

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ABSTRACT

Siloam, a village in the Northern province of South Africa has groundwater reportedly characterised by concentration of fluoride greater than 1.5 mg/L permissible limit. Regional investigation has been done to determine the possible fluoride sources in the northern province of South Africa, but no localised investigation has been documented. The World Health Organization and South Africa National Standard permissible limit is 1.5 mg/L for a duration of time. Therefore, this study focuses on investigating the sources of fluoride in the groundwater of Siloam village in response to reported high incidences (80%) of dental fluorosis in Siloam village. This study also elaborates more on the hydrochemical and geochemical processes favouring the release of fluoride into the groundwater of Siloam village. Two (2) surface rocks, one (1) surface clay deposit, twelve (12) borehole cuttings and four (4) groundwater samples were used for this study. Temperature, total dissolved solids (TDS), conductivity (EC) and pH of the groundwater were determined using a combined multimeter because these parameters are proxy indicators of geogenic influence on groundwater fluoride concentration. Total fluoride in the groundwater samples and the leachates obtained during a leaching experiment were determined using Ion Chromatograph (IC) and Fluoride Ion Selective Electrode (FISE). X-ray fluorescence spectrometry is the most preferred method for rock analysis by earth scientists because it is faster and does not require ambiguous training on the part of the analyst, therefore, it is mostly the standard methods used in whole rock chemistry. Elemental composition and mineralogy were determined using X-ray Fluorescence (XRF) and X-ray diffraction (XRD), respectively. Clay, greywacke, argillaceous sedmients and basalt were analysed. Results obtained indicated that the groundwater fluoride concentration ranges from 3.92 to 4.95 mg/L, which are far above the WHO permissible limit and South African standard. *Insitu* temperature reading obtained ranges from 25 to 48°C thus classifying the groundwater to be hot and tepid. The groundwater pH ranges from 8.1 to 9.1 which indicates an alkaline water condition. The groundwater conductivity ranges from 330 to 730 µS/cm while the Total dissolved solids ranges from 130.12 to 423.07 mg/L. Groundwater proxy indicators showed geologic sources to be responsible for the high fluoride concentration in the groundwater of Siloam village. Hydrochemical investigation revealead that the mineralisation of groundwater in Siloam village is as a result of rock water interaction and the process of groundwater enrichment is through base ion exchange and reverse ion exchange. The dominant water type in the village was identified to be Na-Cl water type and the abundance of sodium (Na) is due to the heavy weathering of plagioclase of the parent rocks. Total fluoride content of the rocks and soils of the village ranges from 10 to 2000 mg/L. The leachable fluoride, however, ranged in concentration from 0.27 to 14.88 mg/L under induced temperature and 0.05 to 10.40 mg/L without temperature. Mineralogical investigation revealed the abundance of smectite clay, which is known for its enrichment and leaching of fluoride into groundwater sources, thus, the research question and assumption about the possible source of fluoride and the assumption that fluoride increases downwards towards the aquifer were answered. Leaching experiments identified the main contributors of fluoride to groundwater in Siloam village as smectite clays and the muscovite present in the sandstone, greywacke and basalt. Time based leaching experiment, geochemical modelling and dating of different hydrogeological unit was recommended.

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LIST OF ABBREVIATIONS

Al	Aluminum
B	Boron
Be	Berilium
DWAF	Department of Water Affairs and Forestry
C	Carbon
Ca	Calcium
Ca^{2+}	Calcium ion
$CaCO_3$	Calcium carbonate
CBE	Charge balance Index
Cl	Chloride
CAI	Chloro-Alkaline Index
CIDA	Canadian International Development Agency
EC	Electrical Conductivity
ENE	East North East
F	Fluoride
Fe	Iron
FISE	Fluoride ion selective electrode
GPS	Global Positioning System
H	Hydrogen

IC	Ion chromatography
K	Potassium
Kg	Kilogram
Lab	Laboratory
L	Litre
Li	Lithium
LOI	Loss on Ignition
Mg	Magnesium
Mm	Millimetre
M	Meter
mM	Millimolar
Mn	Manganese
Mya	Million years ago
Na	Sodium
Na_2O_2	Sodium Peroxide
N/A	Not available
NWN	North West North
O	Oxygen
OH	Hydroxide
Pb	Lead

SACS	South African Classification System
Si	Silicon
T	Temperature
Ti	Titanium
TDS	Total Dissolved Solid
TISAB	Total Ionic Strength Adjustment Buffer
U	Uranium
WHO	World Health Organization
WSW	West South West
Wt	Weight
XRFS	X-ray Fluorescence Spectroscopy
XRD	X-ray Diffraction

LIST OF UNITS AND SYMBOLS

°	Degree
>	Greater than
<	Less than
µg/L	Microgram per litre
µS/cm	Micro-Siemen per centimetre
µm	micronmeter
Kg	Kilogram
L	Litre
mg/Kg	Milligram per kilogram
mg/L	Milligram per litre
mm/a	millimetre per annum
mM	millimolar
mS/cm	Micro-Siemen per centimetre
ppb	Part per billion
ppm	Part per million
%	Percentage

CONTRIBUTIONS FROM THIS STUDY

TOPIC	ARTICLE/ CONFERENCE	STATUS
Contribution of sedimentary rocks to groundwater fluoride: A case study of Siloam village, Limpopo South Africa.	2nd WSU-UNIVEN Conference, Polokwane South Africa.	Presented
Source assessment and health implication of fluoride in groundwater of Sub-Saharan Africa: A review.	Article and Presentation at the 35th AAG conference, New Orleans Louisiana, USA	Under peer-review Presented
Hydrogeochemistry of fluoride-rich groundwater of Siloam village South Africa.	Article	In Progress

1. INTRODUCTION

1.1 Preamble

This chapter gives the background of the study, the statement of problem and motivation behind the study, the objectives of the study and research questions. A brief description of the study area in the context of rainfall, geology, topography and temperature are also covered.

1.2 Background of the Study

Water plays an important role in the existence of life. Access to safe drinking water is extremely important to health, therefore it is a basic human need, irrespective of socioeconomic background (WHO, 2011). Estimates show that deaths from water related complications and inadequacies supersede deaths from violence and unrest (WHO, 2012). Water is of biochemical and economic importance to the developed, developing and under developed world (Braune and Xu, 2010). Groundwater is considered as a relatively safe alternative source of water for drinking and other domestic uses due to its quality when compared to other sources of water. It is mostly used without further treatment (Brindha and Elango, 2011). Groundwater has become indispensable and in developing countries of Africa up to 75% of the population depend on it as their major source of water (ECA, 2000; UN, 2000). Fluoride (F), an inorganic anion of fluorine, is the 13th most abundant element in the earth's crust (Weinstein and Davison, 2003). However, its concentration in water varies from place to place and from region to region all over the world. F is an essential ion that is present in most groundwater and surface water in trace amounts or as a major ion with high concentration (Dar et al., 2010; Fantong et al., 2009). Fluoride is a vital mineral for the development of bones and tooth cavities in the body (Edmunds and Smedley, 2005). Intake of correct F concentration plays an important role in the formation and development of teeth and healthy bones (Brindha and Elango, 2011).

The permissible limit of fluoride in drinking water by World Health Organization (WHO) is 1.5 mg/L (WHO, 2003), of which higher levels can be of risk to human beings (Yeongkyoo et al., 2010). High concentration of F^- in drinking water has raised concerns globally due to its ability to cause skeletal and bone deformation, cancer and dental abnormality such as tooth discolouration and dental fluorosis (Malago et al., 2017; Edmunds and Smedley, 2005; Kut et al., 2016). Fluoride concentration in drinking water can be considered safe if it falls between 0.5mg/L and 1.5 mg/L. Fluoride concentration below 0.5 mg/L, which is the lowest beneficial limit set by WHO, below which preventable dental caries may arise especially when water of low fluoride concentration is consumed by children under the age of five (Ncube and Schutte, 2002). Low intake of fluoride also causes osteoporosis in which bones and teeth degenerate (Thompson 2012).

In groundwater, the level of fluoride is dependent on factors like geology, chemical and physical properties of aquifer, the acidity of rock and soil as well as the depth of the well (Salve et al., 2008). F contamination in groundwater is less pronounced in tropical areas where humidity is high (Frencken, 1992). Lower rate of evaporation due to high humidity together with high rainfall has a diluting effect on groundwater chemical composition (Frencken, 1992). The geochemical properties of groundwater contaminated by fluoride are often associated with neutral to alkaline pH (Jacks et al., 2005), low calcium concentration, high sodium and bicarbonate concentrations (Kundu et al., 2001; Smedley et al., 2002; Edmunds and Smedley, 2005; Chae et al., 2007).

The concentration of fluoride in groundwater increases due to rock-water interaction (reaction time of water with the aquifer minerals) as a result of long residence time (common in geologic formations of low porosity) and evapotranspiration (Brindha and Elango, 2011). The occurrence of natural fluoride in water is usually from the reaction between surface or groundwater with soil and rock containing fluoride-mineral (Rango et al., 2008). Such groundwater is usually associated with deep aquifer systems and a slow groundwater movement (Frencken, 1992). Fractured aquifers are a good source of water in some parts of the world (Manda et al., 2006). Fractured basement aquifers are generally developed in-between a fractured precambrian intrusive and/or metamorphic rocks and an overlay of weathered rock/regolith (Wright, 1992). Ultramafic igneous and volcanic rocks have a fluorine concentration of about 100 mg/L while the fluorine concentration of alkalic igneous rocks are usually >1000 mg/L (Frencken, 1992). Sedimentary rocks have a fluorine concentration from 200 mg/L (limestone) to 1000 mg/L (shales) (Frencken, 1992). Metamorphic rocks have a fluorine concentration from 100 mg/L (regional metamorphism) up to more than 5000 mg/L (contact metamorphism) (Frencken, 1992). In these rocks, the original minerals are enriched with fluorine by metasomatic processes (Frencken, 1992).

Fluoride contamination of groundwater is influenced by fluoride rich host rock (Brindha and Elango, 2011). Fluoride is released into groundwater through weathering and leaching of the fluoride bearing mineral in the rock. Other possible sources of fluoride in groundwater include minerals in rocks and soils, such as fluorite, apatite, amphiboles and micas (Bardsen et al., 1996; Rao and Devadas, 2003). South Africa is among the notable places in the world experiencing a regional scale endemic fluorosis as a result of fluoride contaminated groundwater (McCaffery and Willis, 2001). The sources of the fluoride contaminated groundwater are attributed to fluorine-bearing rocks (McCaffery and Willis, 2001).

1.3 Problem Statement

Several studies have reported the presence and levels of fluoride and other geochemical constituents in the groundwater of Siloam village (Odiyo and Makungo, 2012; Makungo, 2008; Durowoju et al., 2015; Shabalala et al., 2015; Olivier et al., 2008, 2010, 2011). Inferences have been made that the possible source of fluoride in groundwater at Siloam village has to do with the geologic units present in the area rather than from anthropogenic sources. Due to erratic supply of potable water by the government in rural areas of South Africa, residents of Siloam village have resorted to the use of untreated groundwater from individual and communal boreholes as well as geothermal springs for their domestic water needs. However, high fluoride concentrations of up to 6.08 mg/L have been reported in those water sources (Olivier et al., 2008, 2010; Durowoju et al., 2015). The source needs to be determined hence the extent of contamination can be mapped out.

McCaffery and Willis (2001) worked on the regional source of fluoride in groundwater in the northern part of South Africa, precisely Limpopo province, which has the highest record of fluoride in the country, but Siloam village was left out in their investigation. However, Onipe (2016), attempted an investigation on the possible geogenic source of fluoride in the groundwater of Siloam village by studying a few surface rocks from Siloam village. Although, the study was not indepth due to few sampling points, and thus a generalised statement could not be drawn about the source of fluoride concentration in the groundwater. Rather, the contribution of fluoride concentration in the sampled rock units to the groundwater was established.

All the inferences drawn about the possible sources of fluoride in groundwater at Siloam village were by studying the chemistry of groundwater with major emphasis on geothermal springs (Durowoju et al., 2015; Olivier et al., 2008, 2010, 2011), but no research has been documented on the geologic and hydrologic character of fluoride in Siloam, other than an attempt by Onipe (2016), that only had a narrow focus on Siloam village's surface rocks.

Anthropogenic source of fluoride is mostly attributed to industrial and large agricultural effluent. Siloam village, however, lack industries and large agricultural farms capable of contaminating groundwater with high fluoride. The high fluoride in groundwater responsible for molten teeth and fluorosis as reported by Odiyo and Makungo (2012) is therefore attributed to geologic sources that have been speculated but have not yet been established.

1.4 Motivation

Weathering process of fluoride-rich mineral in rocks as well as fluorine leaching and enrichment processes in soil and long contact time between groundwater and fluoride bearing rocks cause the solubility and leaching of F^- into water from minerals and soils containing it. This results in a high groundwater F^- concentration above the permissible limit of 1.5 mg/L; thus, causing deformities such as molten teeth, dental and skeletal fluorosis. All water type in Siloam either from deep seated aquifers or shallow aquifers have been reported to be high in fluoride. Despite the difference in the aquifer rocks and groundwater movement pathways, inferences were drawn that the possible source could be fluorite. However, the groundwater is undersaturated with respect to fluorite therefore raising questions about the possible fluoride source. This study is motivated at answering the questions by establishing possible geologic sources of fluoride from the rocks and soils in Siloam. Therefore, this study will serve as a confirmatory work in the search for possible natural sources of fluoride in groundwater at Siloam village. The geogenic sources of fluoride in Siloam village will break new ground for more research and point to the best remediation technique for F^- removal.

1.5 Research Objectives

1.5.1 Main Objective

The main objective of this research is to investigate the geologic sources of fluoride in groundwater

1.5.2 Specific Objectives

- To evaluate the total F^- concentration in groundwater, soil and rocks samples
- To determine the hydro-geochemistry of groundwater
- To identify the mineral phases, present in the surface rock units, subsurface rock units and aquifer rock unit of the study area in relation to fluoride in the groundwater
- To determine the relationship among the different rock units, soil and groundwater and how they influence the groundwater fluoride.
- To evaluate the leachable fluoride present in different rock units and soil
- To establish if Siloam has one regional aquifer or different smaller aquifer units in relation to the sources of fluoride in groundwater.

1.6 Research Questions

Main Reseach Question

- What is the source of fluoride in groundwater of Siloam village

Sub-reasearch Questions

- What are the mineral phases of the aquifer materials, surface rock and clay deposit in Siloam Village?
- What is the hydrogeochemistry of groundwater in the study area
- What relationship exists among the aquifer rocks, surface rock, subsurface units, soil and groundwater
- How much fluoride can be leached out from rocks and soils into groundwater
- How many aquifer type exist in the village

1.7 Study Area

Siloam Village is located within Makhado Municipality, Vhembe District in Limpopo Province of South Africa. Siloam Village in this study includes the northern flank of Tswime Mountain where Mphephu thermal spring is located. It is 60 km northeast of Makhado and is approximately 45 km west of Thohoyandou. Siloam Village falls under surface water Quaternary catchment A80A of the Nzhelele River catchment which is located in the northern region of Limpopo Province, South Africa (Makungo et al., 2010). The Nzhelele River flows in the northwest direction, towards Nzhelele Dam (Olivier et al., 2011). Figure 1.1 shows the location and geographical features of Siloam village.

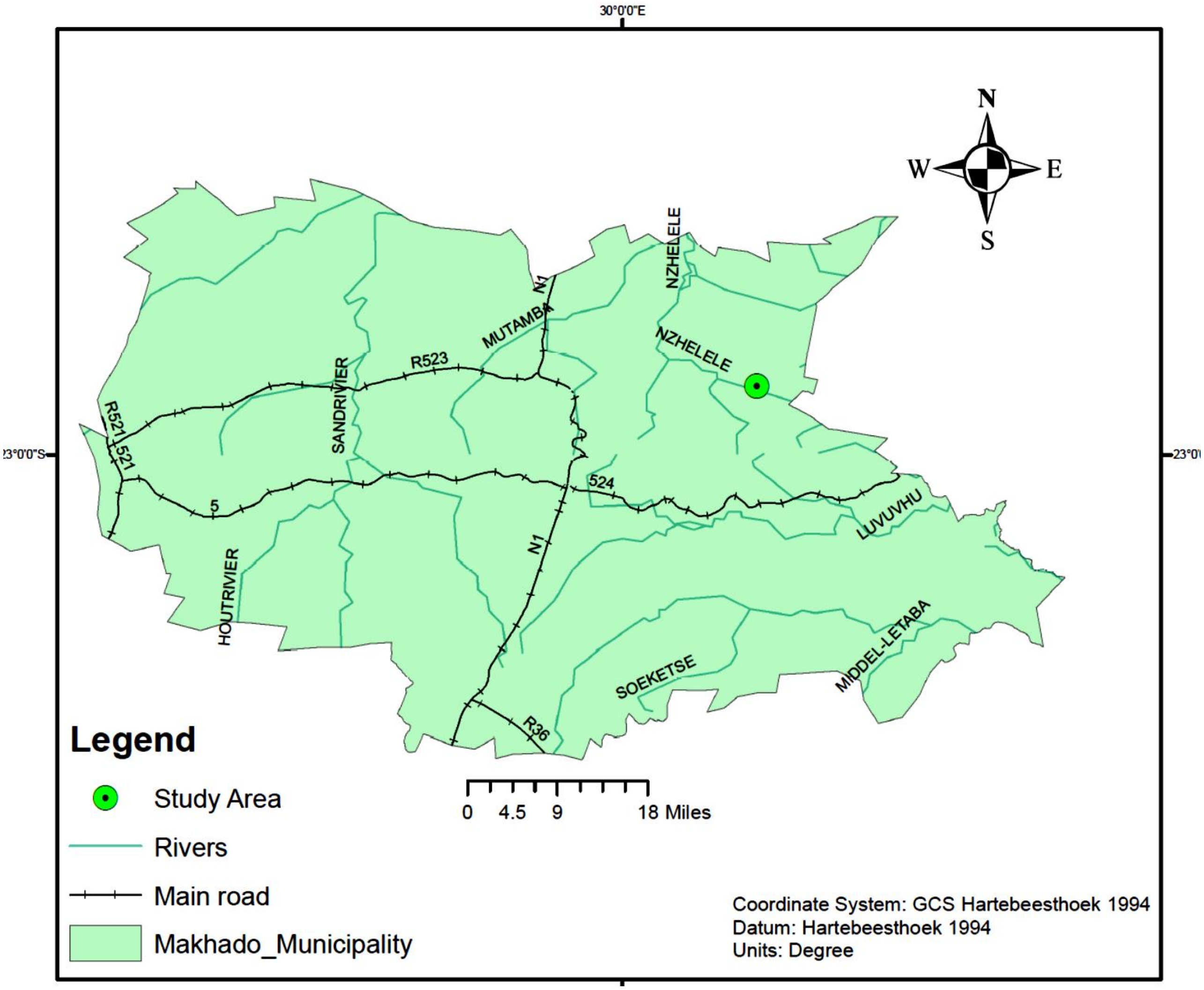

Figure 1.1: Location of the Study area

Siloam Village is found within the geographic grid of latitudes 22°53'15.8'' S and 22°54'5'' S and longitudes 30°11'10.2'' E and 30°11'23.5'' E (Figure 1.1), at an elevation ranging from 800 m to 860 m above sea level (Makungo, 2008). Siloam Village is located on the downwind/leeward side of the Soutpansberg mountain and has a semi-arid climate (Odiyo and Makungo, 2012).

1.7.1 Temperature

In Siloam Village, high temperature variations are usually observed in different seasons of the year. Winter and summer are the two main prevailing seasons of the area of study, with temperature in winter ranging from 16^0C to 22^0C and summer temperature ranging from 22^0C to 40^0C (Makungo, 2008)**.** This high temperature is an important factor that drives increased consumption of fluoride rich groundwater especially by people involved in manual labour like cattle grazing, which is a common occupation in the area.

1.7.2 Rainfall

The mean annual rainfall in Siloam Village ranges from 350-400 mm per annum (Makungo et al., 2010). Rainfall is seasonal and occurs during the summer months; from October to March (Makungo et al., 2010). More than 80% of the rainfall occurs in the summer months and only about 20% occurs in the winter months (DWAF, 2001). Rainfall is largely influenced by the Soutpansberg Mountains and moist air approaches the Soutpansberg Mountain from the southeast (i.e. Thohoyandou) and consequently the highest rainfall occurs on the southern and eastern slopes of the Soutpansberg (DWAF, 2001). Siloam Village experiences high evaporation rate of 1300-1400 mm/a, which is far greater than the annual rainfall rate (Odiyo and Makungo, 2012). The low rainfall could results in low recharge rate and thus reduces the dilution effect of rainfall on the fluoride rich groundwater.

1.8 Geology of the Study Area

Siloam Village lies within the Soutpansberg Group. Soutpansberg Group is a Mokolian age extensively faulted succession that provides a link between the pre-and post-Bushveld age (younger than 1800 mya) rocks (Brandl, 2002). The Soutpansberg succession is an east to west trending asymmetrical rift overlying the Palala shear belt (Brandl et al., 2006). The Palala shear belt separates the Kaapval craton in the South and the Limpopo belt in the North (Brandl et al., 2006). The area has been through different post-deposition tectonic and erosional activities. The evolution of Soutpansberg started with the deposition of basaltic lava as a result of volcanic activities, followed by the deposition of syn-rift sequence of sedimentary rock. The area was subjected to an extensive erosional period of non-deposition after which resistant sandstone-quartzite was deposited (Barker et al., 2006). This was followed by the unconformable deposition of Karoo supergroup which altogether went through the process of block-faulting (Johnson et al., 2006). The sequence is best developed from north of Siloam fault to Musekwa mountains (Brandl, 2002). Figure 1.2 explains the lithostratigraphy in the Siloam which is located on Soutpansberg geological group.

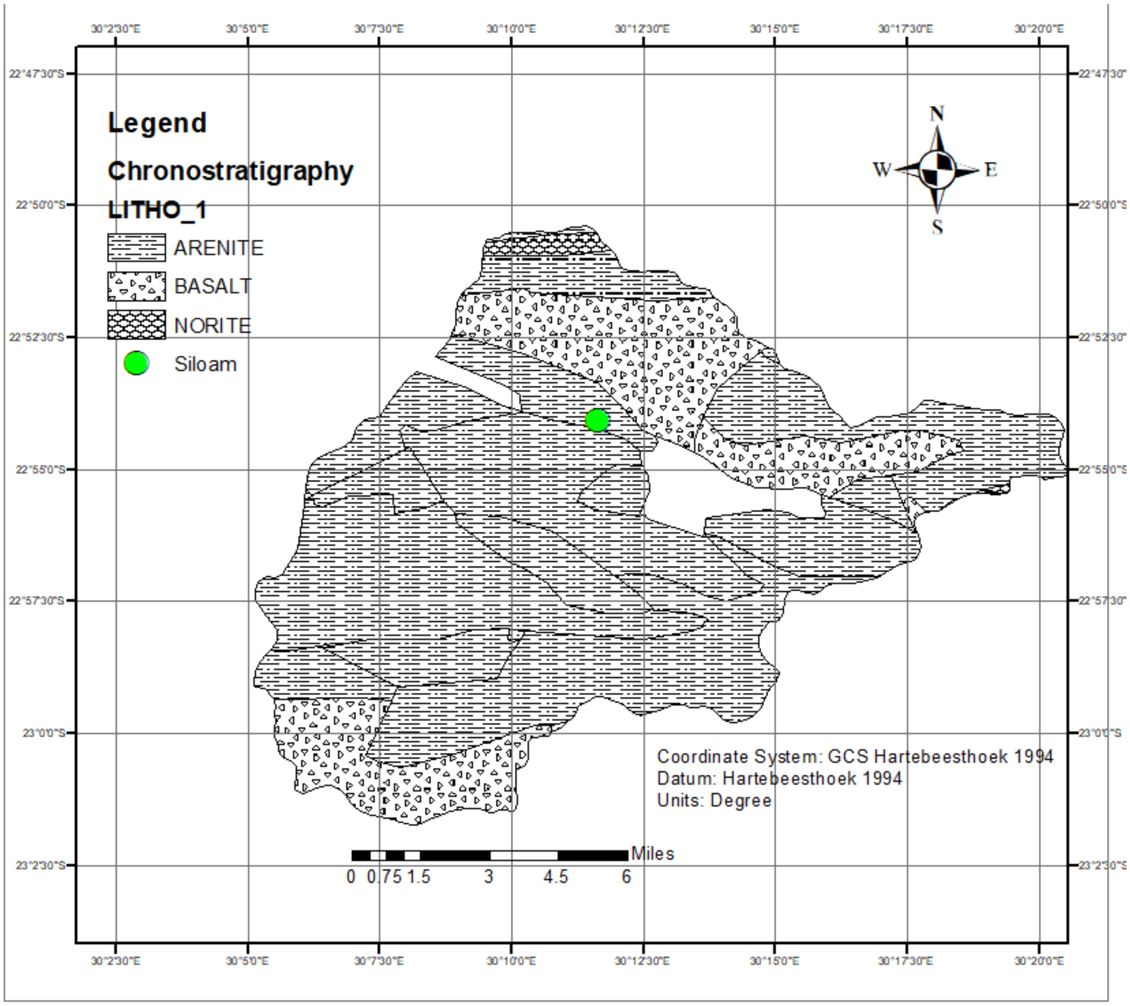

Figure 1.2: Geology map of the study area

The extensive erosional activity is evident by the presence of abudance of clay minerals and weathered rock deposit. Fluoride bearing minerals may have been wethered off the parent materials and deposited in the soil.

2. LITERATURE REVIEW

2.1 Preamble

This chapter presents a concise review of the literature relating to the geogenic source of fluoride in groundwater. The literature review covers previous studies by other authors as well as the geochemistry and chemistry of fluoride. Literature on geohydrology and geology of Siloam village are also covered in this chapter. Lastly, different methods of analyses related to this study are also reviewed.

2.2 Introduction

Fluoride concentration in water is very important because when present in permissible level it contributes to bone growth and helps in the development of strong enamel (Yeongkyoo et al., 2010). But in high concentration, it causes serious and irreversible deformation of bones and skeleton leading to skeletal and dental fluorosis. A research conducted in Sri Lanka showed that even if two areas are very close in geography, opposite endemic diseases can be prevalent due to their different environmental fluoride concentrations (Wu et al., 2004). F^- occurs in almost all types of waterbodies, either groundwater or surface water, but in varying concentration; although its concentration depends on some notable factors.

According to Brinda and Elango (2011), fluoride contamination of groundwater is from natural source (host rock). There is always a positive correlation between fluoride, sodium and bicarbonate, and negative correlation between fluoride and calcium. Amongst the natural sources of fluoride in groundwater, the aquifer material is the major contributor, followed by other sources such as volcanic ash (found in volcanic active regions) and fly ash (found in coal combustion areas). In groundwater, fluorite found in igneous and sedimentary rocks is mostly under-saturated but in rare cases saturated and over-saturated. In aquifer material, fluoride occur as selliate, fluorite, cryolite, fluoroapatite, apatite, topaz, fluoromica, biotite, epidote, amphibole, mica, clays, villamaninite and phosphorite. In Kenya, major dental and skeletal deformations have been linked to the amount of fluoride consumed in water by communities, mainly from boreholes and streams.

Table 2.1 shows reported fluoride concentrations in southern african countries. High fluoride concentration is a common occurrence in southern Africa's groundwater (Table 2.1). Countries in southern Africa include Zimbabwe, Malawi, Mozambique, Angola, Lesotho, Botswana, Namibia, Eswatini and South Africa. Although countries like Mozambique may possibly have high fluoride in its groundwater due to the bordering of the East Africa Rift valley system, no data or study has been published on the status of fluoride in groundwater of the country rather all has been a speculation of the existence of high fluoride in groundwater.

Namibia which is regarded as one of the driest countries in sub-Sahara Africa suffers from high groundwater fluoride greater than 1.5 mg/L threshold (Table 2.1). Groundwater fluoride concentration as high as 3.0 mg/L has been reported by Bolliger (2017). High fluoride in groundwater is predominant in the Cuvelai-Etosha basin to the North (Bolliger, 2017). Studies in Zimbabwe show that fluoride concentrations greater than 1.5 mg/L occur in Gokwe district of the North-West region of the country (Mamuse and Watkins, 2016). The source is suggested to be fluoridic coaly and carbonaceous rocks of the Lower Karoo Aquifer.

In Eswatini, groundwater fluoride concentration exceeding 2 mg/L can be found in the highveld and Middleveld areas of the country (CIDA, 1992) while concentrations up to 18 mg/L occur in the lowveld areas (Manyatsi and Brown, 2009). The highveld areas are underlain by masses of granite, Middleveld areas are underlain by granite and gneissic rocks while the lowveld areas are underlain by the sedimentary rocks of Karoo supergroup. Although fluorspar has been identified in several places in the country, it has little or no contribution to the fluoride concentration of Eswatini's groundwater. Therefore major contribution of groundwater fluoride comes from a different source other than the fluorospar deposit because the the fluorospar is undersaturated. In the presence of favourable climatic and topographic factor, major contribution of fluoride can come from Mica minerals in the sedimentary Karoo supergrop. As noted by CIDA (1992), the groundwater in the lowveld area is saline as a result of stagnancy. This could indicate long retention time of groundwater, which is one of the major factor that increases fluoride concentration in groundwater.

Geothermal springs of Choma district in Zambia is a major groundwater source to the community but it has concentrations of fluoride up to 10.10 mg/L (Shitumbanuma et al., 2007). It was suggested that the fluoride source could be from the Mica and Amphibole mineral groups present in the granitoid mass of the Choma-Kalomo batholith (Shitumbanuma et al., 2007).

Table 2.1: Fluoride occurrence and associated rock types in Southern Africa

Country	Fluoride Concentration(mg/L)	Reference	Source Rock	Associated Rock Type	References
Botswana	2.93	Titus et al., 2009	Granite, Gneiss	Igneous, Metamorphic	Linn, 2009
Lesotho	N/A	N/A	N/A	N/A	N/A
Malawi	0.26 – 7.58	Sajidu et al., 2008	Alluvial	Sedimentary	Malawi Gov, 1986 Chimphamba et al., 2009
Mozambique	N/A	N/A	N/A	N/A	N/A
Namibia	1.5 – 3.0	BGR, 2007	Carbonate rocks	Sedimentary	Bolliger, 2017 Mendelsohn et al., 2013
South Africa	0 – 42.05	Ncube and Schutte, 2002	Granite, clays	Igneous, Metamorphic and Sedimentary	Ncube and Schutte, 2002; Thole, 2013 Onipe 2016
Eswatini	18	CIDA, 1992		Igneous and Metamorphic	CIDA, 1992
Zambia	10.10	Shitumbanuma et al., 2007	Granitoid	Igneous	Shitumbanuma et al., 2007
Zimbabwe	>1.5	Mamuse and Watkins, 2016	Carbonate rocks	Sedimentary	Mamuse and Watkins, 2016

N/A: not available, BGR: Federal Institute for Geosciences and Natural Resources

The groundwater fluoride concentration of about 2 mg/L to 10 mg/L (Table 2.1) in Malawi occurs within the alluvial aquifers of the rift valley escarpment rather than the weathered basement aquifers (Chimphamba et al., 2009). The Qangwa Ngamiland district of North-West Botswana is prominent for slightly high fluoride concentration of about 2.93 mg/L (Titus et al., 2009). The area is underlain by Qangwadum basement complex, comprising of granitic gneiss and augen gneiss with minor development of medium grained biotite muscovite granite (Linn, 2009) which could have been the source of this high groundwater fluoride. South Africa is among the notable places in the world suffering from regional scale endemic groundwater fluoride contamination (Ncube and Schutte, 2002). Permissible fluoride exceedance occurs in almost all regions of South Africa. Groundwater fluoride concentration as high as 42.05 mg/L (Table 2.1) has been recorded in South Africa (Ncube and Schutte, 2002). Studies have documented 803 areas in South Africa affected by high fluoride in groundwater (Thole, 2013), although F^- origin was not established. South African geothermal springs have also shown varying degrees of fluoride concentrations from 0.18 mg/L to 11 mg/L (Kent, 1949; Olivier et al., 2008; Olivier et al., 2010; Durowoju et al., 2015). According to Ncube and Schutte (2002), studies show that fluoride bearing minerals occur in almost all rocks of South Africa. High groundwater fluoride in observed in areas underlain by sedimentary rock, granite, metamorphic and volcanic rocks. A map was developed to depict fluoride occurrence in Southern African countries and their concentration range (Figure 2.1).

Occurrence of high groundwater fluoride in South Africa is found in almost all geological formations, especially in most igneous rocks (Fayazi, 1994). However, in South Africa, Cryolite occur to a lesser extent than fluorspar. Fluorspar is found mostly in phosphate bearing rocks, but it is also widely associated with granite and dolomitic formations. The majority of these deposits, however, are in small and scattered pockets normally found in the granite of the Bushveld type, the dolomite and the limestone deposits of the Highveld (Rawhani, 1986). South Africa's most economically significant deposits of fluorspar occur in dolomites of the Malmani subgroup (Transvaal sequence) of the North-West Province and Felsic members of the Bushveld Complex (Munzhelele, 1998). Minor occurrences are known to occur in Kwazulu Natal. Fluorspar deposits are also found in some of the alkali and carbonatite complexes in Limpopo Province, which are of the post Bushveld age. South Africa's reserves of fluorspar are the world's second largest (Munzhelele, 1998). Below are different authors who have investigated different rock sources in South Africa in order to establish possible direct sources of fluoride in groundwater and surface water

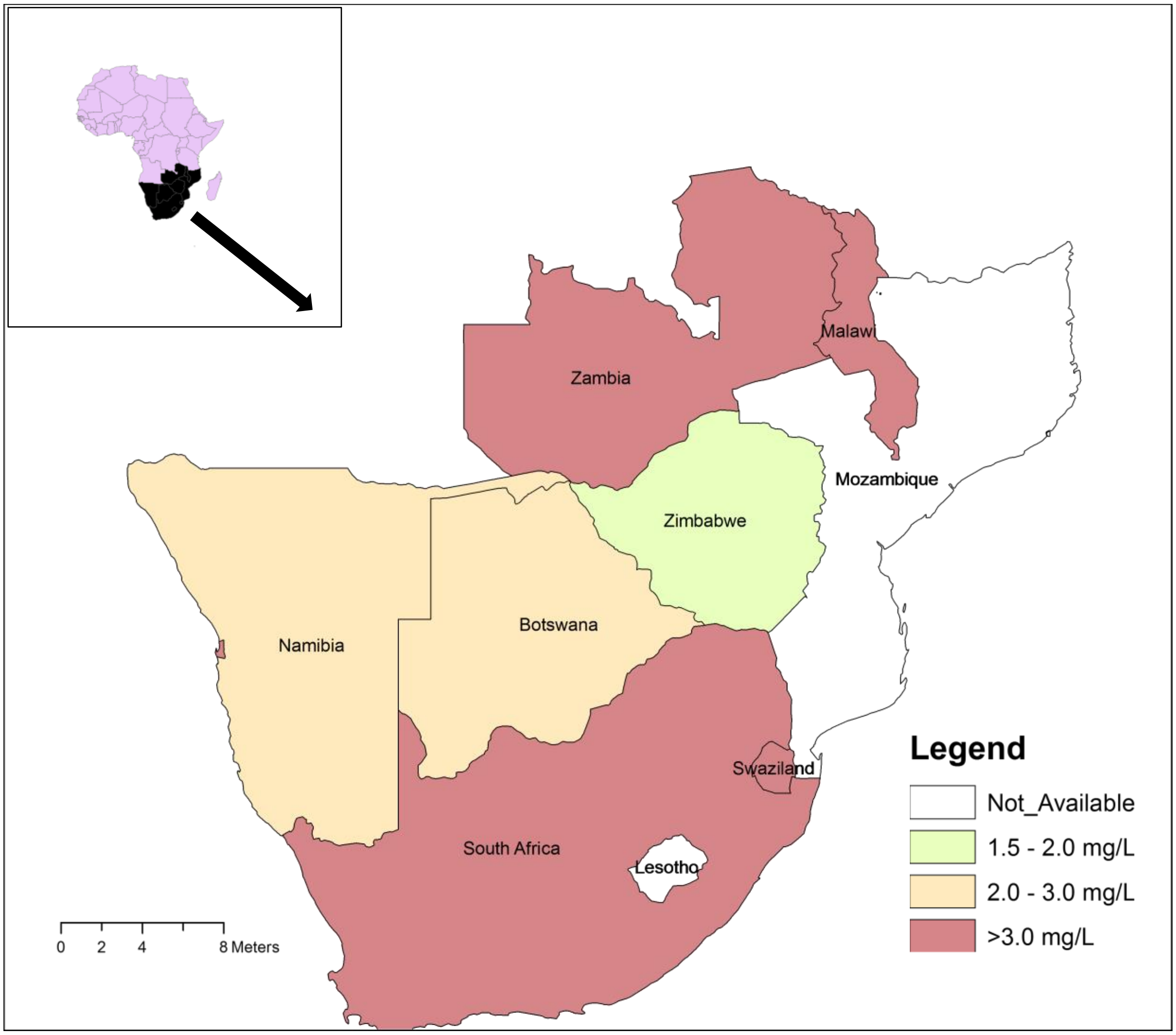

Figure 2.1: Map of Southern Africa showing groundwater fluoride concentrations

Ockerse (1946) investigated the sources of endemic fluorosis in Pilanesberg, Warmbath and Pretoria saltpan areas of South Africa. The study attempted to understand the relationship between the rocks, soils and groundwater of the areas. His work suggested that the fluoride in groundwater emanates from the Ecca formation of the Karoo super group underlying the area. Fayazi, (1994) suggested that the Karoo sedimentary strata contained fluorite derived from the surrounding Bushveld Granites during episodes of arid erosion. Clarke (2000) investigated the sources of high fluoride in groundwater of Namaqualand area of Eastern Cape, South Africa. Her work focused on the source and distribution of fluoride in the Namaqualand complex. She sampled only four major lithology and from her results she made the following conclusions:

- The presence of fluorite in rocks does not necessarily mean it is the main contributor of fluoride in groundwater. In the presence of unfavourable climatic and hydrogeologic conditions, fluorite can be undersaturated in groundwater. Fluorite saturation can be affected by certain factors like groundwater pH, groundwater residence time and rainfall dilution effect.
- Villiaumite is one of the fluoride-containing minerals more soluble than fluorite. If they are both present, Villiaumite would also contribute to the fluoride concentration in the water.
- Weathered samples contain less fluoride than fresh rock samples.
- Fluoride concentration is low at high calcium concentration and vice versa.

Multitude of dissolution and weathering processes as well as cation and anion exchange, $CaCO_3$ precipitation and evaporation rate, serve as controlling factors in the concentration of fluoride in groundwater.

McCaffery and Willis (2001), investigated the mobility of fluoride in the hydro-geochemical environment of the North and North-West Province of South Africa, in order to show relationships between fluoride-enriched groundwater and fluoride source rocks, mineralized areas and soil. From their work, certain findings were made, and these include:

- Fluoride concentration would be minimal at the soil surface but increases downwards towards the fresh rock boundary.
- The highest concentration of fluoride released (through leaching experiment) comes from rocks and soil with highest F concentration. Although during the experiment, favourable leaching conditions were assumed and this may not be the case in nature. Therefore, homogenous and favourable dissolution conditions were assumed.
- Fluoride concentration in rock shows little variation to seasonal changes.
- The distribution of fluoride in soils and rocks is similar to the distribution of fluoride in groundwater.

Onipe (2016) elucidated on the contribution of some surface rock units in Siloam Village to groundwater fluoride in the area. From his work, he established that muscovite present in one of the generics of sandstone in Siloam village also contributes to the high concentration of fluoride in groundwater of the village, unlike previous inferences that state that fluorite is the only likely source of high fluoride concentration in the groundwater of the village.

2.3 Chemical Properties of Fluorine

Fluorine is the ninth element in the periodic table and the 13th most abundant element on earth. It belongs to group 7 elements (the halogens) and has an atomic number of 9. It exists in one oxidation state as fluoride and one stable isotope (19 F). Fluoride is a negative ion of fluorine which bonds with almost all cations (Kauffman, 2005). The electron affinity of Fluorine atom makes it easy to bond with other elements it comes in contact with (DWAF, 1996). Fluorine is the lightest element in group 7 and the most electronegative element which cannot be oxidised to a positive state in the periodic table. Fluoride is able to substitute hydroxyl ions in the silicate structures of micas, amphiboles and tourmaline, due to its similar charge and ionic radius (Clarke, 2000). It rarely occurs free in nature but combines chemically to form fluorides; therefore, in minerals, fluorine is generally found as fluoride ion (Gaciri and Davies, 1993). Fluorine forms compounds with every element except helium, neon and argon.

2.4 Geochemistry of Fluorine

Fluorine is commonly considered to be relatively high in terms of concentration in most silicic igneous rocks due to residual solutions, magmatic differentiation into silicic igneous fractions and vapours (Fleischer and Robinson, 1963). However, such is mostly not the case as some igneous rocks are low in silica and have high concentration of fluorine in their most differentiated rocks. The concentration of fluorine in soil varied between 20 – 500 mg/kg (Kabata-Pendias and Pendias, 1984) while surface water contains about 100 µg/L of fluorine (Clarke, 2000). Fluorine occurs naturally as fluoride ion in association with rock-forming minerals such as fluorite [CaF_2], topaz [$Al_2SiO_4(F,OH)_2$], apatite [$CaF_2.3Ca_3(PO_4)$], amphibole group [$AB_2C_5T_8O_{22}W_2$, where A = O, Na, K, Ca, Pb, Li; B = Na, Ca, Mn^{2+}, Fe^{2+}, Mg, Li; C = Mg, Fe^{2+}, Mn^{2+}, Al, Fe^{3+}, Mn^{3+}, Ti^{4+}, Li; T = Si, Al, Ti^{4+}, Be; W = (OH), F, Cl, O_2], villiaumite [NaF], cryolite [Na_3AlF_6], ralstonite [$Na_xMg_xAl_{2-x}(F, OH)_6\,H_2O$] and phlogopite [$KMg_3(Si_3Al)O_{10}(F,OH)_2$] (Clarke, 2000). However, of all the minerals listed above, fluorite, apatite, micas, amphiboles, and villiaumite are of utmost significance to the geochemistry of fluoride in groundwater (Shah and Danishwar, 2003).

In most environments, fluorite has been the most dominating mineral which determines the geochemistry of fluoride in groundwater with some exceptions in sedimentary basin environment and a few igneous environments (Boyle, 1992). Villiaumite is more soluble than fluorite and when present in a rock, can contribute greatly to the fluoride concentration in groundwater especially those associated with aluminum (Al) deficient (peralkaline) intrusive body (Clarke, 2000). Micas, amphiboles and apatite have low solubility, therefore, their contribution to the concentration of fluoride in groundwater is determined by pH values as they are only soluble at low pH below 7 (Apambire et al., 1997). The concentration of complexing and precipitating ions such as Ca, Na, Fe, Al, B, Si, Mg and H can determine the concentration range of fluoride in groundwater (Apambire et al., 1997). The solubility of fluorite is enhanced in alkaline water because there is decreased concentration of Ca^{2+} (McCaffery and Willis, 2001).

2.5 Geochemistry of Fluorine in Soil

Liu et al. (2014) worked on the geochemical process of fluorine in soil and noted two major dynamic geochemical processes of soil fluorination with regards to groundwater and surface water. The two major geochemical processes in the fluorination of soil is basically fluorine enrichment and leaching. Fluorine enrichment process is responsible for the increase of fluorine in soil while the leaching process is responsible for the removal of soil fluorine by infiltrating and percolating water in the process, therefore enriching groundwater with fluoride. The concentration of fluoride in groundwater and surface water is determined by the dominating geochemical factors (enrichment and leaching) at play. If the dominating geochemical process is the enrichment process, then there will be low concentration in surface water but if the dominant factor is leaching, then there will be higher concentration of fluoride in ground and surface water especially in arid and semi-arid regions. The adsorption and desorption of fluorine in soil by clay minerals is responsible for enrichment and leaching of fluorine. However, various clay minerals found mostly in sedimentary basins increase the fluoride concentration in water up to 30 mg/L by a process of anion exchange which involves the displacement of OH for F (Apambire, 2001). This process causes the pH to increase to the alkaline values on pH scale (Apambire, 2001). Mobility of fluoride in soil depend on factors such as pH, soil type and the concentration of fluoride present (Ncube and Schutte, 2002). Adsorption of F in soil is favoured in low pH environment (acidic sediment).

2.6 Abundance of Fluoride in Rock Forming Minerals

The relative abundance of fluorine in F^- bearing minerals differs from each fluoride bearing mineral to the other. Fluorine ranges from main to accessory constituent of the chemical formula of its constituting mineral (Clarke, 2000). Muscovite and biotite are primary rock-forming minerals which may contain about 1 wt% of fluorine, while fluorapatite, topaz and fluorite may contain 3.8 wt%, 11.5 wt% and 48 wt%, respectively, as accessory minerals (Maria and Laura, 2015). Cryolite, a rare earth element, may also contain up to 54 wt% of fluorine (Maria and Laura, 2015). Fluoride ion and hydroxyl ion have the same charge and almost the same radius therefore they can isomporphously replace each other in the octahedral sheet of mineral structure (Brigatti and Guggenheim, 2002).

2.7 Stratigraphy of Soutpansberg group

Different authors have proposed different classifications but the mostly widely accepted stratigraphic classifications of Soutpansberg group and Karoo supergroup are the South African Commission of Stratigraphy (SACS)(1980) and Brandl (1999) classifications. According to these accepted classifications, the Soutpansberg group was subdivided into six formations namely: Tshifhefhe formation, Sibasa formation, Fundudzi formation, Wyllie's formation, Musekwa formation and Nzhelele formation.

2.7.1. Tshifhefhe Formation

This is the oldest and basal discontinuous formation of the Soutpansberg group, primarily comprising of clastic, shale, greywacke and conglomerate, which have been epidotised (Barker et al., 2006). Due to the epidotization, the rocks of Tshifhefhe formation are greenish grey coarse grained feldspathic quartzite, grits and conglomerate (Brandl, 2002). They rest uncomformably on the gneiss of Swazian age (Brandl, 2002). Although the common part of the Tshifhefhe formation is believed to be an extended part of the underlying granitic rock (Barker et al., 2006).

2.7.2. Sibasa Formation

This formation is about 3000 m to 3300 m thick in Sibasa region, consisting of sequence of cyclically erupted basalt (Brandl, 2002) with intercalations of clastic sediments (Shale, Greywacke, quartzite and minor Conglomerate) which could be as thick as 400 m (Brandl, 2002). This formation thins out to the east, west and north-west of Sibasa (Brandl, 2002). Sibasa formation could sometime contain andesite which are locally trachytic with inter-beds of tuff, agglomerate, ignimbrite and subordinate beds of sandstone, grit, conglomerate, siltstone and mudstone (Bumby et al., 2002). Epidotization is evident by the colour range of black to green of the basalt of Sibasa formation (Brandl, 2002). The radiometric age of Sibasa formation was dated by Barton (1979), to be 1749 ± 104 Ma.

2.7.3. Fundudzi Formation

This formation is about 1900 m thick and consists of arenaceous and argillaceous rocks with a few thin pyroclastic beds (Bumby et al., 2002). The top of the bed is intercalated with epidotised basaltic lava and rests uncomformably on rocks of Sibasa formation (Barker et al., 2006). This formation is found to have the highest thickness around Lake Fundudzi in the eastern side of Soutpansberg (Brandl 2002). However, laminated whitish and pinkish quarzitic sandstone and quartzite occur locally in this formation (Bumby et al., 2002).

2.7.4. Wyllie's Poort Formation

This formation consists of clastic sediments with thickness of about 1500 m (Barker et al., 2006; Bumby et al., 2002). The formation is dominated by resistant pink quartzite-sandstone and the basal contact interpreted as regional unconformity (Barker et al., 2006). According to Visser (1989), the highest Soutpansberg peak is made up of this formation. The relative age of this formation is 1700 Ma (Jansen, 1976). Minor lenticular intercalations of basaltic lava and pyroclastic rock occurs locally in the eastern region (Barker et al., 2006). This formation's deposition is considered to be associated to fluvial conditions.

2.7.5 Musekwa Formation

This formation is made up of volcanic assemblages of about 400 m thickness (Brandl, 1999) and predominantly consists of basalt, which are similar to that of the Sibasa formation (Brandl et al., 2006). This formation is found occurring around Mphephu section of Siloam valley and is associated with highly magnetic iron-rich zone (Barker et al., 2006). Bomb-like volcanic fragments occur locally in tuffaceous layers (Barker et al., 2006).

2.7.6. Nzhelele Formation

This is the topmost and the youngest formation in the Soutpansberg group. This formation is maximally preserved at a thickness of about 600 m (Barker et al., 2006) to 2000 m (Bumby et al., 2002). It comprises of red argillaceous and arenaceous sediments with intercalation of volcanics consisting of basaltic lava and several pyroclastic rocks (Barker et al., 2006). The volcanic assemblages are believed to be at the base of this formation with the deposition of argillaceous and arenaceous sediments on it (Brandl, 2002). The volcanic assemblages are predominantly made up of basaltic lava while the argillaceous and arenaceous sediments consist of tuff, reddish-brown shale, sandstone, conglomerate and quartzite (Bumby et al., 2002). Figure 2.2 shows the lithology log of Soutpansberg geological group.

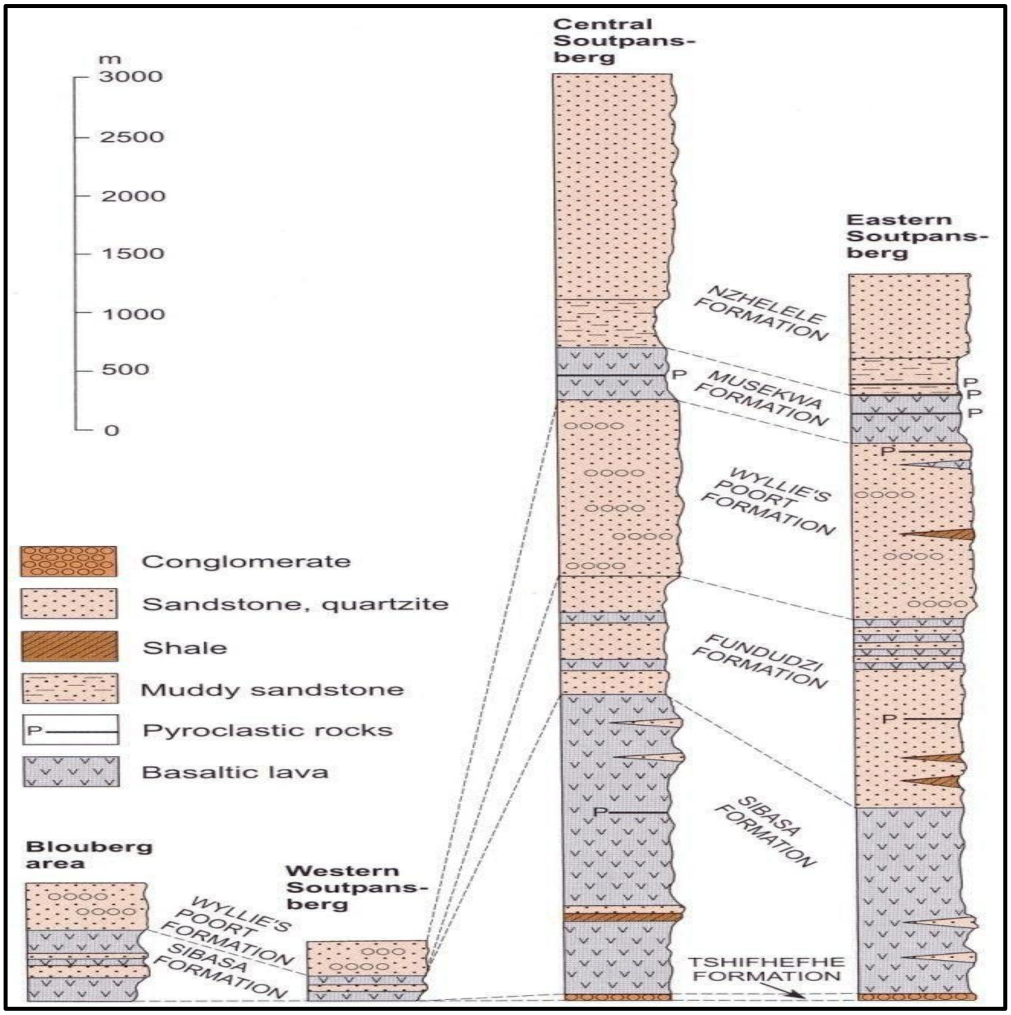

Figure 2.2: Stratigraphy of the Soutpansberg Group in the western, central and eastern Soutpansberg areas, as well as the Blouberg area (Barker et al., 2006).

However, an outlier formation categorised as a member of Soutpansberg group occurs southwest of Tshipise. It is called Stayt formation and consists essentially of volcanic rocks with a few accompanying sedimentary rocks (Bumby et al., 2002). The volcanic rocks are made up of conglomerate at the base and followed by basic lava of reasonable thickness (Bumby et al., 2002). The basic lava deposition is followed by shale of reddish-brown colour and pale-coloured quartzite (Bumby et al., 2002). However, Barton (1979), noted that this formation has the same age as the Sibasa formation.

2.8 Structural Settings

The Soutpansberg strata shows a 30^0 dipping towards the north-northwest direction with pronounced extensional faults categorised as the dominant East-North-East (ENE) which is parallel to the regional strike and the less dominant North West (NW) to North West North (NWN) (Barker et al., 2006); Brandl, 2002). The dominant ENE trending faults were believed to be old and started occurring as far back as the formation of Soutpansberg strata. The Soutpansberg are unfoliated, are not regionally strongly fractured but often found locally fractured in some places (Brandl, 2002). There is a heavy presence of fault planes intruded diabase dykes and shale-quartzite interface intruded sill (Brandl et al., 2006). Due to the nature of the geological formation in Siloam area, groundwater is stored and transmitted through fractures and faults (Brandl, et al., 2006). The maximum vertical displacement does not exceed 500 m and the throw is either to the north or south (Brandl, 2002). Figure 2.3 shows major and minor faults as well as the distribution of the formations in Soutpansberg group.

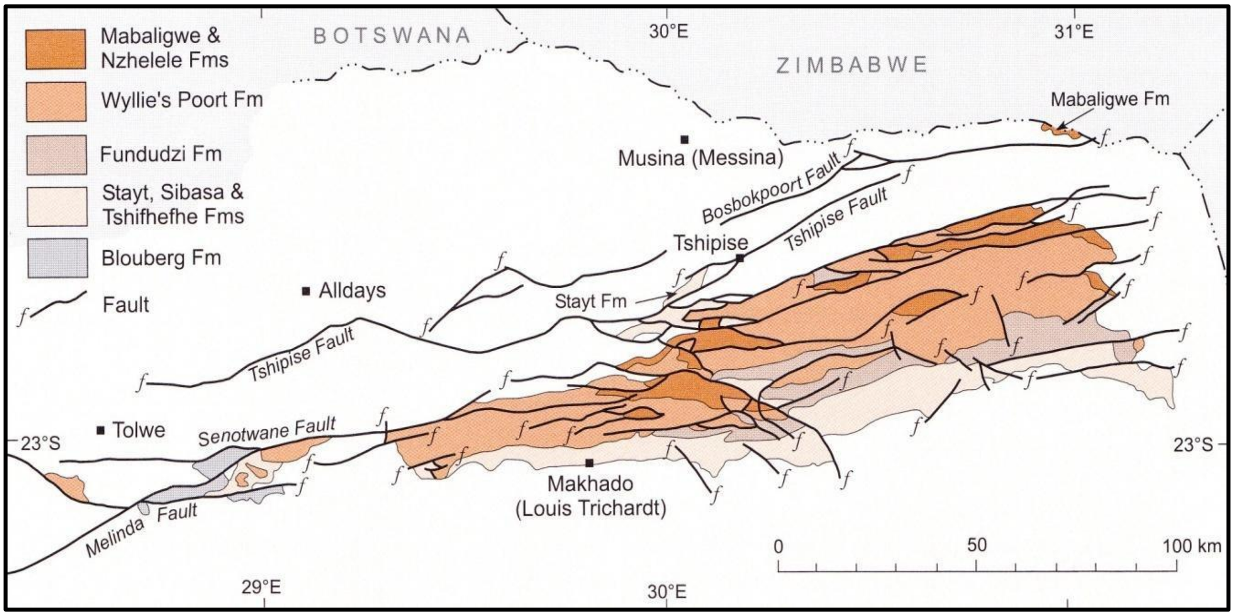

Figure 2.3: Distribution of the formations in the Soutpansberg Group as well as the Blouberg Formation (Barker et al., 2006).

2.9 Geohydrology

The aquifer type in the Soutpansberg group can be grouped as either fractured aquifer or intergranular aquifer type with groundwater hydraulics being controlled by fault, shear zone, dolerite dykes and sills (Du Toit and Sonnekus, 2010; 2011). Sibasa formation has both fractured rock aquifer and intergranular rock aquifer but has poor to moderate aquifer potentials. Fundudzi, Wyllie's and Nzhelele formations have only fractured rock aquifer. Nzhelele, however, has moderate aquifer potential while Wyllie's formation has low aquifer potential and Fundudzi formation having very low aquifer potential (Havemann, 2013). Areas with poor water quality indicate shallow sandy overburden and open fracture systems (Du Toit and Sonnekus, 2010; 2011).

2.10 Impact of High Fluoride Concentration on Human Health

Fluoride is momentous in the skeletal and dental framework of the body. Abnormal (overdose or underdose) intake of fluoride causes irreversible detrimental effect on the consumer. Particularly in children, the ingestion of higher concentration (> 1.5 mg/L) of fluoride has been documented to cause dental and skeletal fluorosis (Ncube and Schutte, 2002; Ghorai and Pant, 2005). Soil is an important resource in the survival of human race, therefore, its fluoride concentration is an important hotspot for study (Liu et al., 2014). A unique type of endemic fluorosis exists, and it is referred to by Wu et al., (2004) as coal-combustion type fluorosis. This type of fluorosis is caused by the mixture of coal with clay soil of high fluorine concentration. During the enrichment of soil with fluorine, surface soil forms weathering crust with humid climate thereby resulting in coal-combustion type of fluorosis (Liu et al., 2014). Fluoride ingestion at very high concentration causes crippling fluorosis. Fluoride is also known for its interference with body calcium (Sauerheber, 2013), causing hypocalcemia in case of higher fluoride intake, and hypercalcemia in case of low fluoride intake. Consumption of high groundwater fluoride can either have a direct or indirect implication. Effects of high fluoride ingestion include: dental fluorosis and browning of teeth, skeletal fluorosis, crippling fluorosis and hip dislocation. However, indirect effects of ingestion of high fluoride concentration include: hypocalcemia (Sauerheber, 2013), retarded growth, IQ loss, loss of mobility (Fawell et al., 2006; Reddy et al., 2003; Shomar et al., 2004; Kut et al., 2016) and psychological effect (McCaffery and Willis, 2001). Figure 2.4 shows different fluoride concentrations and different health hazards associated with them.

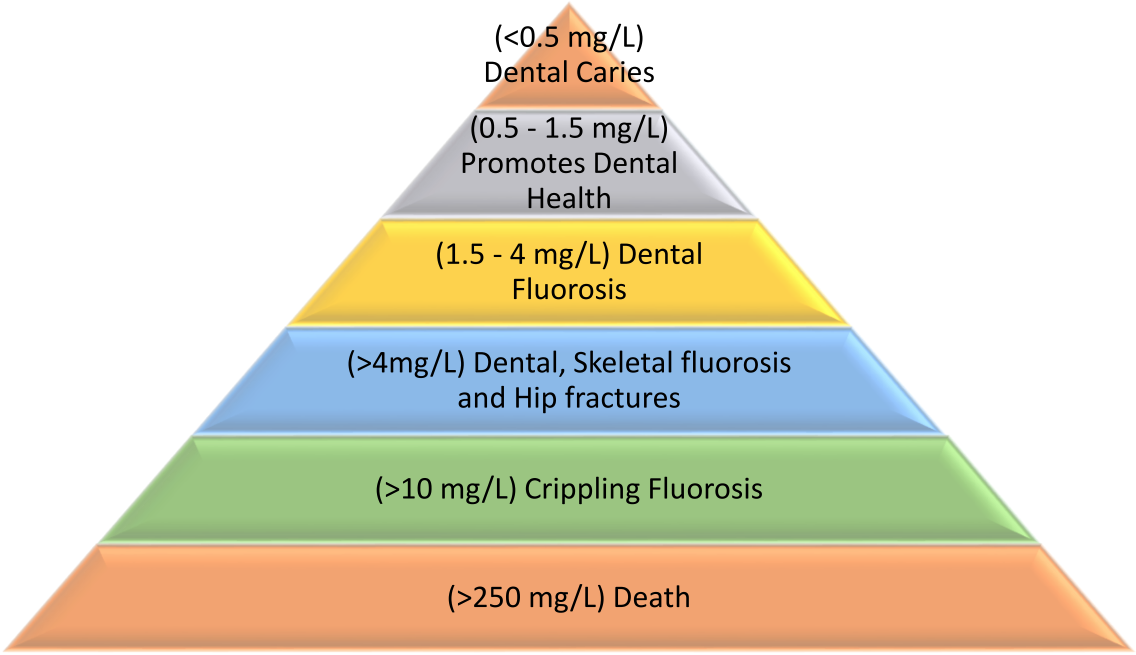

Figure 2.4: Classification of Fluoride concentration and its effect Modified after Durowoju et al. (2015)

osteoporosis, arthritis, thyroid disorder, infertility, alzheimer's syndrome and cancer have all been liked indirectly to high fluoride consumption (Kut et al., 2016). During the enrichment of soil with fluorine, surface soil forms weathering crust with humid climate thereby resulting in coal-combustion type of fluorosis (Liu et al., 2014). The effect of the combination of coal combustion and soil with high fluoride results in coal-combustion type endemic fluorosis.

2.11 Analytical Techniques in Fluoride Source Investigation

2.11.1 X-ray Fluorescence (XRF)

X-ray fluorescence spectrometry is the most preferred method for rock analysis by earth scientists because it is faster and does not require ambiguous training on the part of the analyst; therefore, it is preferred to atomic absorption spectrometry (La Tour, 1989). A striking advantage it has is that it can be used for quantitative analysis of rock samples by measuring the spectral energies produced by the sample, therefore revealing the types of elements present (Brouwer, 2010). XRF can be used for qualitative analysis where the concentration of each element can be obtained by measuring the intensities of the emitted spectrals from the samples (Brouwer, 2010). Although elemental interference could occur during XRF analysis due to the presence of minerals of highly variable composition and structure, the interference can either be broadly classified as overlap effect or absorption effect (La Tour, 1989). The combination of all these effects result in mass effect which occurs as a result of absorption of fluorescence radiation by co-existing elements (La Tour, 1989). This interference, however, can be corrected just by proper sample preparation (La Tour, 1989).

2.11.2 X-ray Diffraction (XRD)

X-ray Diffraction is an analytical method suitable for determination of mineral phases in rock samples (McCaffery and Willis, 2001). XRD analysis is carried out using a diffractometer. The spacing of atoms in most rock and soil minerals structure is almost the same as the X-ray wavelength used in X-ray diffractometers (Nesse, 2012). This attribute makes it possible for X-rays to be diffracted by regular spaced atoms that comprise crystals in minerals (Nesse, 2012). XRD has more advantage over other conventional methods of mineral phase identification because of its accuracy and convenience and thus no reference material is needed (Hillier, 2000; Gualtieri, 2000). The most widely used X-ray diffraction method is the powder method due to its powerful and convenient mineral identification technique. However, major sources of error in XRD analysis include the chemical and structural characteristics of clay minerals present in rock samples during analysis, error that arise during grinding process (Srodon et al., 2001), instrumental error, sample preferred orientation error and recording errors (Srodon et al., 2001; Nesse, 2012).

2.11.3 Fluoride Ion Selective Electrode (FISE)

FISE is a type of ion selective electrode that deals exclusively with the detection of fluoride ion in solution (Yang, 2005). It is useful both in the field and in the laboratory and works by measuring the concentration of fluoride ion in solution when the sensors on the electrodes come in contact with aqueous solution containing fluoride (Yang, 2005). However, as effective as this method is, it has its limitation. Fluoride ion selective electrode method encounters frequent interference from other high valence cations (Yang, 2005). This problem can, however, be solved by the addition of TISAB (Total Ionic Strength Adjustment Buffer) to the water sample and standards to mask all interferences from other ions (Yang, 2005). Apart from the function of TISAB as a masking agent, it performs other functions like adjustment of pH where it adjusts the pH of water sample to about 5.4, thus eliminating the effect of pH on the outcome of the result.

2.11.4 Ion Chromatography (IC)

IC is an analytical method used in the determination of anions and cations (Shimizu et al., 2006). When using IC to determine Fluoride in rock samples, elements in the rock samples are transferred into solution after alkaline fusion (Anazawa et al., 2001). In IC, the retention time, peak height and peak area of fluoride and chloride are affected by a large amount of matrix elements from the samples (Shimizu et al., 2006). The interference can be overcome by diluting the solution after alkaline fusion, using standard addition method (Shimizu et al., 2006). This can be achieved by using small test portion of about 30 mg (Shimizu et al., 2006). Electrical Conductivity (EC) values can also be used in determining the necessity of dilution (Durowoju, 2015). EC value above 500 µS/cm requires 5 times dilution and above 1000 µS/cm requires 10 times dilution (Durowoju, 2015).

2.11.5 Optical Mineralogy

Optical mineralogy is the aspect of geological science that deals with the study of optical properties of rock minerals (Hirsch, 2012). Optical mineralogy as a branch of geological science deals with thin section and polished section. Thin section is the process of making rocks and minerals transparent enough for optical study by mechanically reducing the thickness of rock or minerals to 30µm (Hirsch, 2012). Thin section slides are 24 mm x 46 mm and the sliced rock is attached to a glass slide with an epoxy (Nesse, 2012). The slide is always covered with another slide. The epoxy generally always has a refractive index of 1.54 (Hirsch, 2012; Nesse, 2012).

Although unlike other mineralogical methods of analysis like XRD, some minerals cannot be detected in thin section under microscope probably due to the existence of such minerals in small grains or due to cutting out of the minerals from the part of the thin section prepared (Battaleblooie et al., 2012). Therefore, both XRD and thin section are used to complement each other. Thin section study can either be studied under plane polarised light (PPL) or cross polarised light (XPL). In PPL, light can be constrained to vibrate in only a single plane by a polarising filter while in XPL thin section minerals are viewed between two perpendicular Polaroid filters (Lang, 2015). Minerals under PPL exhibit pleochroism in which colour change depends on orientation of grain relative to polariser (Lang, 2015). Isotropic substance appears dark when viewed under XPL because the polarised light that passes through it is unaltered, and when it hits the analyser it is blocked (Lang, 2015). This property makes minerals exhibit different colours under PPL and XPL.

2.12 Hydrochemical and Geochemical plots in Fluoride Source Investigation

2.12.1 Piper and Ternary Diagram

Piper trilinear diagram is a hydrogeological tool for visualizing the dominant major ions controlling the groundwater and surface water chemistry of an area. Piper trilinear diagram (Piper, 1944) evaluates the evolution of the water and relationship between rock types and water composition (Ravikumar et al., 2015). Major cations and anions are plotted in ternary triangles as shown in Figure 2.5. The apexes of the cation triangle consist of Mg, Ca and Na+K while the apexes of the cation triangle consist of SO_4, Cl and HCO_3+CO_3. The cation and Anion ternary plots are projected into a centrally placed diamond which determines the dominant water chemistry as shown in Figure 2.5 .

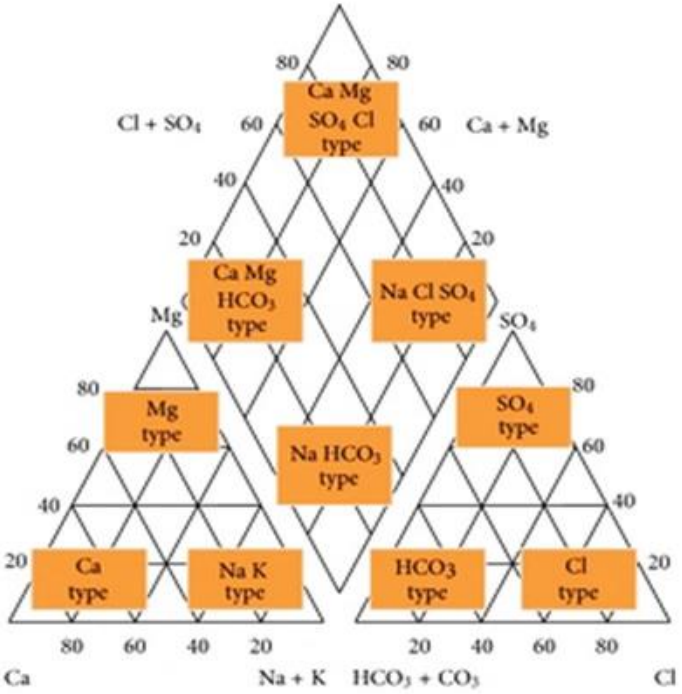

Figure 2.5: Piper diagram showing water type (Piper, 1944; Al Farraj et al, 2012)

2.12.2 Durov Diagram

Durov diagram or Durov plot is similar to piper plot, although Durov diagram is advantageous over the Piper diagram in revealing some geochemical processes that could affect groundwater genesis (Ravikumar et al., 2015). This plot illustrates cations and anions in relativity to TDS and pH. Illustration and interpretation of Durov's diagram is shown in Figure 2.6.

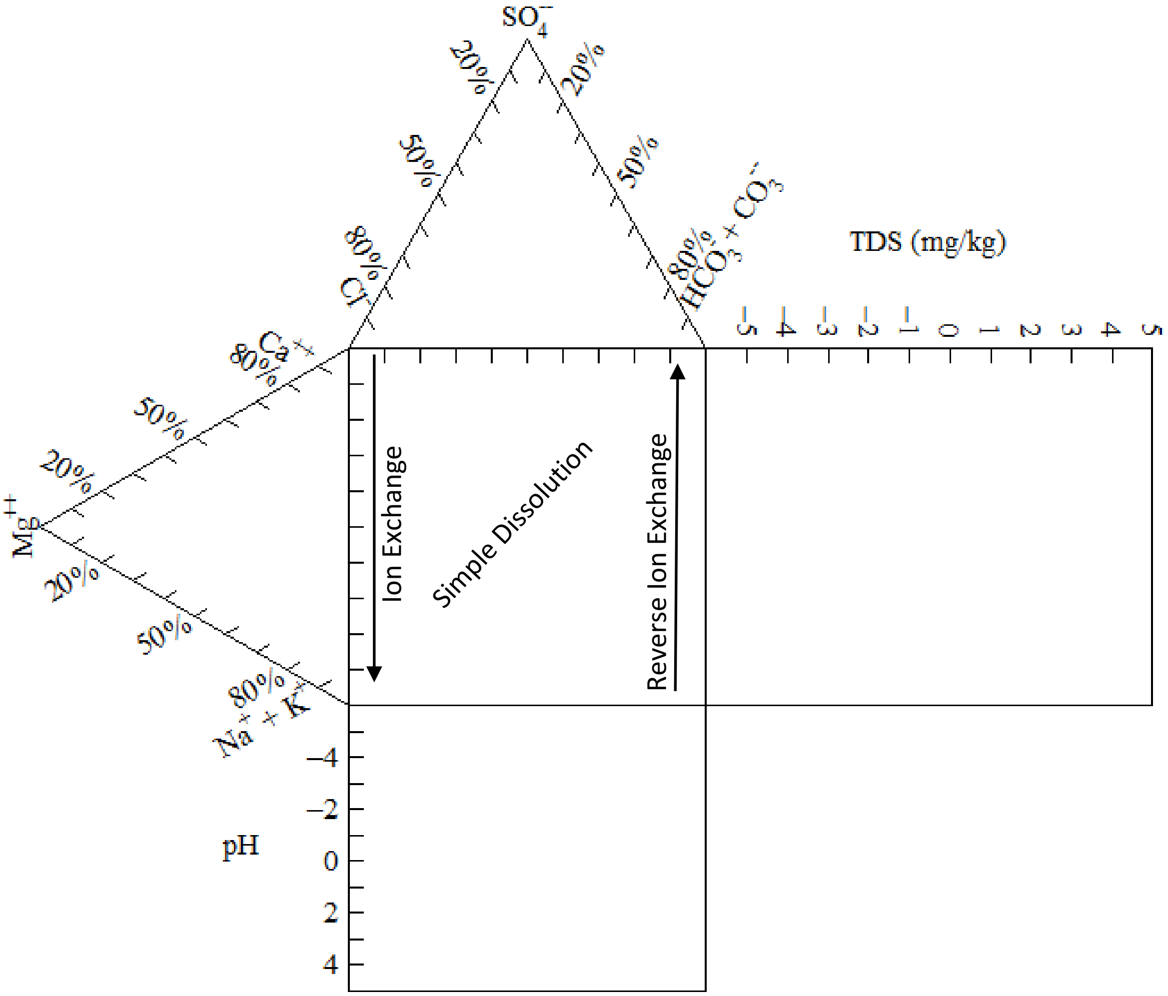

Figure 2.6: Durov Trilinear diagram

2.12.3 Gibbs Diagram

Gibbs plot is used to illustrate natural processes of evaporation-crystallization, rock-water interaction/weathering and atmospheric precipitation (Gibbs, 1970). This plot can also be used to illustrate the dominant factor responsible for the mineralization of groundwater. A simple illustration and interpretation of Gibbs diagram is shown in Figure 2.7.

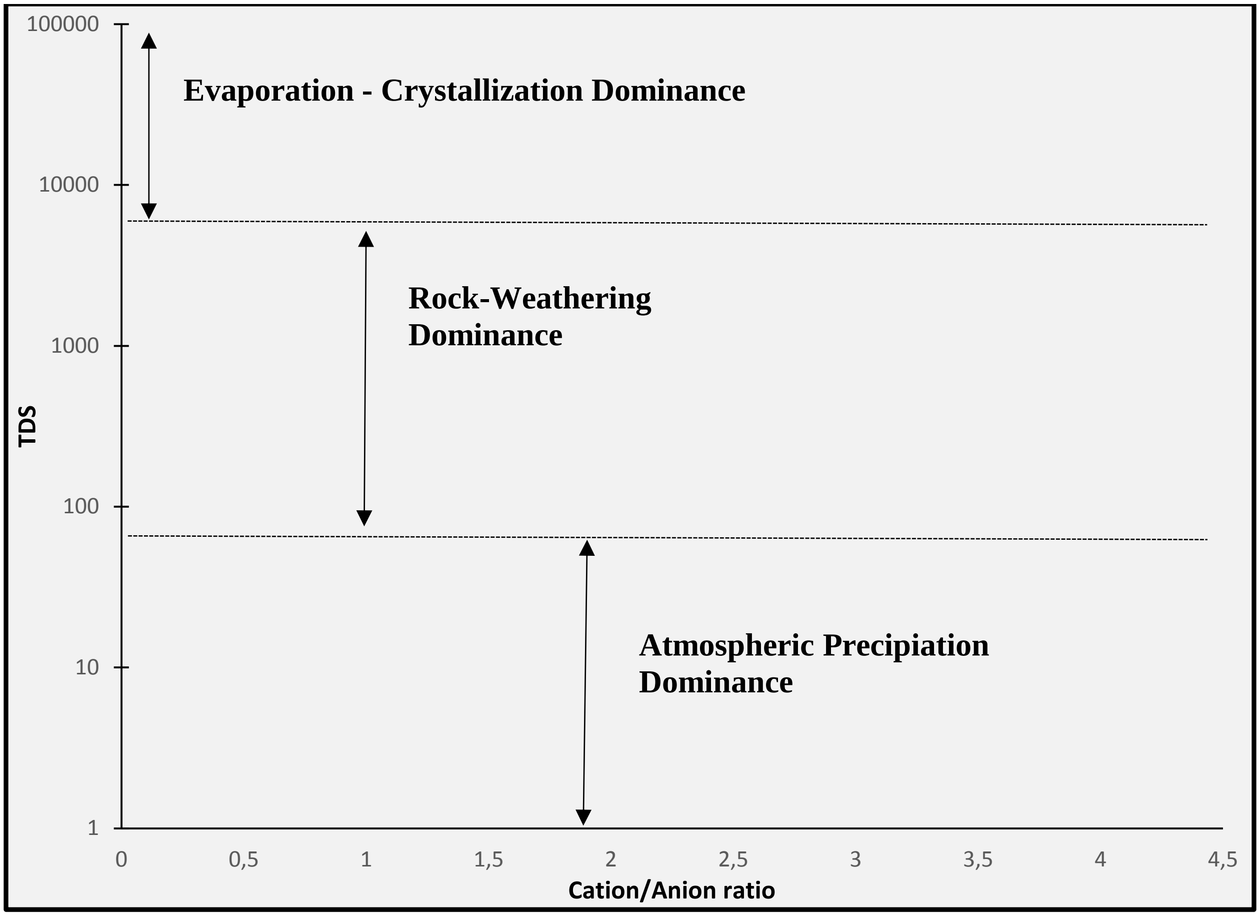

Figure 2.7: Gibbs diagram modified after Gibbs (1970)

3. RESEARCH METHODOLOGY

3.0 Materials and Methods

3.1 Preamble

This chapter explains the specific procedures and methods used in the determination of possible geogenic source of fluoride in groundwater at Siloam Village.

3.2 Sampling

3.2.1 Rock and Soil Sampling

Two types of rock samples were collected. Surface rocks and borehole cuttings. Clay deposits in the area were also sampled. The major outcropped rock at the study area was sampled. Samples were taken in duplicates according to McCaffery and Willis, (2001). The samples were collected irrespective of season as fluoride concentrations in rocks over short period of time show no variation to seasonal changes (McCaffery and Willis, 2001). The samples were taken in August 2017. However, road-cuts were not available and thus made the rock sampling a bit challenging due to poor accessibility to available outcrops. Figure 3.1 shows the drilling process and borehole cut samples were taken during drilling exercise at two sampling points (Figure 3.2). The cut samples were collected after every 5 m depth and stored in a sealable polythene bag, before being transported to the laboratory for storage. The drilling operation took place in August and September 2017. Drilling of boreholes were recommended by Onipe (2016) because analytical informations from the surface rocks were not enough to clearly show the major contributors of fluoride to groundwater at Siloam Village. Also, drilling of borehole is necessary to understand the general trend of fluoride at depth towards aquifers and in Table 3.1, the geographical coordinates, elevation and depths of all sampling points were also recorded.

Figure 3.1: Drilling operation at Siloam Village

Figure 3.2: Rock and soil sample collection from borehole cuttings

3.2.2 Water Sampling

The samples were collected as shown in Figure 3.3, from two monitoring boreholes, and 2 other private boreholes. The samples were collected using plastic cups as recommended by Harvey (2000). For each location, the samples were collected three times in a 1 L sampling bottle before they were transported to the laboratory for further analysis. As suggested by Weaver (2007), the bottles were pre-rinsed with the water to be sampled, to avoid cross contamination.

Figure 3.3: Groundwater sampling at one of the boreholes

Table 3.1: Summary of samples and GPS coordinates of sampling points

Study Area	Sample type	Sample ID	Elevation / Depth(m)	GPS coordinate	No of samples
			WATER SAMPLES		
Siloam	Monitoring borehole 1 (BH1)	BH1	N/A	22° 53’ 34.008” S 30° 11’ 47.22” E	1
	Monitoring borehole 2 (BH2)	BH2	N/A	22° 53’ 38.148” S 30° 11’ 18.52” E	1
	Individual Borehole 1 (H1)	H1	N/A		1
	Individual Borehole 2 (H2)	H2	N/A		1
			ROCKS AND SOIL SAMPLES		
	Surface Soil Sample	S1	776 (e)	22° 53’ 34.83” S 30° 11’ 45.56” E	1
	Surface Rock Sample 1	SR2	798 (e)	22° 54’ 22.8” S 30° 10’ 44.0” E	1

Surface Rock Sample 2	SR3	1048 (e)	22° 52’ 02.5” S 30° 12’ 09.7” E	1
Borehole 1 Cuttings	X	65 (d)	22° 53’ 34.008” S 30° 11’ 47.22” E	6
Borehole 2 Cuttings	Y	40 (d)	22° 53’ 38.148” S 30° 11’ 18.528” E	6

e: elevation, d: depth, N/A: Not available

3.3 Sample Preparation

3.3.1 Rock and Soil sample preparation

The XRD samples were prepared according to the standardised PANalytical backloading system, which provides nearly random distribution of the particles, while the XRF samples were prepared as pressed powders. The preparations were carried out at the Department of Mining and Environmental Geology Laboratory and Department of Hydrology and Water Resources laboratory, both in University of Venda, and XRD and XRF Facilities of the Department of Geology, University of Pretoria, South Africa. The rock samples were split, washed, dried crushed and pulverised. Splitting into chips was done by a hydraulic splitter after which the split chip was washed and treated with ultrasound wave to remove any loose impure particles. After washing, the samples were dried overnight in an oven to remove excess water introduced during washing of samples. A jaw crusher was used to crush the samples (Figure 3.4) and the crushed samples were split to obtain approximately 100 mL of the sample. The aliquot was further reduced to finer grain by pulverising for about Five (5) minutes to reduce the particle size of the sample to less than 40 µm diameter using a Retsch Rs 200 miller (Figure 3.4).

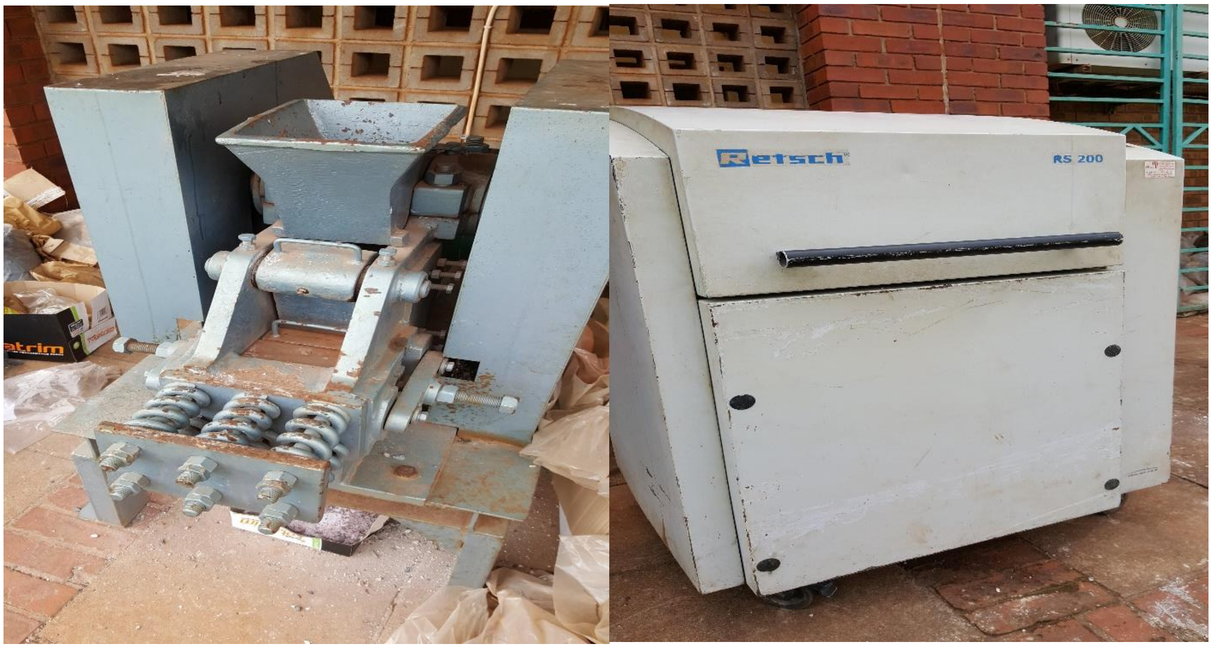

Figure 3.4: Jaw crusher and Retsch milling equipment used for crushing and pulverisation

The surface rock samples were washed, sun-dried and crushed using a jaw crusher. The crushed samples were transferred into Retsch Rs-200 pulveriser (Figure 3.4) as explained above and milled for 5 min. The milled samples were transferred to a paper bag and oven dried at 110°C for 6 hours using 80 L Labotech Ecotherm Oven Model 276 at the Department of Hydrology and Water Resources of University of Venda (Figure 3.5). The borehole cut samples were firstly oven dried at 110°C for 6 hours using a Labotec Oven. After Oven drying, the samples were milled to less than 20 µm and transported in a sealable polythene bag to Agricultural Research Council Laboratory in Pretoria and Mintek Laboratories in Johannesburg for leachable fluoride analysis and total fluoride analysis, respectively.

Figure 3.5: Labotec oven during drying of samples

Samples for total fluoride in solids analysis were prepared by weighing 0.2 g of the samples in a nickel crucible, 2 g of $CaCO_3$ (sodium carbonate) and 2 g of Na_2O_2 (sodium peroxide). The mixture was fused manually to aid leaching, using a low flame bunsen burner in a fume box. Auto fusion was avoided to prevent burning of the nickel crucibles and ensure that Na_2O_2 does not get moist. 250 mL plastic beakers were pre-washed in a heated Ecobath using concentrated HCl (Hydrochloric acid). The heated crucibles were transferred into 250 mL plastic beakers where 50 mL of deionized water and 8 mL of HCl was added. The mixtures were covered with a plastic lid and placed on warmbath until the samples were leached out of the crucibles. The crucibles were washed with de-ionized water to make sure that all the leachate were removed from the crucibles. The solutions were transferred into 100 mL volumetric flask and diluted to mark. Blank was prepared by fusing 2 g of $CaCO_3$ and 2 g of Na_2O_2. The fused mixture was transferred into a 250 mL beaker and 100 mL of deionized water and 16 mL of concentrated HCl were added. The mixture was allowed to leach out and the crucible rinsed with distilled water. The leachate was transferred into a 200 mL volumetric flask and filled to mark with de-ionized water. Calibration was carried out using 0.1 ppm, 1 ppm, 10 ppm, 100 ppm and 1000 ppm fluoride standards. The standards, samples and blanks were all mixed in equal proportion with TISAB II in a 1:1 ratio.

Calibration of pH meter was done using buffers 6.00 and 4.00. The Slope was 97.9% which fell within the recommended slope limit of 95% to 105%. The pH of the samples and blanks were adjusted to 6.00 using 50% NaOH (sodium hydroxide) and HCl. The pH was adjusted because at pH below 5, hydrogen ions complex a portion of the fluoride ions, forming HF or HF_2, which cannot be detected by the fluoride electrode. Likewise, in a solution with pH above 9, the electrode responds to hydroxide ion as well as to fluoride ion giving an exaggerated reading.

Samples for leachable fluoride in solids were prepared by mixing 10 g of the sample with 100 ml of distilled water at a ratio of 1:10. The samples were prepared in duplicate to ensure that each sample is represented under induced temperature and normal room temperature. The first set of samples were shaken in a warm bath at normal room temperature for 6 hours. The second set of samples were shaken in a warm bath at a temperature of 42°C. Because of the clay contents of the sample the mixture was centrifuged for 10 minutes at a speed of 3000 rpm (Figure 3.6). The centrifuged samples were decanted and filtered using a 9 cm filter paper. The resultant mixture was then further filtered using a 40 µm syringe filter to ensure that all impurities that could block the IC column was removed. The EC of the samples were below 500 µs/cm hence dilution was not required. The pH meter was calibrated using pH buffers 4.00 and 7.00.

Figure 3.6: Pulverised rocks and soils samples inside centrifuge

3.3.2 Water Sample Preparation

The samples collected for major anions were preserved in a refrigerator at a temperature of about 4^{o} C and analysed within seven days of collection. For fluoride analysis, the samples, standards and TISAB were removed from the storage refrigerator and placed in a Labotec warm bath at room temperature. It is imperative that all reagents and sample temperature remains the same because temperature changes above 25°C affects the readings. pH meter was calibrated using Orion Verserstar pH buffer 4.00 and 7.00. The slope of the pH meter was recorded as 97.8% which falls within the recommended pH range for analysis. The samples for major anions and cations were prepared at Agricultural Research Council in Pretoria, South Africa by filtering the water samples through a 40 µm syringe filters using a 20 mL syringe. The EC of the samples were below 500 µs/cm hence dilution was not done

3.4 Experimental Analysis

3.4.1 Mineral Phase Identification and Quantification Analysis

The minerals in the rocks and soils of Siloam Village were identified and quantified using X-ray diffraction method of analysis. The samples were analysed using a PANalytical X'Pert Pro powder diffractometer in θ–θ configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å). The phases were identified using X'Pert Highscore plus software. As suggested by Doebelin and Kleeberg (2015), the relative phase amounts (weight%) were estimated using the Rietveld method (Autoquan Program). The analysis was carried out at the XRF and XRD facilities of the Department of Geology, University of Pretoria, South Africa. The equipment was switched on and allowed to warm-up for 30 min before any measurement was carried out. The handle of the stage was pulled down to allow loading of samples into the goniometer. After sample mounting on the sample holder, high voltage was activated and the intensity of diffracted X-rays was continuously recorded as the sample and detector rotated through their respective angles. A peak in intensity occurs when the mineral contains lattice planes with d-spacings appropriate to diffract X-rays at that value of θ. The angle of the peaks were used to identify the mineral phase while the intensitites of the peaks indicated the abundance of each mineral.

3.4.2 Total Oxide Analysis

The total rock and soil oxides were measured using X-ray Fluoresence analytical method. The ARL Perform'X Sequential XRF instrument with Uniquant software was used for the analyses. The software analysed for all elements in the periodic Table between Na and U, but only elements found above the detection limits were reported. The values were normalised, as no LOI was done to determine crystal water and oxidation state changes. The analysis was also carried out at the XRF and XRD facilities of the Department of Geology, University of Pretoria, South Africa. The concentration of 23 elements in rocks and soil samples of Siloam Village were measured by comparing their intensity with internationally accepted internal database. The intensities for all elements were corrected automatically for line interference and absorption effects due to all the other elements using the fundamental parameter method.

3.4.3 Total Fluoride Analysis

Total fluoride analysis was carried out using Fluoride Ion Selective Electrode. This method was also used to determine the fluoride concentration in groundwater at Siloam village and the total fluoride content of the rock and soil samples. The groundwater analysis was carried out on the third day of sample collection using Fluoride Ion-Selective electrode Orion Versastar Advanced Electrochemistry meter at the Department of Hydrology and Water Resources of the University of Venda, South Africa, while the fluoride in solids were analysed 2 weeks after sample collection at Mintek Laboratories, Johannesburg, South Africa using Metrohm fluoride meter with reference electrode. Internal calibration was used to calibrate the equipment. Calibration standards 0.1 ppm, 1 ppm, 10 ppm and 100 ppm were used to calibrate the equipment. Orion TISAB II was used as the ionic strength adjustment buffer and the TISAB II was mixed in equal volume of 50 mL with 50 mL of samples and buffer. The TISAB used were TISAB pre-mixed with standard at ratio 1:1. Labotec Magnetic stirrer was used to ensure that the mixture of TISAB and sample was thorough and accurate during measurement.

Each rock and soil samples were prepared and analysed in a 150 mL beaker by inserting the measuring electrode and the reference electrode in the beaker while a magnetic stirrer shakes the mixture. The millivolts (mV) of the standards were recorded before the mV of the samples. The fluoride content was evaluated by plotting fluoride concentration on a logarithmic scale versus the mV readings on a linear scale. The slope was measured as the difference between the two standards, the concentration of which are decades apart. However, water samples were also measured in a 150 mL beaker with Orion Versastar combined reference and measuring electrode. The measurement was taken directly because the Orion Versastar Advanced Electrochemistry meter is capable of measuring directly unlike metrohm fluoride meter used for fluoride in solids which required a reference electrode.

3.4.5 Physicochemical Analysis

As shown in Figure 3.7, the physicochemical parameters were measured *insitu* using pH, EC and temperature multimeter (Multi 340i/SET) and was also measured in the laboratory. The measurements for each sample was carried out in triplicate and the mean value calculated to ensure maximum accuracy and precision.

3.4.4 Leaching Experiment

This method was used to determine the leachability of fluoride and other major cation and anions from the rock and soil samples. IC was used for both normal samples and the temperature induced samples. The Ion Chromatograph was allowed to stabilise for 15 min prior to analysis. The eluent used was Dionex AS22 which is made up of 45 mM Na_2CO_3 and 1.4 mM $NaHCO_3$. The pH, EC and alkalinity of the water, soil and rock samples were pre-measured using Mantech Titrasip Autotitrator (Figure 3.8) to ensure that the unknown samples fall within the recommended pH and EC limit for using Ion chromatograph. The analysis was carried out at the Agricultural Research Council, Pretoria, South Africa using Dionex Model DX 500 Ion Chromatograph (Figure 3.9)

Figure 3.7: Measurement of physicochemical parameters

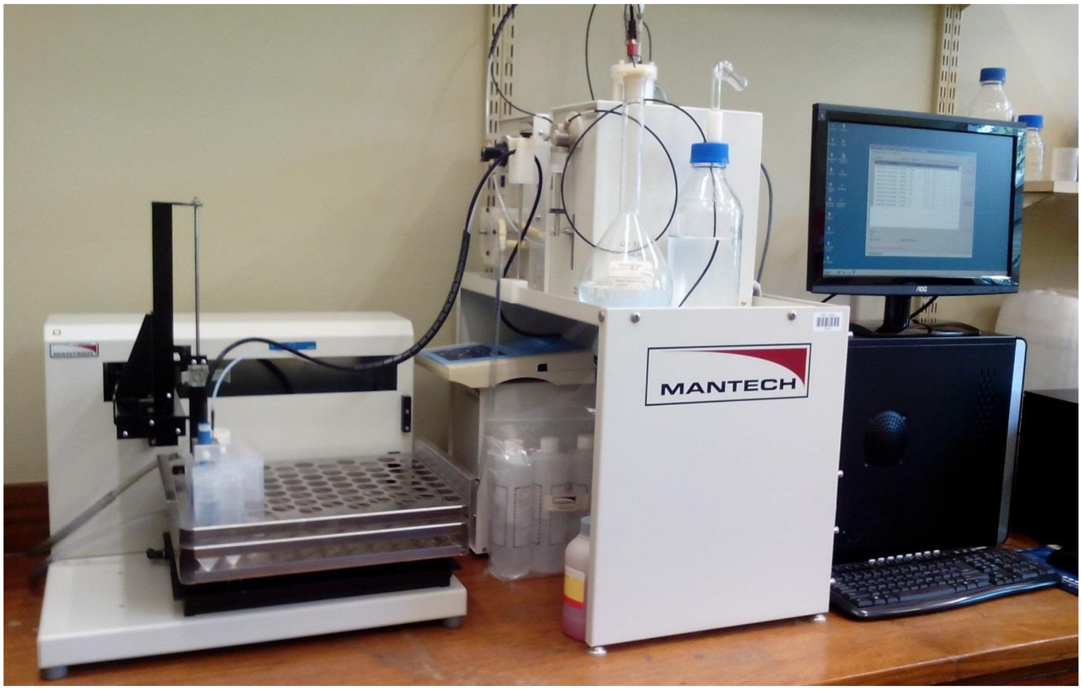

Figure 3.8: Mantech Titrasip Autotitrator used for determination of pH, EC and alkalinity

Figure 3.9: Ion chromatography (Dionex Model DX 500) used for the determination of the major anions

3.5 Quality Control and Assurance

3.5.1 Sample Collection

- During sampling, fresh samples were obtained and the samples were representative of the bulk material.
- The representation was ensured by avoiding sampling from detached rock boulders.
- However, for water sampling, sampling bottles were pre-rinsed to avoid cross contamination and the samples were placed on ice during transportation to the storage and from the storage to the laboratory in an air-tight cooler.
- Soil samples were stored in air-tight, sealed polythene bags.

3.5.2 Sample Preparation

The following quality control procedures as noted by La Tour (1989), was observed during preparation of samples for both XRF and XRD analyses:

- To eliminate contamination of pulverised aliquot by analyst hand, plastic gloves was used immediately after pulverisation of the samples.
- Contamination of samples from previously pulverized sample was minimised by the pulverisation of pure quartz and washing of the pulverising pot to clean the container in-between each sample pulverisation. Although, this may introduce SiO_2 contamination which is negligible compared to the silica content of the samples.

- Excessive pulverisation was avoided to reduce the chances of contamination of samples
- Calibration was carried out on all instruments used for all analysis and the manufacturer's instructions were followed

- Instrumental errors from misalignment of instrument and sample positioning in the diffractometer was minimised by proper calibration and inclusion of sample blanks of known *d-spacing* (spaces between adjacent lattices).
- Recording error was minimised by electronic and manual recording because multiple run on the same sample yield different peak values.
- The effect of sample preferred orientation on the intensity of the samples was minimised by grounding the sample below 20 μm.
- For safety, gloves, laboratory googles, face mask and Lab boots were worn at all times.

3.5.3 Experimental Analysis and Quality Assurance

- Equipment calibration was done according to the manufacturer's specifications.
- All experimental analysis was carried out in triplicates to ensure maximum accuracy and precision.
- Cross contamination of liquid samples was avoided by pre-rinsing of apparatus with de-ionized water

- The stirring bar and other apparatus were well rinsed with de-ionized water and in some cases washed with washing liquid.

- During total fluoride in solids analysis, the temperature was kept constant at 25°C because increased temperature has a direct effect on the pH and vice versa by causing an increase in the pH value. An increase in the pH value affects the reading of fluoride ion selective electrode by reading hydroxide ion as well as fluoride ion thereby exaggerating the values of the fluoride content of the samples

- The Lab temperature was kept between 24 – 25°C for all experimental procedures.
- During total fluoride in solid analysis, the pH was kept constant at 6.00 using 50% NaOH or HCl where applicable.
- Blanks were used in all the analytical methods to cross-check the accuracy and precision of the equipments.

3.5.4 Data Validation

Water sample data was validated using charge balance. For every solution, neautrality must be maintained. Aqueous solutions must be electrically neutral. This means that in solutions, the total sum of all the positive charges (cations) must equal the total sum of all negative charges (anions), therefore charge balance was used to determine eliminate the following errors:

- lab errors (serious or systematic errors during analysis)
- some dissolved species (major ions) are not measured
- using *unfiltered* samples that contain particulate matter which dissolves upon addition of acid (for preservation purposes)

The CBE was calculated using equation 4.1, and adjustment made where necessary.

$$\boldsymbol{CBE} = \frac{\boldsymbol{\sum cations - | \sum anions |}}{\boldsymbol{\sum cations + | \sum anions |}} \times \mathbf{100} \quad \text{………(4.1)}$$

The charge balance error (CBE) must not exceed ±5%. For this study, the charge balance was determined using Aqion Hydrochemical Numerical software, version 6.6.11, with United States Geological Survey (U.S.G.S.) software PhreeqC as an internal numerical solver.

4. RESULTS AND DISCUSSION

4.1 Preamble

This chapter presents the results and discussion of all analyses and experimental work carried out in the evaluation of the geogenic source of fluoride in groundwater at Siloam Village. The results are summarised and discussed under different headings.

4.2 Groundwater Physicochemical Quality Parameters

The physicochemical groundwater quality parameters for Siloam village are reported in Table 4.1. The EC and the TDS values for all the locations sampled within Siloam Village were within the recommended limits of <150 µS/m and <450 mg/L, respectively (DWAF, 1996). Therefore, they pose no threat to the health of those that consume the water. The monitoring borehole sites in Siloam Village (BH1 and BH2) and one private household 1 groundwater has pH values of 8.17, 8.10 and 8.86, respectively (Table 4.1). Household 2 sample has a slightly higher pH value of 9.19. All sampling points in Siloam village have pH values above 7.0, therefore the groundwater is alkaline (Table 4.1). These pH result support the finding of Odiyo and Makungo (2012) and Durowoju (2015) that the groundwater of Siloam village is generally mostly alkaline. Although these pH values are above the neutral value of 7.0, they are still within the recommended South African Guidelines value of 5.0 to 9.5 for domestic water use (DWAF, 1996) except for household 2. The pH of individual boreholes H1 and H2, however are above the WHO recommended limits of 6.5 to 8.5 (WHO 2011) for drinking water but are within the South African recommended limit of 5.0 to 9.5 (Table 4.1). Alkaline pH favours increased fluoride concentration as a result of reduced Ca^{2+} concentration (McCaffery and Willis, 2001). This makes the water favourable for the solubility of common fluoride bearing minerals in groundwater at Siloam. Groundwater with high concentration of sodium ion and carbonate species as well as pH greater than 8 mostly have F concentration exceeding 1 mg/L (Rivett et al., 2006). High groundwater pH is a proxy indicator of long residence time of groundwater-rock interaction (Kim, 2003; Kim et al., 2008)

Table 4.1: Physico-chemical parameters of Siloam groundwater

	pH	**EC (µS/m)**	**TDS (mg/L)**	**Temperature (°C)**	**Alkalinity (mg/L)**	**CBE (%)**
BH1	8.17	69.00	296.45	25.00	25.50	0
BH2	8.10	73.00	423.07	27.00	17.50	0
H1	8.86	63.00	305.73	48.00	10.00	3.95
H2	9.19	33.00	130.12	45.00	12.00	0

BH1 & BH2: Monitoring boreholes 1 and 2, H1 and H2: Household boreholes 1 and 2,

Siloam village is known for its high temperature gradient due to the occurrence of tectonic activities in the form of geothermal activity. Siloam village alone is endowed with two geothermal springs and this is evidence of geothermal activities below the ground surface. The village has undergone different tectonic faulting, fracturing, post-tectonic deposition and an extensive erosional period of non-deposition (Barker et al., 2006). This extensive tectonic activity has allowed the development of minor aquifers of different properties which are evident from the temperature differences between aquifers, some of which are close to each other like BH1 and H1. The temperature results of groundwater in Siloam Village are given in Table 4.1. The monitoring boreholes BH1 and BH2 at maximum depths of 65 m and 40 m, respectively, have temperatures of 25°C and 27°C, respectively, while private boreholes of households H1 and H2 have temperatures of 48°C and 45°C, respectively (Table 4.1). Based on temperature difference, the aquifer in Siloam village can be broadly classified as tepid and hot groundwater aquifer. Groundwater temperature classification is presented in Table 4.2.

Table 4.2: Temperature classification

Temperature range (°C)	**<25**	**25 - 34**	**34 - 42**	**42 - 50**	**>50**
Classification	cold	tepid	warm	hot	scalding

(Olivier et al., 2008; Kent, 1949; Hoffman, 1979; Winfield, 1980; Boekstein, 1998; Chidley, 1985)

Generally, temperature has a direct effect on chemical reactions as it speeds up the rate of chemical reaction and dissolution. The fluoride concentrations in H1, H2, BH1 and BH2 are 4.55 mg/L, 4.95 mg/L, 4.02 mg/L and 3.92 mg/L, respectively. Figure 4.1 shows a graphical relationship between temperature and fluoride. Fluoride concentration is higher in hot water aquifer of wells H1 and H2 (Figure 4.1) than in cold water aquifers (BH1 and BH2). At H1 and H2, the temperature of the groundwater was 45°C and 48°C yielding fluoride concentrations of 4.55 mg/L and 4.95 mg/L, respectively (Figure 4.1). At BH1 and BH2, however, fluoride concentrations of 4.02 and 3.92 occured at groundwater temperatures of 27°C and 25°C, respectively (Figure 4.1).

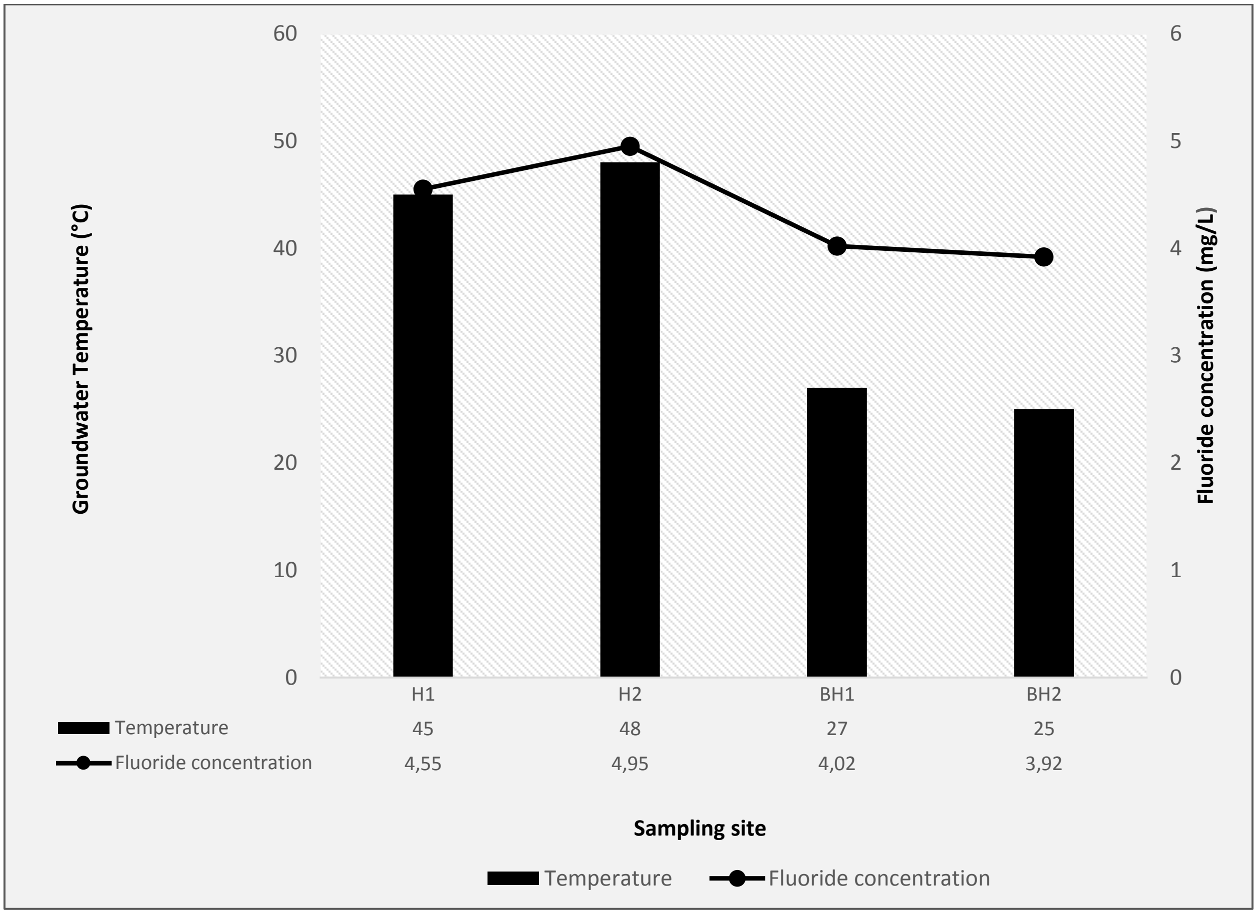

Figure 4.1: Plot of temperature against fluoride concentration

The plot of groundwater temperature vs fluoride concentration in groundwater at Siloam village shows that at higher temperature, there is high fluoride concentration while at lower temperature, the fluoride concentration is low. The temperature change of 23°C resulted in 1.03 mg/L increase in fluoride concentration in groundwater (Figure 4.1). This is a significant increase in fluoride concentration. A similar trend was reported in Ethiopia by Tekle-Haimanot et al., (2006), where 80% of the groundwater samples obtained in the geothermal springs of the rift African valley area contained fluoride concentrations above 3.0 mg/L and 30% contained fluoride concentration above 13.0 mg/L compared to the cold spring in the same area with maximum fluoride concentration of less than 3.0 mg/L. High geothermal temperature causes an increased dissolution of fluoride bearing formations and thus increases the fluoride concentration in groundwater (Odiyo and Makungo, 2012). A two-tailed test by Odiyo and Makungo (2012) showed that there is a significant difference between the fluoride concentration values in geothermal waters and tepid groundwater at Siloam village. Correlation analysis (Table 4.3) on the physicochemical parameters show that almost all the parameters have significant correlating impact on each other except for the impact of alkalinity on TDS and vice versa. The correlation Table shows how temperature affects the pH of groundwater in the area. The strong positive correlation coefficient between pH and temperature shows that an increase in temperature gives an increase in the pH of groundwater towards the alkaline side of the pH scale, which in turn favours the dissolution of fluorine bearing minerals into the groundwater because of a reduced Ca solubility. Although this sometimes is not the case.

Table 4.3: Correlation of groundwater Physicochemical parameters

	pH	*Temperature*	*EC*	*TDS*	*Alkalinity*	*Fluoride*
pH	1					
Temperature	**0.928842**	1				
EC	-0.88298	-0.651	1			
TDS	-0.8302	-0.58397	0.937949	1		
Alkalinity	-0.78932	-0.91189	0.51812	0.322035	1	
Fluoride	**0.837406**	**0.888851**	-0.84828	-0.96807	-0.33431	1

A direct proportionality occurs between the correlation of TDS and EC because Ec is a measure of ionic charge. The correlation results (Table 4.3) show that a very strong correlation exist between EC and TDS which is supported by the equation below (Hayashi, 2008)

$$TDS = 0.67 \times EC \text{ .... } (4.2)$$

Therefore, an increase in the electrical properties of groundwater at Siloam village gives an increase in the total dissolved solid properties of the water. However, a strong negative correlation also occurs between pH and EC, pH and TDS, pH and alkalinity and vice versa. This inverse proportionality means that an increase in pH causes a sharp decrease in the EC, TDS and alkalinity. However, TDS and alkalinity show weak correlation to each other and vice versa. It is to be noted, however, that alkalinity which is the capability of the groundwater to resist change in pH reduces at an increased pH and increased temperature. This is supported by the correlation coefficient in Table 4.3 where strong negative correlation occurs between pH and alkalinity as well as pH and temperature. The correlation tables show that Temperature and pH have significant effects on each other as well as the dissolution of fluoride in groundwater at Siloam village.

4.3 Groundwater Hydrochemistry

Groundwater chemistry is directly linked to its quality therefore it is imperative to understand the complex geochemical processes occurring below the surface of the earth through different geochemical facies present. The major anions and cations in the groundwater of Siloam village were analysed using IC and are reported in Table 4.4:

Table 4.4: Groundwater Chemical parameter

Sample ID	F (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	PO_4^{3-} (mg/L)	CO_3^{2-} (mg/L)	HCO_3^- (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	B (mg/L)
H1	4.55	0	0.17	153.3	16.45	1.15	1.8	8.54	118	2.73	3.54	0	0.01
H2	4.95	0	1.31	38.9	10.55	1.52	2.4	9.76	62.7	2.21	0.82	0	0.02
BH1	4.50	0	3.22	80.14	17.56	3.29	0	31.11	124	5.15	27.8	15.8	0.03
BH2	3.92	0	83.95	103.23	25.88	4.59	2.7	15.86	170	4.67	12.8	3.72	0.05
STD	1.50	4.00	44.0	250	500	N/A	20.0	N/A	400	400	200	100	1.5

STD: Maximum limit. N/A: Not available

Generally, groundwater chemical composition at Siloam village appears to be within permissible limit for drinking and other activities except for the occurrence of high concentration of fluoride in all the four wells and nitrate in well BH2 (Table 4.4). In each of the four boreholes, the fluoride concentration exceeds the generally accepted WHO permissible limit of 1.5 mg/L (Table 4.4). This supports the findings of Odiyo and Makungo (2012) and Durowoju et al. (2015). They reported the presence of high fluoride in groundwater in Siloam village and its effect on human health. The nitrate concentration of BH2 exceed the DWAF (1996) permissible limit of 44 mg/L (Table 4.4). Nitrate contamination is a growing problem throughout the world and ingestion by infants can cause methaemoglobinaemia and eventual death (Fewtrell, 2004). High concentration of nitrate above the permissible 44 mg/L is considered a good pointer of anthropogenic pollution source (Kim et al., 2005). Nitrate source is mostly from septic tanks, pit latrines and fertilizers. The water table in well BH2 occurs at 28 m below the surface thus it is a shallow well and this makes it easy for infiltration of sewage from nearby septic tanks. The source of high concentration of nitrate in well BH2 could be from septic tank located less than 20 m uphill from the well. Calcium concentrations in all the boreholes occured below 30 mg/L which falls within the class I recommended operational limit of <150 mg/L and below class II maximum allowable limit of 150 mg/L- 300 mg/L (DWAF, 2005). Therefore, its concentration is generally low in the area. Calcium and fluoride were plotted against each other in order to determine a general relationship between them (Figure 4.2).

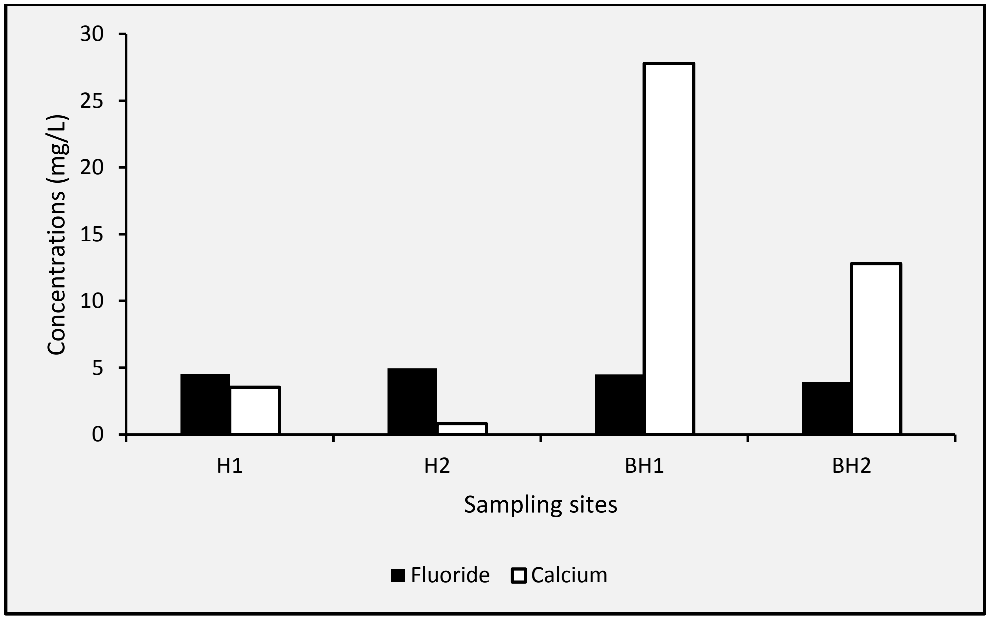

Figure 4.2: Plot of Fluoride against calcium

From Figure 4.2, the highest fluoride concentration occurs at H2 while the lowest calcium ion concentration also occurred at H2. Fluoride occurrence in borehole H1 at concentration of 4.55 mg/L is more than the calcium concentration of 3.54 mg/L. However, at borehole BH1, the highest concentration of calcium occurs at 27 mg/L, and at borehole BH2, 12.2 mg/L concentration of calcium occurs. At boreholes BH1 and BH2, the occurrence of high fluoride concentration is also accompanied by a slightly high calcium concentration, whereas in boreholes H1 and H2, high fluoride concentration occurs at low calcium concentration. However, groundwater high in calcium often contain fluoride concentration less than 1mg/L (Rivette et al., 2006) most likely because high concentration of calcium reduces the solubility of CaF_2 thus inhibiting the release of fluoride into the groundwater (Chae et al., 2007). It is to be noted that the opposing trend between fluoride and calcium is not always the case as seen in Evangelina spring in Limpopo South Africa (Durowoju et al., 2015). The chemistry of the groundwater at Siloam village partially agrees with the opposing factor of solubility between calcium and fluoride because it appears that geothermal temperature plays an important role in the inverse solubility trend between fluoride and calcium. This phenomenon can be better explained by statistically correlating fluoride and calcium in the two predominant water types in Siloam village (hot and tepid groundwater). Table 4.5 shows the correlation analysis of fluoride and calcium in hot and tepid groundwater at Siloam village.

Table 4.5: Correlation table for Calcium and fluoride in hot and tepid groundwater

Hot groundwater		
	Calcium	*Fluoride*
Calcium	1	
Fluoride	**-1**	1
Tepid groundwater		
Calcium	1	
Fluoride	**1**	1

The relationship between fluoride and calcium in Siloam village can either be direct or inverse relationship depending on the temperature range of the groundwater (Table 4.5). A very strong negative correlation exists between fluoride and calcium in hot groundwater of Siloam village while a strong positive correlation occurs between fluoride and calcium in the tepid groundwater at Siloam village. The very strong positive correlation denotes that at an increasing fluoride concentration, the calcium concentration increases while strong negative correlation denotes that at increasing fluoride concentration, the calcium concentration decreases. Therefore, the relationship between calcium and fluoride in groundwater at Siloam village shows that geothermal temperature could affect the solubility and concentration of fluoride and calcium in groundwater.

Understanding the geochemical evolution of groundwater is important in determining the dominant cations and anions in such water which in turn gives a better understanding of the source of infiltration or where the groundwater comes from. Generally, throughout the sampled boreholes, the value of calcium is low, this could be because of the alkaline nature of the water which affects the solubility of calcium therefore causing the faster dissolution of fluoride bearing mineral and release of fluoride into the groundwater at Siloam village. High – elevated Na+, suggest dissolution of Na-feldspar. The Major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) were plotted against major anions (SO_4^{2-}, HCO_3^{-} and Cl^{-}) on a piper trilinear diagram, in an attempt to understand the water type dominant in the groundwater of Siloam Village (Figure 4.3). The piper trilinear diagram below gives an evolutional history of the groundwater and the dominating water type in the sampled aquifers at Siloam village. A trilinear piper plot by Durowoju (2015) shows that the geothermal springs of Siloam village in both summer and winter months were dominated by Na-Cl ions. Therefore, seasonal changes do not have effect on the groundwater type and dominant cation and anions.

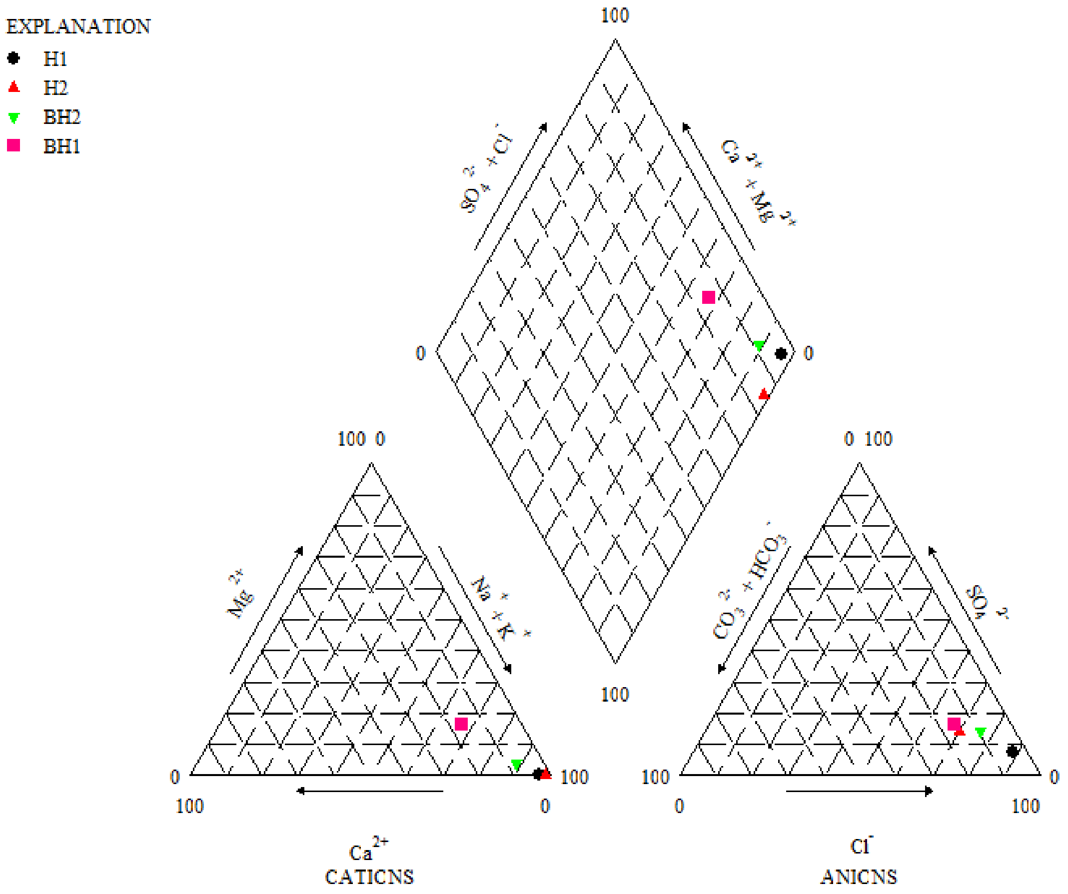

Figure 4.3: Piper diagram of major anions and cations in groundwater

From the piper trilinear diagram, the hydrochemistry of the groundwater at Siloam village is plotted on the Na-Cl region of the trilinear diagram therefore denoting that the water type is the Na-Cl dominated water. The detailed explanation of Piper diagram with diagram is highlighted in chapter 2, section 2.12.1. However, the hydrochemistry was plotted on the Na-Cl side of the trilinear diagram because the chemistry of the water is majorly dominated by Na and Cl ions. Piper diagram divides water into Six basic types based on the dominating cation and anion. The divisions are:

1. *Ca-HCO_3 type*
2. *Na-Cl type*
3. *Ca-Mg-Cl type,*

4. *Ca-Na-HCO_3 type*
5. *Ca-Cl type*
6. *Na-HCO_3 type*

The chemistry of groundwater and the dominant groundwater type are determined by the geology and subsurface rocks present in the area. Although exceptions can be made in situations where dissolution factors like residence time, climate and rainfall, are not favourable for fluoride migration from the rock to groundwater as experienced in Eswatini (CIDA, 1992). Groundwater with high fluoride in Korea occurs mostly within the basement aquifer and are dominantly Na-HCO_3 water type influenced by granitoids and metamorphic rocks (Chae et al., 2007). However, in Siloam village, results from the study of Durowoju (2015) and Olivier et al., (2011) conform to that of this study indicating that the dominant water type is Na-Cl in groundwater. Groundwater mixing from different sources do not occur in the study area because the water is predominantly and 100% Na^+- Cl^- type. Further confirmation was performed using stiff diagram which diagrammatically shows the dominant anions and cations in groundwater samples in meq/kg.

Stiff diagram (Figure 4.4) shows the major ionic contents of each borehole based on the water type. The stiff diagram shows the dominating impact of Na-Cl groundwater type in Siloam village. The dominance of Na in the groundwater could be from weathering and dissolution of plagioclase tectosilicate mineral end member which is evident by the abundance of clay minerals in Siloam village, which were formed from the weathering of feldspar. This Na-Cl type of water is typical of brine and deep ancient groundwater. Brine refers to high concentration of Na-Cl ion in water. Most groundwater is siloam area is dominated by Na-Cl which shows that the water is brine in nature. It mostly occur as a result of long resident time with rocks therefore causing migration of minerals from the rock to groundwater. Thus Na-Cl water type indicate ancient groundwater with ample residence time with the aquifer materials. This is evident by the dominance of the alkali ion in form of Na^+. Therefore, the groundwater is of an alkaline type as illustrated by Ravikumar et al., (2015) and is dominated by increasing alkali concentration (Na^+).

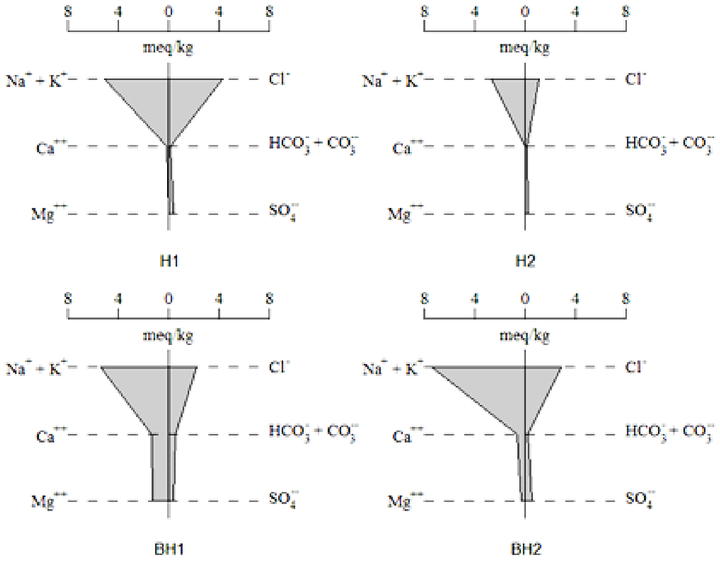

Figure 4.4: Stiff diagram for groundwater in Siloam village

Groundwater from all the sampled locations in Siloam village are from a very deep aquifer as illustrated by the piper and confirmed by the stiff diagram but could rather find its way to shallow aquifers by upward movement via numerous major and minor faults present in the area. Example of such fault is the ENE trending Siloam fault which influences most of the geothermal springs in the area. This finding conforms with the findings of Durowoju (2015). However, the piper and stiff diagram were disadvantageous because they could not show the specific order of major ion concentration in each well which is an important factor to determine the hydro chemical process responsible for the domination of Na^+ and Cl^- in the groundwater at Siloam Village.

The XY plot (Figure 4.5) shows clearly the order of dominating components in the groundwater at Siloam village. From Figure 4.5, Borehole H1 shows a higher concentration of Cl^- than Na^+. This shows that unlike the other boreholes where the predomination facie is $Na^+ > Cl^-$, borehole H1 has a predominating hydro-chemical process of $Cl^- > Na^+$. This implies that the hydrochemical process responsible for the Na and Cl enrichment of BH1, BH2 and H2 is different from the hydrochemical process responsible for the enrichment of BH1. Hounslow (1995) noted that if Cl^- exceeds Na^+, then the hydrochemical process responsible for the enrichment is most likely reverse ion exchange / reverse softening. However, if Na^+ commensurates Cl^-, then dissolution of halite is the hydrochemical process responsible for the enrichment of Na^+ and Cl- (Hounslow, 1995). In boreholes H2, BH1 and BH2, Na^+ concentration supersedes Cl^- concentration which is likely as a result of ion exchange/ brine softening. However, to confirm the hydrochemical process assumption, the hydrochemical data of BH1, BH2, H1 and H2 were plotted on Durov's diagram (Figure 4.6). The diagram shows that the hydrochemical data clusters occur around Na^++ K^+ and Cl^- quadrant, and this denotes that the dominant water type occurs because of ion exchange and reverse ion exchange.

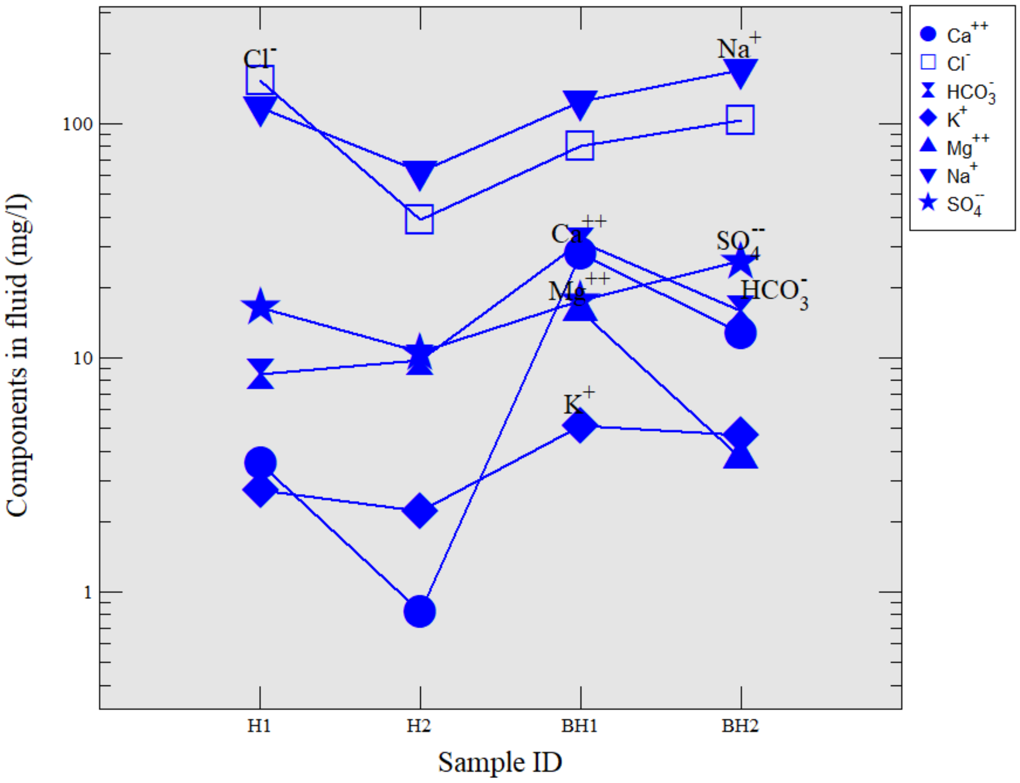

Figure 4.5: XY Plot for groundwater at Siloam Village showing dominant cations and anions

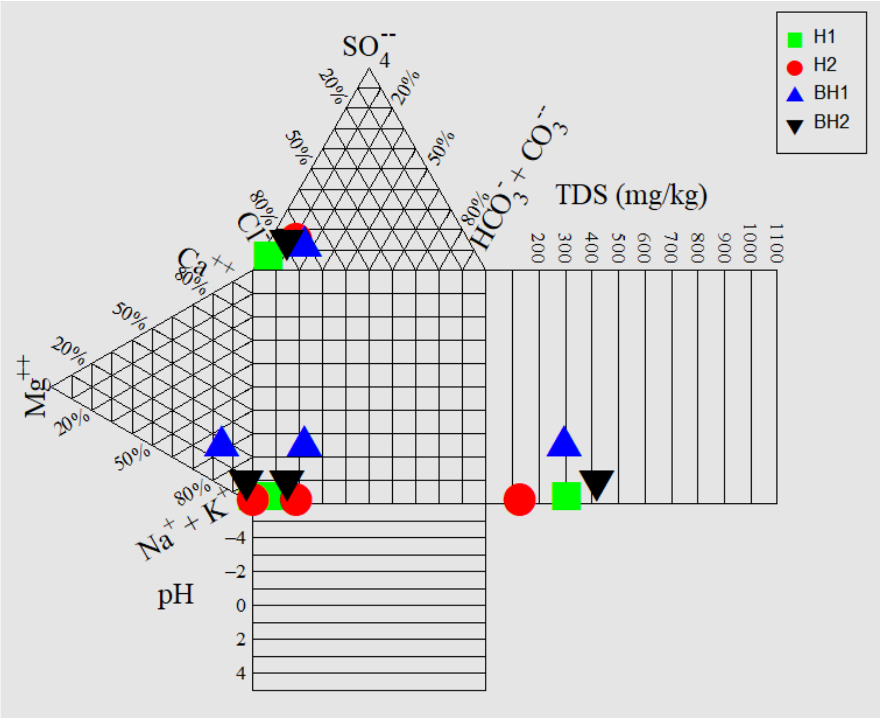

Figure 4.6: Durov diagram showing the hydrochemical process governing the groundwater at Siloam village

However, the occurrence of Cl^- > Na^+ hydro-chemical process in borehole H1 denotes that although the prevailing water type is Na^+ - Cl^-, the dominance of the water type is as a result of reverse ion exchange or reverse natural softening of saline water rather than normal ion exchange. The occurrence of sulphate (SO_4^{2-}) in groundwater is mostly assumed to be influenced by the dissolution of gypsum or the neutralisation of acid water by limestone or dolomite (Hounslow, 1995). Gibbs plot (Figures 4.7 and 4.8) was used to determine the major geological process responsible for the mineralisation process in the groundwater at Siloam Village.

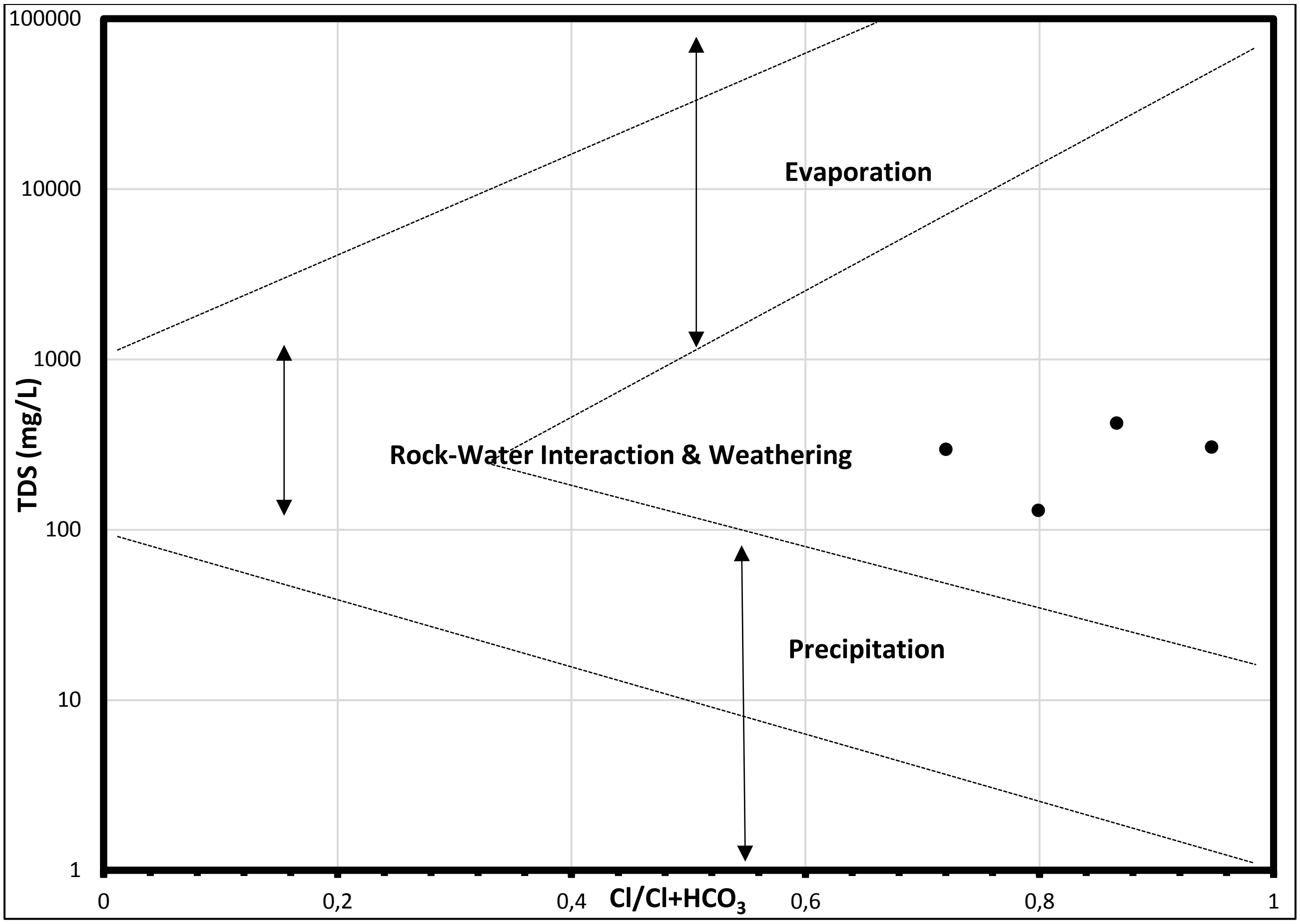

Figure 4.7: Gibbs plot showing dominant anion mineralisation process of groundwater in Siloam Village

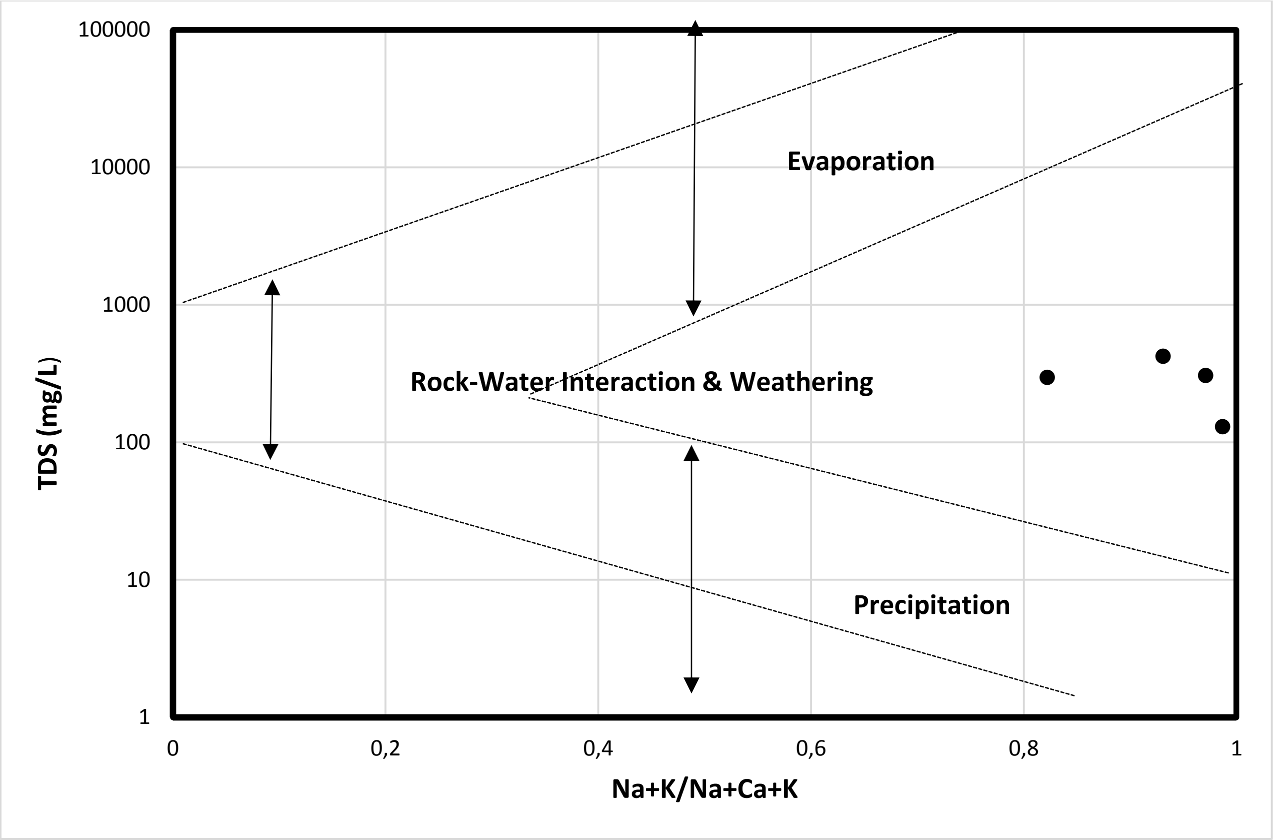

Figure 4.8: Gibbs plot showing dominant cation mineralisation process of groundwater in Siloam village

The total dissolved solids were plotted against major anions and cations on Gibbs diagram to determine the geochemical process responsible for the chemical constituents of groundwater at Siloam village (Figures 4.7 & 4.8). For anions, TDS was plotted against equation 4.3 , while for cations TDS was plotted against equation 4.4.

$$\text{Anions} = \frac{\text{Cl}}{\text{Cl} + \text{HCO}_3} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4.3)}$$

$$\text{Cations} = \frac{\text{Na} + \text{K}}{\text{Na} + \text{K} + \text{Ca}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{(4.4)}$$

The Gibbs diagram shows that rock water interaction and weathering of the rock and soil components (Overburden and Aquifer) in Siloam village are the geological factors responsible for the chemical signature of groundwater in the village. Gibbs diagram elaborate more on the Na-Cl dominant water type indicated by Piper plot. The plot of Na/Cl (Figure 4.9) is a good indicator of the type of weathering responsible for the dominance of Na in groundwater. Mayback (1987) noted that Na/Cl ratio greater than one (1) is an indication of silicate weathering otherwise the source of Na is from another source other than silicate weathering

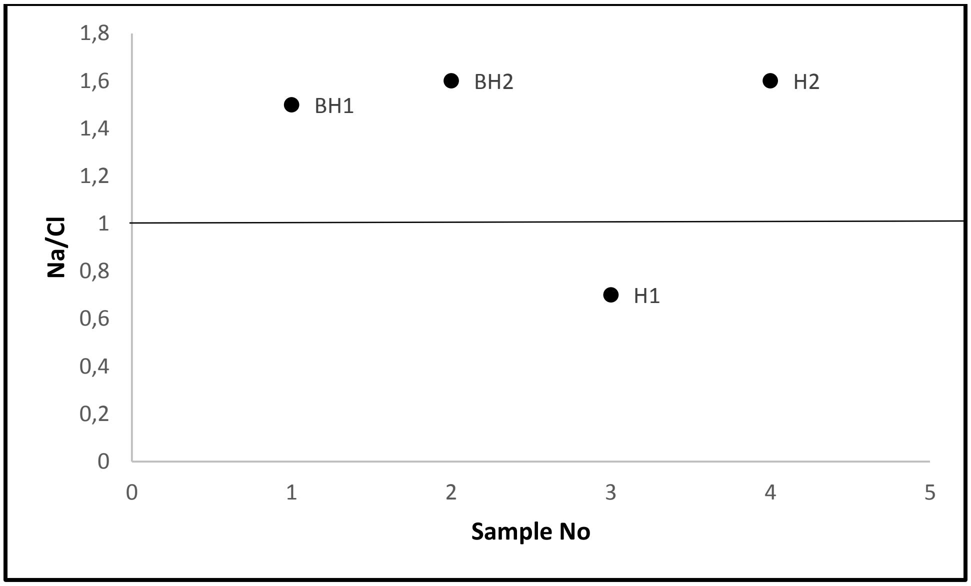

Figure 4.9: Plot Showing Na/Cl ratio

From the Na/Cl ratio plot, 75% of the samples (BH2, BH1 and H2) show predominant silicate weathering while 25% (H1) of the samples show other sources of Na^+ other than silicate weathering. This other source is the reverse ion exchange. The dominant Na^+ in the groundwater at Siloam Village is as a result of the weathering and chemical alteration of tectosilicate minerals in the form of Plagioclase feldspar (Na rich feldspar) or sheet silicate minerals in the form of chlorite, due to rock-water interaction over a period of time resulting in base ion exchange between the rocks, soil and groundwater. Chloro-Alkaline Indexes (CAI) were calculated from equations 4.5 & 4.6 to determine if the Na^+ is from base ion exchange or from reverse ion exchange. In ion exchange process, the Ca and Mg from the groundwater is exchanged with the Na^+ and K^+ from the host rock or surrounding rocks. CAI 1 and CAI 2 were plotted in Figures 4.10 & 4.11.

$$CAI\ 1 = \frac{[Cl^- - (Na^+ + K^+)]}{Cl^-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4.5)$$

$$CAI\ 2 = \frac{[Cl^- - (Na^+ + K^+)]}{SO_4{}^{2-} + HCO^-{}_3 + CO_3{}^{2-} + NO^-{}_3} \quad \ldots\ldots\ldots\ldots\ldots\ (4.6)$$

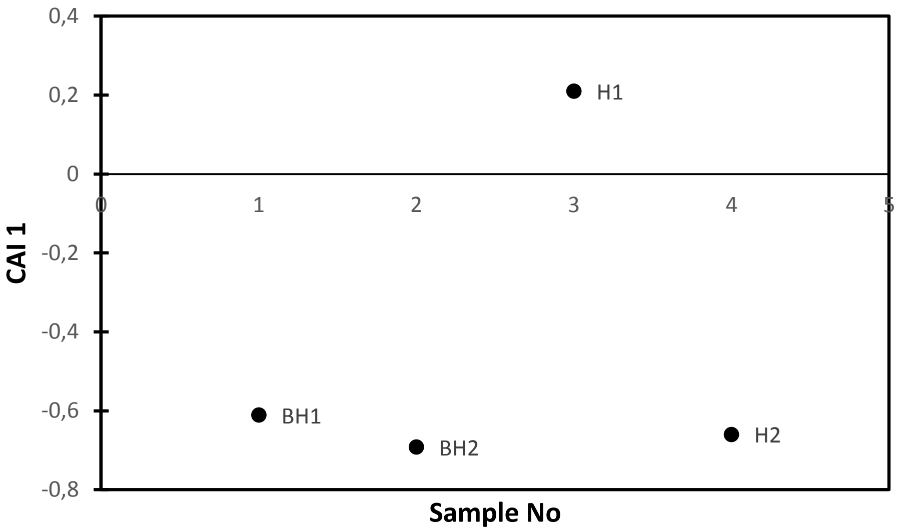

Figure 4.10: Chloro-Alkaline Index 1 for enrichment process

Both CAI 1 and CAI 2 (Figures 4.10 & 4.11) will give a negative value if the process of Na^+ enrichment is by ion exchange process, otherwise, the process of reverse ion exchange is responsible (Kumar and James, 2013). From CAI 1 and CAI 2 (Figures 4.10 & 4.11), boreholes BH1, BH2 and H2 exhibits a sodium enrichment process by normal ion exchange while borehole H1 shows that the sodium enrichment process is by reverse ion exchange process.

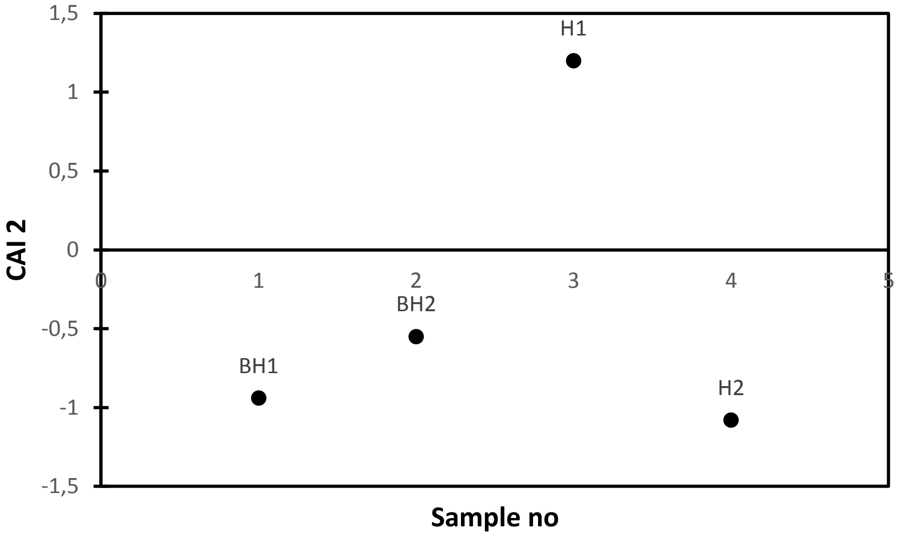

Figure 4.11: Chloro-alkaline Index 2 for enrichment process

4.4 Lithostratigraphy and Mineralogy

Fifteen samples (rock and soil) were obtained for the purpose of this study, with thirteen of those samples from borehole cuttings as shown in Chapter 3 and the other two samples from surface rock and road-cut clay deposit. The borehole cuttings belong to **BH1** and **BH2** and they are represented as **X** and **Y,** respectively, while **SR** represents surface rock samples and **S1** represents surface soil. The lithologic description of the samples is given in Table 4.6 and the lithology log is shown in Figure 4.12

Table 4.6: Lithologic Description of Sampled Rock and Soil

LOCATION	SAMPLE ID	DEPTH (m)	ASSOCIATED GROUP	LITHOLOGY	BRIEF DESCRIPTION
			SURFACE SAMPLES		
S	S1		Soil	Clay	Brown colour with very fine texture
LOCATION	**SAMPLE ID**	**DEPTH (M)**	**ASSOCIATED GROUP**	**LITHOLOGY**	**BRIEF DESCRIPTION**
	SR2		Metamorphic	Epidotised grey wacke	This rock type shows alow-grade metamorphism characteristic and it exhibits an aphanitic texture. It has a green colour due to the abundance of chlorite
	SR3		Sedimentary	Sandstone	Pinkish Sandstone due to the presence of hematite
			BOREHOLE SAMPLES		
BH1	X5	5	Sedimentary	Argillaceous Sediment	Top soil with brittle texture and pinkish-brown colour. Presence of Smectite and hematite noticeable
	X15	15	Sedimentary	Argillaceous Sediment	Dark brown colour with reduced pinkness probably due to the hematite content
	X20	20	Sedimentary	Argillaceous Sediment	Light pink colour due to the heavy presence of clay mineral Smectite and Hematite
	X30	30	Sedimentary	Argillaceous Sediment	Reduction in the pink colour and traces of darker brown colour. Smectite and Hematite still present although at a reduced concentration
	X40	40	Sedimentary	Gray Wacke	Green in colour probably due to the presence of Chlorite mineral and the rock is slightly saturated due to its function being the aquifer rock. Total disappearance of clay minerals of smectite and hematite.
LOCATION	**SAMPLE ID**	**DEPTH (M)**	**ASSOCIATED GROUP**	**LITHOLOGY**	**BRIEF DESCRIPTION**
	X65	65	Sedimentary	Gray Wacke	Green in colour probably due to the presence of Chlorite mineral and the rock is slightly saturated due to its function being the aquifer rock. Total disappearance of clay minerals of smectite and

					hematite noticeable. Index mineral noticed are quartz and chlorite
BH2	Y5	5	Soil	Clay	Light brown in colour with more than 60 wt.% Smectite.
	Y10	10	Soil	Clay	Light brown colour with increased smectite content of more than 70 wt.%
	Y20	20	Soil	Clay	Reduced lightness with two different groups of Smectite namely smectite 1 and 2. Overall smectite content is greater than 75 wt.%
	Y25	25	Soil	Sandy Clay	Dark brown colour with intercalation of clay and sand. Although smectite content is still above 50% but there is reduction in its wt.%
	Y28	28	Igneous	Basalt	Dark colour with dominantly plagioclase feldspar and diopside mineral.
	Y40	40	Igneous	Basalt	Dark colour with dominantly plagioclase feldspar and diopside mineral

S: surface soil, SR: surface rocks BH1: borehole 1, BH2: borehole 2

Chlorite minerals can be found in any major rock group, but they are known to be predominant in low grade metamorphic rocks. Chlorite is also the index mineral for green schist facie (Phillips and Phillips, 1980). Chlorite is found as a common constituent of igneous rocks resulting from hydrothermal alteration of pyroxenes, amphiboles, biotite and garnet (Phillips and Phillips, 1980). In sedimentary basins, Clay-rich sediments derived from the weathering of these igneous rocks are often rich in chlorite (Phillips and Phillips, 1980). This is basically the source of chlorite enrichment in sedimentary terrain. The abundance of chlorite can be seen in Siloam village which is made up of volcano sedimentary sequence. Table 4.7 gives the weight percent (wt.%) and the constituent minerals in all the soil and rock samples collected in Siloam village as analysed by X-ray Diffraction (XRD). The abundance of chlorite is seen especially in borehole cuttings of BH1 at depths 40 m – 65 m where chlorite is seen as much as 38 wt.% of the total rock mass at some depths (Table 4.7). However, the occurrence of chlorite determines the colour of the total rock mass given that the wt.% of chlorite is more than 20% as seen in cuttings X40 and X65 (Table 4.7 & Figure 4.12). From depths 5 m – 35 m in borehole BH1, the pink – brown colour is due to the presence of Smectite and occurrence of hematite. The brown colour may also be due to the presence of plagioclase. However, occurrences of quartz and muscovite mostly do not determine the colour of the whole rock mass because they are mostly colourless to white in colour. The pinkish colour of rock SR2 is due to the occurrence of hematite (Iron oxide).

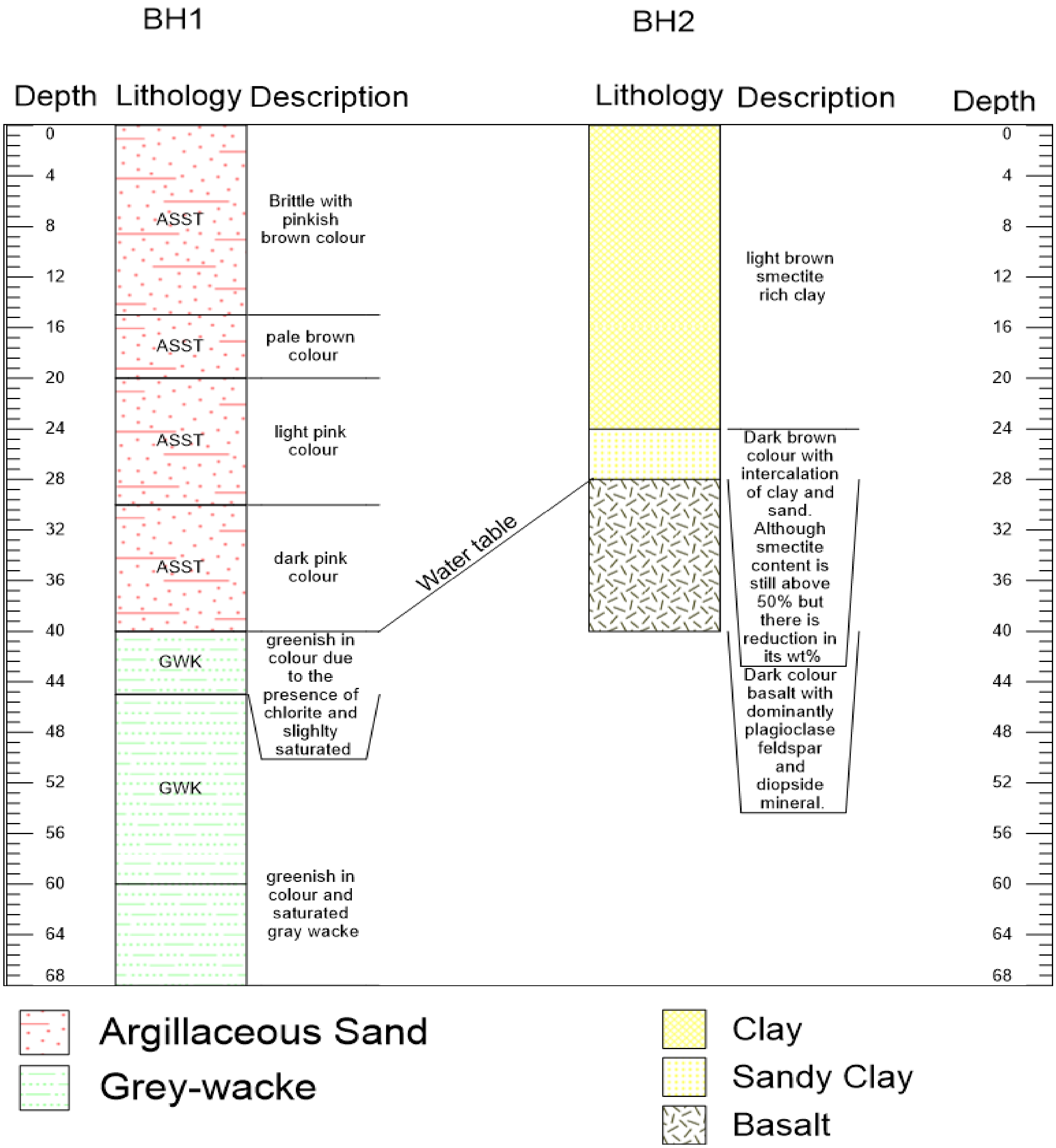

Figure 4.12: Lithology log of boreholes BH1 and BH2

The occurrence of chlorite in the sedimentary terrains of Siloam village and the high abundance of smectite and hematite group shows that the present geologic sequence in Siloam village has undergone a series of weathering and tectonic activities. This explains the abundance of Na^+ in groundwater at Siloam Village because of ion exchange and possible reverse ion exchange during the process of weathering of silicate minerals like plagioclase and chlorites.

Table 4.7: Mineral constituents and percentage weight of rocks and soils

S1		**SR2**		**SR3**		**X5**	
	weight%		weight%		weight%		weight%
Diopside	2.76	Chlorite	28.41	Hematite	0.67	Chlorite	4.21
Hematite	1.7	Diopside	20.5	Muscovite	1.6	Hematite	9.41
Orthoclase	8.04	Epidote	21.63	Quartz	97.73	Muscovite	32.41
Plagioclase	32.38	Hematite	0.17			Orthoclase	2.65
Quartz	8.36	Plagioclase	14.82			Quartz	35.99
Smectite	44.26	Quartz	14.47			Smectite	15.33
Sepiolite	2.49						
X15		**X20**		**X30**		**X40**	
	weight%		weight%		weight%		weight%
Chlorite	5.42	Chlorite	4.59	Chlorite	5.42	Chlorite	38.92
Hematite	7.87	Hematite	5.07	Hematite	7.27	Muscovite	12.33
Muscovite	33.77	Muscovite	33.07	Muscovite	41.15	Plagioclase	17.35
Orthoclase	1.87	Quartz	44.76	Quartz	30.04	Quartz	25.99
Quartz	34.44	Smectite	12.51	Smectite	16.1	Titanite	5.4
Smectite	16.63						
X65		**Y5**		**Y10**		**Y20**	
	weight%		weight%		weight%		weight%
Actinolite	9.22	Orthoclase	7.7	Hematite	0.78	Orthoclase	7.97
Chlorite	26.98	Plagioclase	11.08	Orthoclase	5.61	Plagioclase	9.75
Epidote	12.04	Quartz	12.19	Plagioclase	6.86	Quartz	5.53
Muscovite	7.49	Smectite	69.02	Quartz	8.34	Smectite1	41.2
Plagioclase	16.31			Smectite	78.41	Smectite2	35.55
Quartz	20.72						
Titanite	7.25						
Y25		**Y28**		**Y40**			
	weight%		weight%		weight%		
Orthoclase	14.99	Actinolite	2.08	Actinolite	2.6		
Plagioclase	22.93	Chlorite	4.69	Chlorite	4.72		
Quartz	9.72	Diopside	28.7	Diopside	29.87		
Smectite	52.36	Enstatite	3.02	Ilmenite	5.18		
		Ilmenite	3.89	Muscovite	3.29		
		Muscovite	4.56	Plagioclase	38.27		
		Plagioclase	39.49	Quartz	9		
		Quartz	7.69	Smectite	7.1		
		Smectite	5.88				

S1: Surface soil, SR: surface rock, X: borehole BH1 depth, Y: borehole BH2 depths

From Table 4.7, the general trend of the minerals in Siloam can be seen. The dominant minerals in the village include quartz, chlorite, plagioclase, smectite and muscovite at varying amount and at different depths. Figure 4.13 shows the abundance of major minerals present in the surface soil sample. The maximum peaks were recorded for smectite and plagioclase. From Table 4.7 and Figure 4.13, the high dominance of Smectite and plagioclase is noticeable in soil S1. Montmorillonite was identified as the end member of the smectite group in the sample (Appendix 1). However, clays are known for their role in the release of fluoride into groundwater (Liu et al., 2014). Clays are regarded as active ion exchange agents. Table 4.8 shows the minerals in Siloam village's rocks and soil with their family name and chemical constituents.

Table 4.8: Minerals and their chemical formula

Minerals	**Family Name**	**Chemical Formula**
Chlinochlore	Chlorite	$(Mg,Fe^{2+})_5Al_2Si_3O_{10}(OH)_8$
Diopside	Pyroxene	$MgCaSi_2O_6$
Epidote	Epidote	$Ca_2(Al_2,Fe)(SiO_4)(Si_2O_7)O(OH)$
Hematite	Hematite	$Ca_2(Al_2,Fe)(SiO_4)(Si_2O_7)O(OH)$
Orthoclase	Feldspar	$KAlSi_3\ O_8$
Plagioclase	Feldsppar	$NaAlSi_3O_8 – CaAl_2Si_2O_8$
Quartz	Silicates	SiO_2
Montmorillonite	Smectite	$(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2•n(H_2O)$
Sepiolite	Sepiolite	$Mg_4Si_6O_{15}(OH)_2·6H_2O$
Muscovite	Mica	$KAl_2(AlSi_3O_{10})(F,OH)_2$
Titanite	Silicates	$CaTiSiO_5$
Actinolite	Amphibole	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Ilmenite	Ilmenite	$FeTiO_3$
Kaolinite	Silicates	$Al_2Si_2O_5(OH)_4$
Enstatite	Pyroxene	$Mg_2Si_2O_6$
Andesine	Feldspar	$(Na,Ca)Al_{1-2}Si_{3-2}O_8$
Ripidolite	Chlorite	$(mg, Fe, Al)_6\ (Si, Al)_4O_{10}(OH)_8$

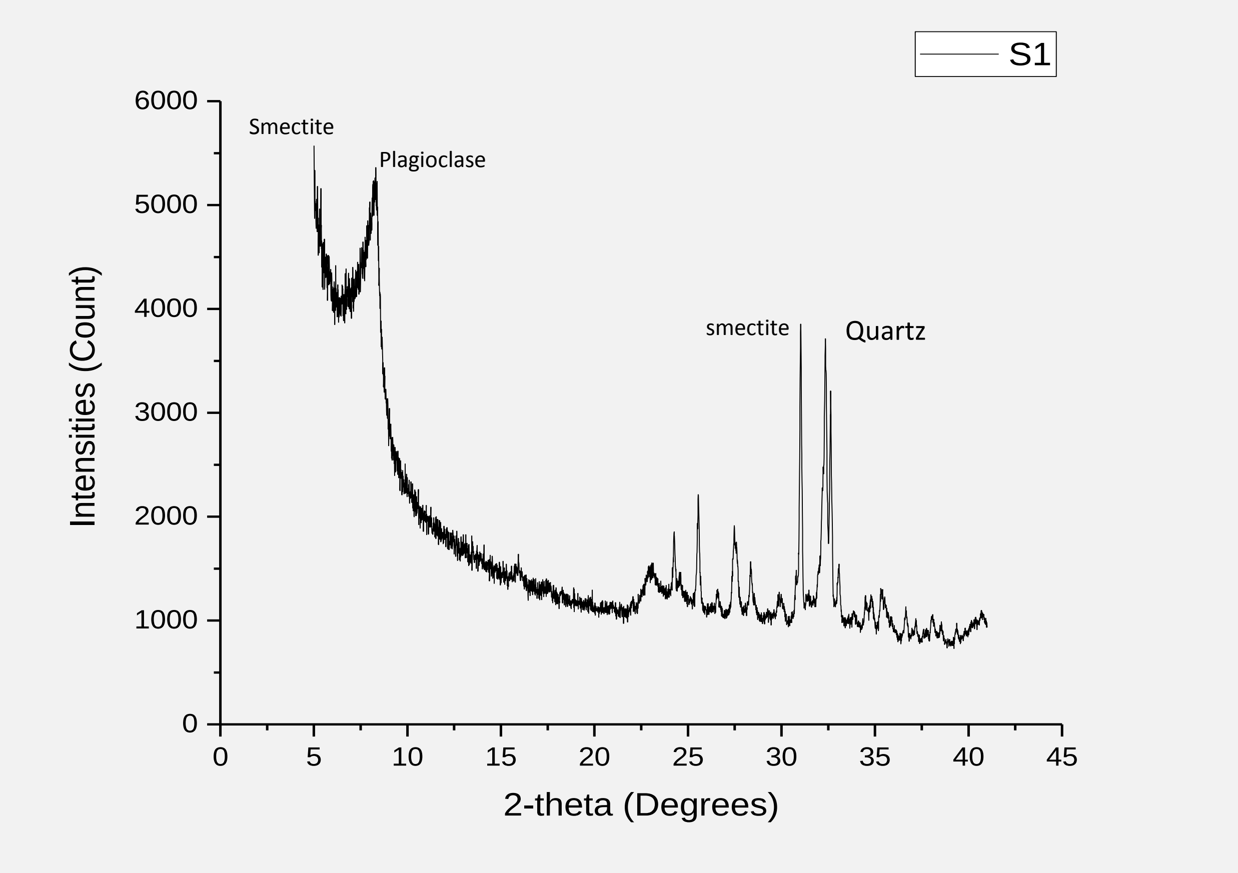

Figure 4.13: XRD plot for S1 showing major minerals and abundance

Muscovite, a common end-member of mica mineral group is known for its contributions to groundwater fluoride. Muscovite as rock forming mineral, when present may contain 1 wt. % of fluorine (Maria and Laura, 2015). Muscovite is an important fluoride bearing mineral because it contains fluorine in its crystal lattices and also contains hydroxyl which can also substitute for fluoride because of their similar ionic charges. Muscovite occurs at about 1.62 wt. % (Table 4.7) in location SR3 which is sandstone at Siloam village and the abundance was observed with the quartz abundance in Figure 4.14. Onipe (2016) noted that muscovite in the surface rocks at Siloam village contributes to the groundwater fluoride of Siloam village rather than fluorite as earlier inferred by McCaffery and Willis (2001) and Odiyo and Makungo (2010). This study supports the investigation of Onipe (2016) because fluorite is absent in the rock and soil formations at Siloam Village. Onipe (2016) also argued that the muscovite present in the surface sandstone at Siloam village can never be the sole contributor of fluoride to groundwater of the area.

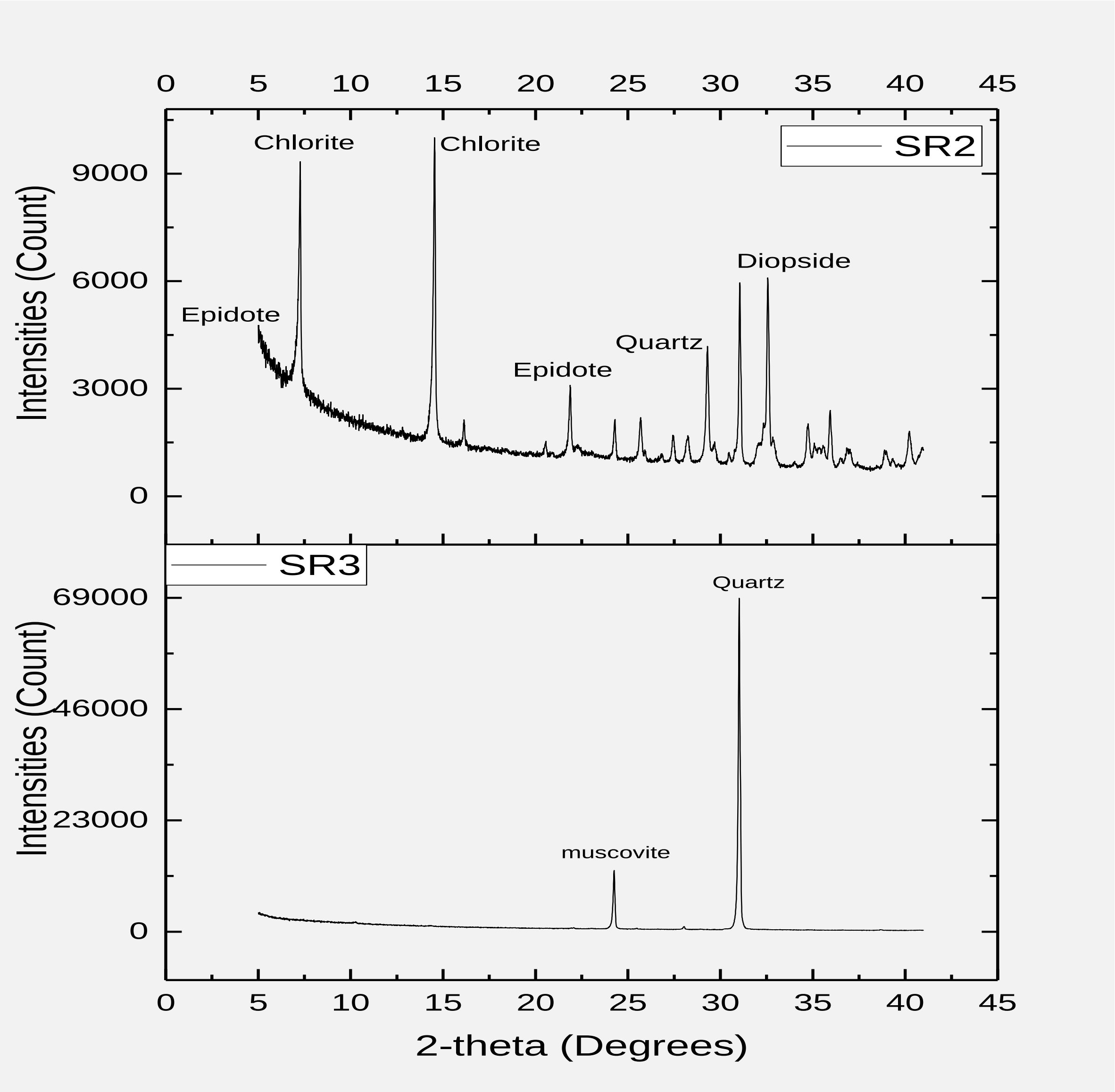

Figure 4.14: XRD plot for SR2 and SR3 showing major minerals and their abundance

Surface rock SR2 contains high proportions of Chlorite and epidote (Figure 4.14). The occurrence of clinochlore, an end member of chlorite is predominant in Siloam village (Appendix 2, Figure 4.14). Chlorite has been linked to fluoride contribution to groundwater mostly due to its hydroxyl content which is displaced by fluoride ion. Generally, chlorite contains fluoride but not as much as its ripidolite. This reason is attributed to the fact that clinochlore (an end membe of chlorite group) has an appreciable number of aluminium in its octahedral layer therefore limiting its fluoride adsorption properties unlike ripidolite that has aluminium in its tetrahedral layer. However, at varying depth in borehole BH1, muscovite occurs as an abundant rock forming mineral rather than its accessory form as found in the surface rock SR2 (Figures 4.14 & 4.15). The concentration of muscovite in wt. % increases from top soil to 30 m below the surface as seen in Table 4.7 and Figure 4.16. The major minerals present in borehole BH1 from depth 5 m to 30 m are Muscovite, Quartz and Smectite (Table 4.7). The abundance of major dominating minerals of borehole BH1 from depth 15 m – 30 m are shown in Figure 4.15.

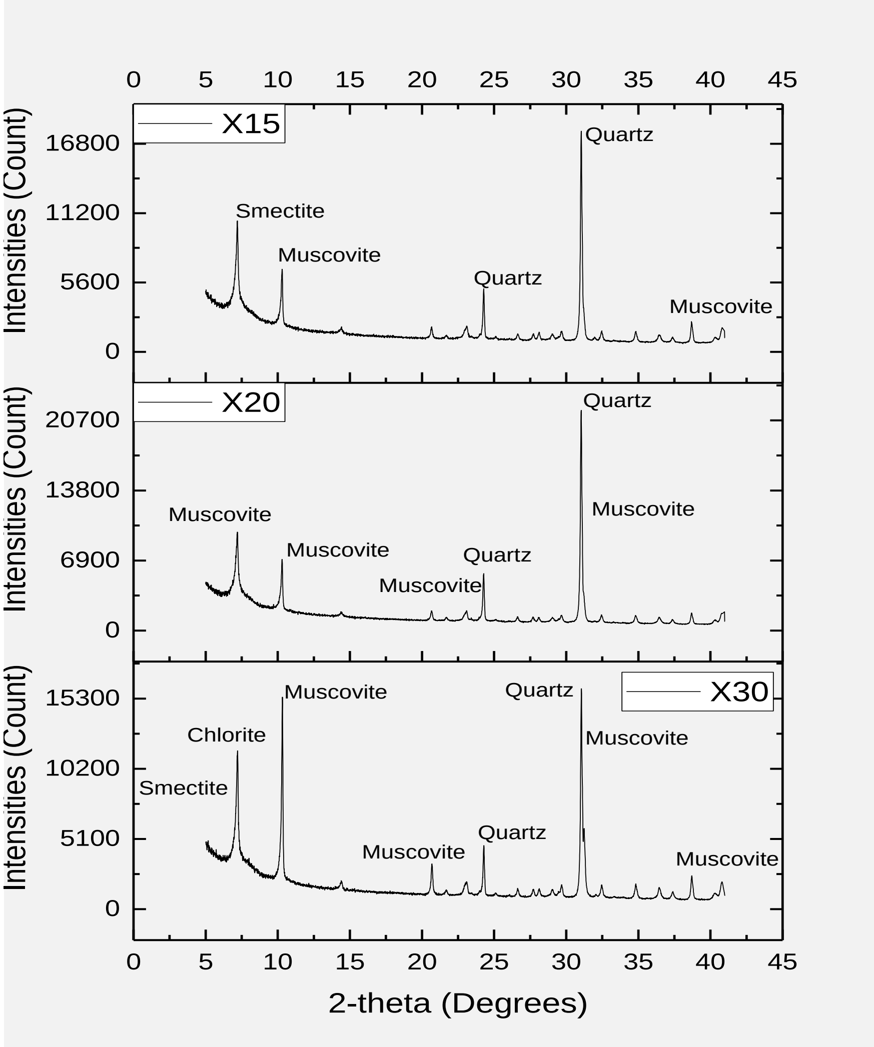

Figure 4.15:XRD plot at depths X15, X20 and X30 showing major minerals and abundances in borehole BH1

The behavioural trend of muscovite in borehole BH1 is shown in Figure 4.16. Fluorine affiliated muscovite increases with depth from 5 m to 15 m, slows down at depth 20 m and picks up its increasing trend again at depth 30 m below ground level before drastically reducing as the depth increases (Figure 4.16).

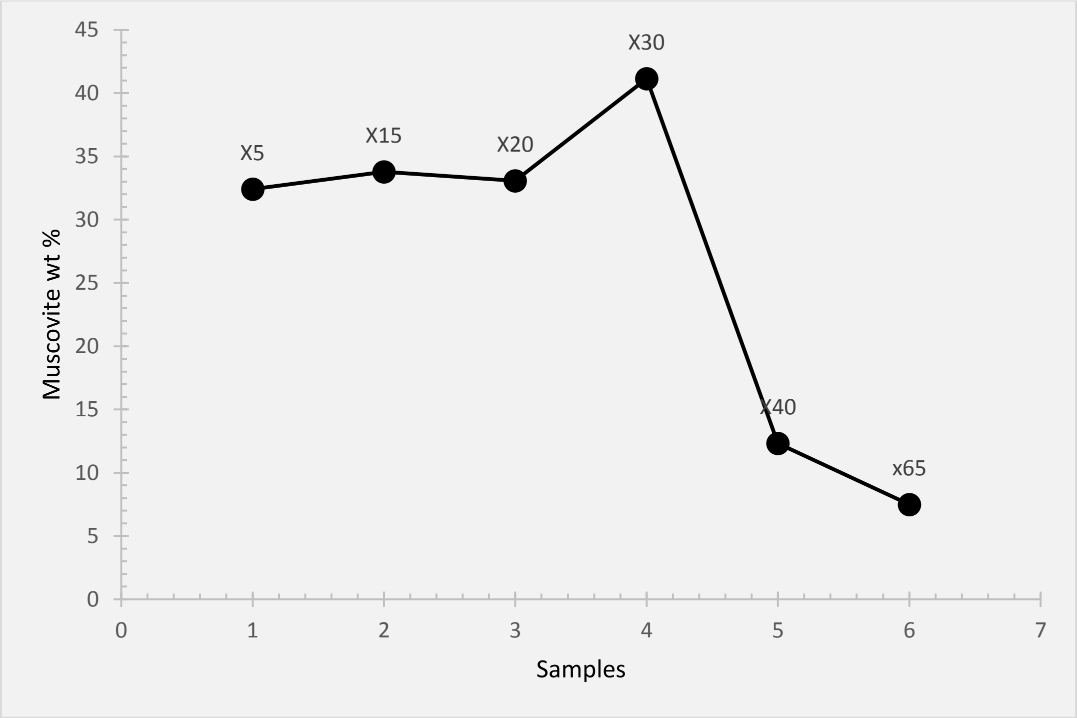

Figure 4.16: Abundance of Muscovite in borehole BH1

Figure 4.17 shows the XRD peaks for the epidotised gray-wacke which is the aquifer rock for borehole BH1. Although muscovite is present, the abundance is not as much as at depths 5 m to 30 m. The grey wacke is dominated by chlorite which explains why the colour is greenish-grey (Table 4.6). The primary minerals present in the rock materials include: Chlorite, Quartz and plagioclase. The intensities and abundance of each mineral are identified in Figure 4.17. The combined presence of muscovite and chlorite at depth X40 and X 65 in borehole BH1 accounts for the slightly high total fluoride concentration of the aquifer due to the exchange of OH with F in their structure. Figure 4.17 also shows a high abundance of plagioclase which denotes that the level of weathering is either absent or low at depth 40 m below the earth surface, therefore there has been no chemical alteration of plagioclase to smectite clay or kaolin as seen at shallow depths before 40 m.

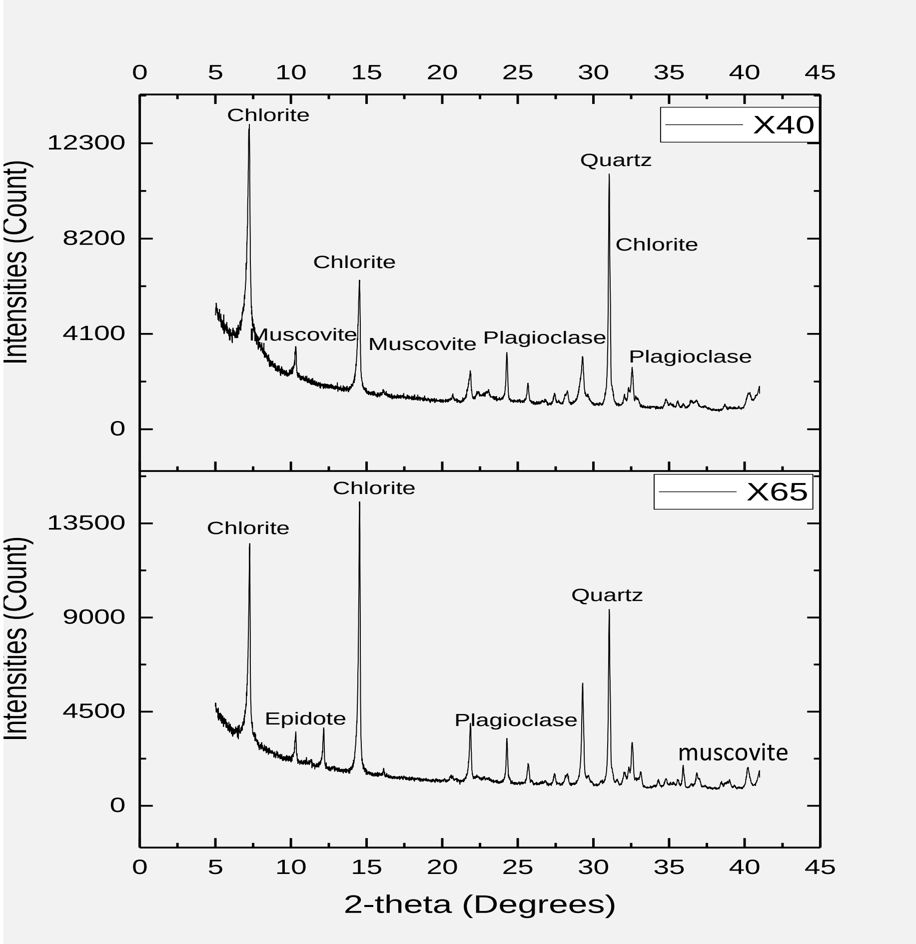

Figure 4.17: XRD plot at depths X40 and X65 showing major minerals and abundance for borehole BH1

Two main dynamic geochemical processes occur in clay, they are the enrichment and leaching processes. Under the dynamic geochemical process of leaching, areas with clay formations and arid to semi-arid climatic conditions, experience high groundwater and surface water fluoride concentration (Liu et al., 2014). Dynamic geochemical process of leaching occurs when fluoride is leached out of clay formation into groundwater through infiltration and percolation of water. Fluorine can easily migrate from clay formations to groundwater during migration of groundwater (Jacks and Sharma, 1995). The clay enrichment geochemical process occurs when fluoride migrates from groundwater to the Soil. Therefore, the process of leaching and enrichment is governed by adsorption and absorption factors (Liu et al., 2014).

In borehole BH2 at Siloam village, Muscovite which is the predominant fluoride bearing mineral in the area is seen to be absent until the depth of 28 m (Table 4.7). Muscovite occurrence was found at depth 28 m to 40 m although at a volume less than 5 wt. %. Figure 4.18 shows the major minerals, their abundance and the peaks in borehole BH2 from depth 0 to 25 m.

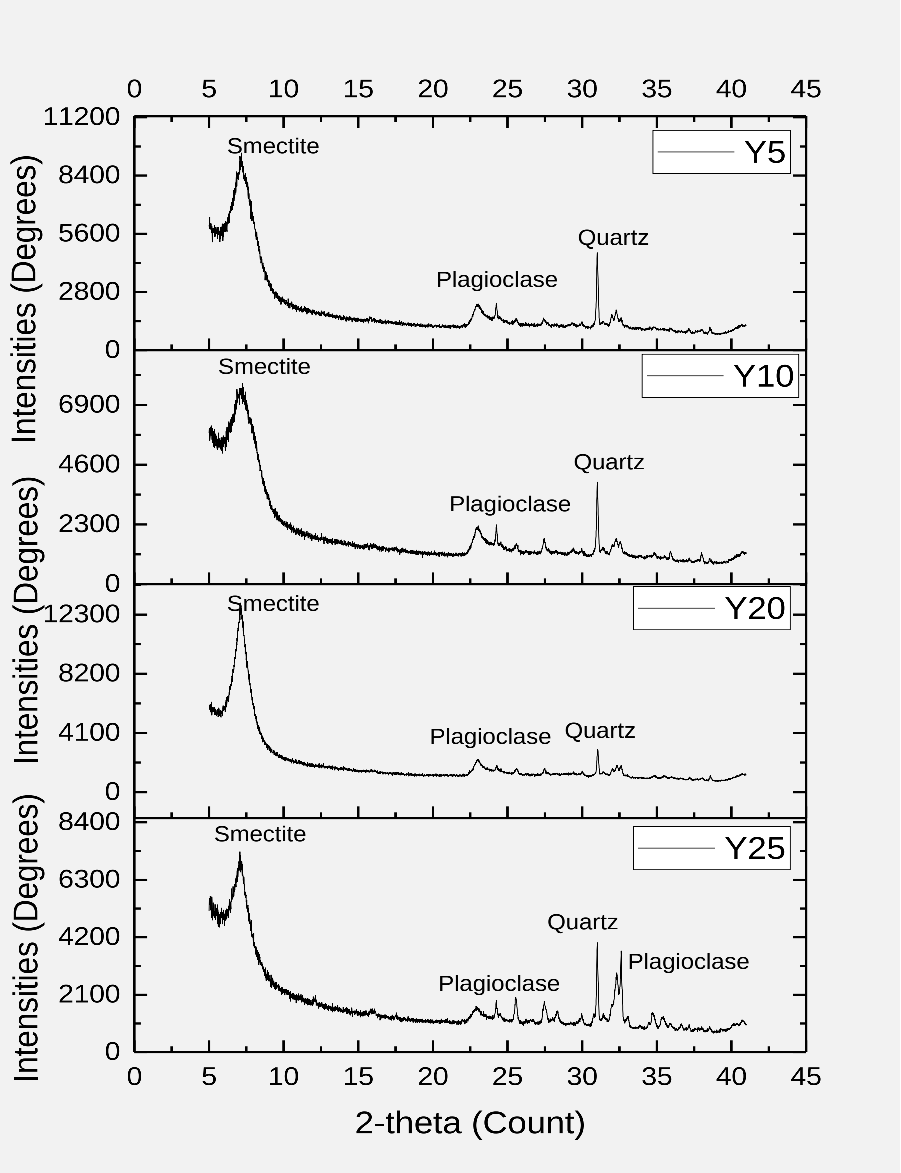

Figure 4.18: XRD plot of depth Y5, Y10, Y20 and Y25 showing major minerals and abundance for borehole BH2

The peaks of smectite at depths Y5, Y10, Y15 and Y20 occur at almost the same count and intensity (Figure 4.18). Smectite is the most abundant mineral at depths Y5 – Y20 (Figure 4.18). Clay could also act as a migration agent for fluoride enrichment of groundwater at Siloam Village. Figure 4.19 describes the abundance of major minerals in borehole BH2 at depths Y28 and Y40.

The abundance of chlorite and plagioclase can be seen in Figure 4.19. Muscovite can also be seen occurring at a lower amount in Figure 4.19. Y28 and Y40 is the basaltic aquifer material of borehole BH2. XRD analysis was carried out in order to quantitatively assess the mineral content, show the mineral phases and general mineral trend of the sampled surface rock types, soils and borehole cuttings in Siloam village.

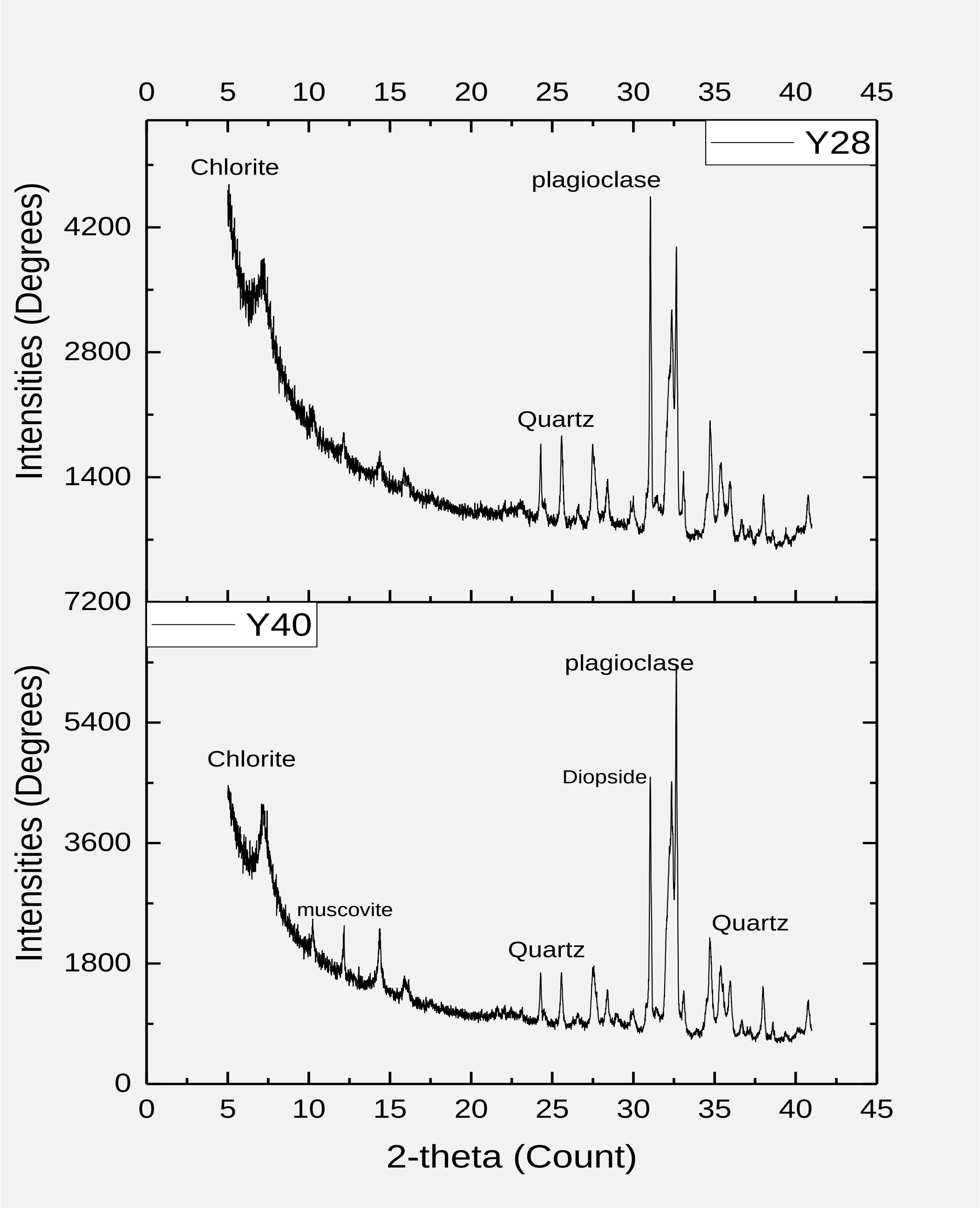

Figure 4.19: XRD plot for Y28 and Y40 showing major minerals and their abundance

The XRD analysis was able to show the minerals associated with fluoride release into the groundwater of Siloam village.

4.5 Total Rock chemical composition

In sedimentary terrain, the most abundant fluorine bearing mineral is associated with mica mineral group and clay minerals especially montmorillonite and kaolinite. Total rock chemistry is important to determine the total rock composition in oxides and elemental properties. The rock oxides were determined using XRF and the total fluorine concentration was analysed separately using Fluoride Ion Selective Electrode. The oxides (Appendix 3) were converted to obtain major elemental constituents of interest using different conversion factors as given in Table 4.9. Figure 4.20 shows the graphical representation of major oxides in the rock and soil of Siloam Village. The village is dominated by high silica content followed by aluminum oxides. The highest concentration of silica occurs at surface sandstone rock of location SR3 (Figure 4.20).

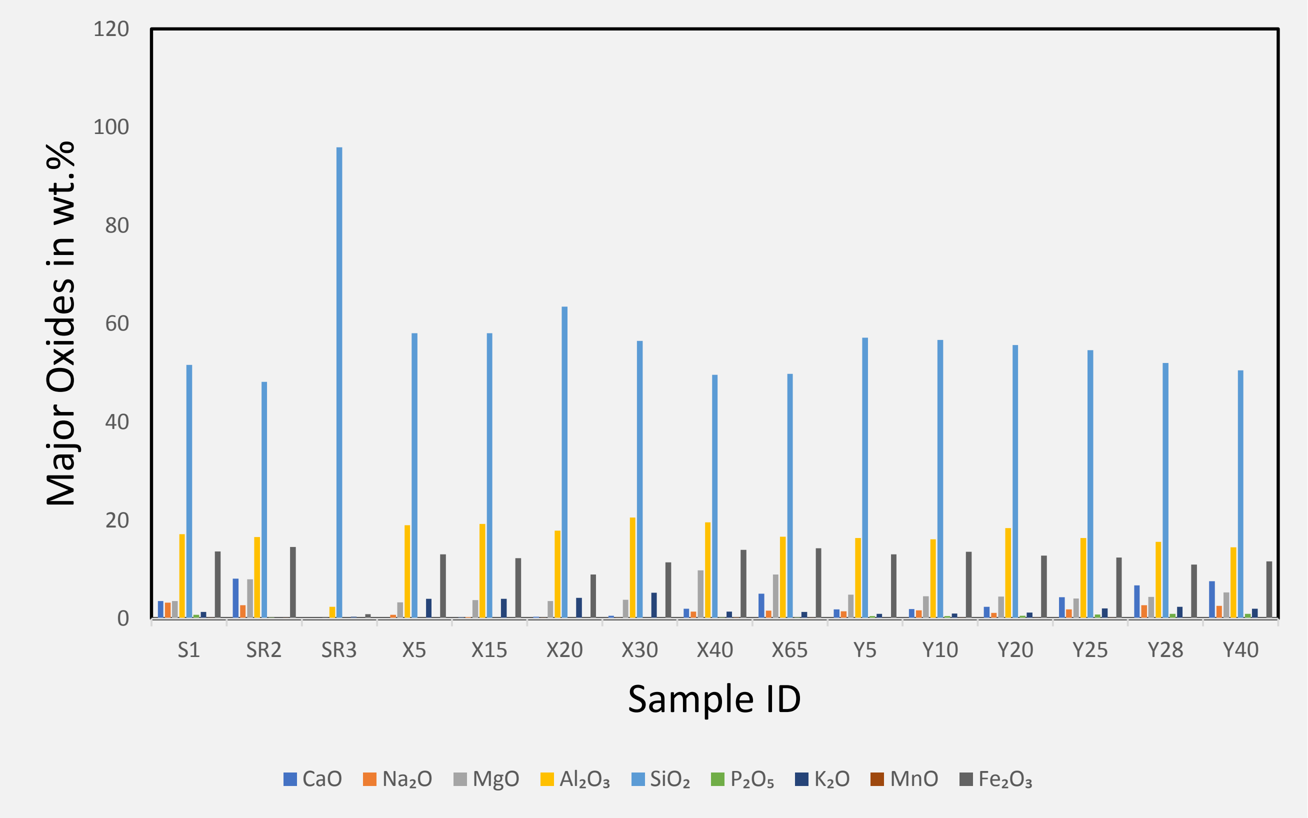

Figure 4.20: Major oxide abundance in sampled rocks and soils

The formula for conversion of Oxides to elemental wt. percent is given as equation 4.7.

$$\text{Oxide wt percent } \times \text{Conversion factor } = \text{ Elemental wt percent} \cdots\cdots\cdots (4.7)$$

The conversion factor is the sum of the atomic weights of the elements in the required formula divided by the sum of the atomic weights in the original formula. The conversion factors for major oxide are given in Table 4.9.

Table 4.9: Conversion factors for major oxides

Oxides	*Conversion Factor*
CaO	0.7143
Na_2O	0.7419
MgO	0.6030
Al_2O_3	0.5293
SiO_2	0.4675
P_2O_5	0.4365
K_2O	0.8301
Fe_2O_3	0.6994
MnO	0.7745

Silica (SiO_2) and quartz (SiO_2) have the same chemical composition but they are different in nature. Silica refers to the total pure silicon dioxide in the rock mass while quartz refers to a mineral with a very high concentration of silica. However, often, quartz occurs as silica with little amount of impurities. Therefore, the name is used interchangeably. Total rock silica could be from quartz and other silicate minerals like feldspars, chlorites and other aluminum and silicate rich minerals. The SiO_2 in Figure 4.20 refers to the total silica content of the rock and soil. Table 4.10 gives the converted oxides in weight percent (wt.%). To determine the total elemental composition of the rock and soil in mg/kg, Table 4.1 is converted using equation 4.8. The results are given in Table 4.11.

$$weight\ \% \ \times 10{,}000 = elemental\ concentration\ (mg/kg)\ldots\ldots.(4.8)$$

Table 4.10: Major elemental compositions of rocks and soils in wt%

	Ca (wt%)	**Na (wt%)**	**Mg (wt%)**	**Al (wt%)**	**Si (wt%)**	**P (wt%)**	**K (wt%)**	**Mn (wt%)**	**Fe (wt%)**
S1	2.542908	2.388918	2.15874	9.088081	24.1417	0.350073	1.120635	0.154126	9.560798
SR2	5.828688	2.025387	4.824	8.78638	22.52415	0.096903	0.030548	0.165743	10.19725
SR3	0.041572	0.02426	0.094068	1.265027	44.83325	0.048452	0.313778	0.004182	0.632957
X5	0.065858	0.574973	2.00196	10.04611	27.14773	0.028154	3.361905	0.056926	9.155146
X15	0.202147	0.255956	2.26728	10.2102	27.16175	0.047142	3.353604	0.072338	8.609614
X20	0.252148	0.140961	2.14065	9.47447	29.66288	0.047579	3.503022	0.074972	6.280612
X30	0.405722	0.146896	2.32155	10.8877	26.4231	0.065912	4.358025	0.083646	7.994142
X40	1.414314	1.075755	5.9094	10.38487	23.19268	0.116982	1.16214	0.177361	9.770618
X65	3.600072	1.194459	5.43303	8.834017	23.2815	0.099959	1.112334	0.161871	10.00841
Y5	1.350027	1.090593	2.94867	8.691106	26.71295	0.233091	0.8301	0.118499	9.155146
Y10	1.378599	1.238973	2.73762	8.558781	26.5166	0.209957	0.863304	0.12392	9.518834
Y20	1.71432	0.845766	2.69541	9.744413	26.01638	0.254916	1.021023	0.121597	8.98729
Y25	3.121491	1.402191	2.46024	8.68052	25.5442	0.372771	1.701705	0.13941	8.714524
Y28	5.157246	2.084739	2.91249	8.20415	23.95938	0.493245	1.99224	0.10146	7.469592
Y40	5.442966	1.943778	3.1959	7.696022	23.6181	0.423405	1.685103	0.117724	8.134022

…….(4.8)

Table 4.*10*, silica has the highest wt. % in Siloam village. This means that the village is dominated by felsic rock and the soil by high silica content. Felsic rocks, which contain relatively high concentrations of SiO_2, tend to have higher concentrations of fluorine than mafic rock (Wedepohl et al., 1978). Table 4.11 shows the total major elemental and fluorine compositions of rocks and soils at Siloam village in mg/kg. Fluorine is an accessory element in minerals and also fluoride is an important trace element in water which has a major effect on people who consume it. Although fluorine is regarded as a trace element, its concentration in some rocks and soil in Siloam village is higher than expected. The total fluorine content of rocks and soil at Siloam Village ranges from 10 mg/kg to 2000 mg/kg (Table 4.11). The average fluorine concentration in Siloam village is about 762 mg/kg (Table 4.11). This is above the permissible limit of 30 mg/kg concentration of fluorine in soil for agricutlture (Department of Environmental Affairs, 2010). The highest fluorine concentration of 2000 mg/kg occurs at a depth of 5 m in borehole BH2 (Table 4.11). The lowest concentration occurs in borehole BH1 at a depth of 30 m (Table 4.11).

The fluorine concentration in clay are typically in the range of 20 – 500 mg/kg (kabata-Pendias and Pendias, 1984). The surface clay deposit S1 has a total fluoride concentration of 431 mg/kg (Table 4.11). However, the Clay formation of borehole BH2 from 5 m to around 20 m depth has the highest concentrations of fluorine (Table 4.11). The Soil of BH2 at depths 5 m and 10 m have more fluorine concentration than the surface rock formations and aquifer rocks in Siloam Village as observed from Table 4.11. This is arguably against McCaffery and Willis (2001) that stated that rock samples have higher fluorine content than soil samples. The clay deposit and argillaceous sediments of Siloam village are from chemical alteration and weathering of plagioclase of parent rock materials therefore giving more room for OH and F replacements. This ion displacement gives a higher room for more storage of fluoride in the crystal lattices of the resultant clay. It is to be noted, however, that clays formed under hydrothermal conditions are mostly rich in fluoride as observed in Siloam (Lagat, 2007) although not always the case as observed in Sagole, Tshipise and Evangelina area of Limpopo South Africa (Durowoju et al., 2015).

Table 4.11: Major elemental compositions of rocks and soils in mg/kg

Sample ID	Ca	Na	Mg	Al	Si	P	K	Mn	Fe	F
S1	25429.08	23889.18	21587.40	90880.81	241417.00	3500.73	11206.35	1541.26	95607.98	431.00
SR2	58286.88	20253.87	48240.00	87863.80	225241.50	969.03	305.48	1657.43	101972.52	1400.00
SR3	415.72	242.60	940.68	12650.27	448332.50	484.52	3137.78	41.82	6329.57	160.00
X5	658.58	5749.73	20019.60	100461.14	271477.25	281.54	33619.05	569.26	91551.46	450.00
X15	2021.47	2559.56	22672.80	102101.97	271617.50	471.42	33536.04	723.38	86096.14	330.00
X20	2521.48	1409.61	21406.50	94744.70	296628.75	475.79	35030.22	749.72	62806.12	290.00
X30	4057.22	1468.96	23215.50	108877.01	264231.00	659.12	43580.25	836.46	79941.42	10.00
X40	14143.14	10757.55	59094.00	103848.66	231926.75	1169.82	11621.40	1773.61	97706.18	850.00
X65	36000.72	11944.59	54330.30	88340.17	232815.00	999.59	11123.34	1618.71	100084.14	770.00
Y5	13500.27	10905.93	29486.70	86911.06	267129.50	2330.91	8301.00	1184.99	91551.46	2000.00
Y10	13785.99	12389.73	27376.20	85587.81	265166.00	2099.57	8633.04	1239.20	95188.34	1500.00
Y20	17143.20	8457.66	26954.10	97444.13	260163.75	2549.16	10210.23	1215.97	89872.90	1200.00
Y25	31214.91	14021.91	24602.40	86805.20	255442.00	3727.71	17017.05	1394.10	87145.24	800.00
Y28	51572.46	20847.39	29124.90	82041.50	239593.75	4932.45	19922.40	1014.60	74695.92	620.00
Y40	54429.66	19437.78	31959.00	76960.22	236181.00	4234.05	16851.03	1177.24	81340.22	620.00

S: surface soil, SR: surface rock, X: borehole BH1 depth, Y: borehole BH2 depth, ion units: mg/kg, depth: m

The aquifer rocks occurring at depth 40 m – 60 m in borehole BH1 and 28 m – 40 m in borehole BH2 have fluorine concentrations ranging from 620 - 850 mg/kg (Table 4.11). The concentration of Fe which is the combined concentration of Fe^{2+} and Fe^{3+} is generally high in Siloam village both in the rock and Soil. This accounts for the general brown and pink colour of different geologic (rocks and soils) formations in the village. The highest Fe concentration occur in surface rock SR2 with a concentration of 101,972.5 mg/kg (Table 4.11). This high concentration of Fe is as a result of high presence of minerals like epidote, diopside and hematite which account for a combined 42.3 wt.% of the total rock mass. The Fe concentration in sampled rock and soil of Siloam village ranges from 6329.57 - 101,972.52 mg/kg (Table 4.11). The lowest concentration of 6329.57 mg/kg occurs at location SR3 (Table 4.11) which is dominated by quartz and muscovite. The Fe in the hematite of location SR3 rock accounts for the concentration of 6329.57 mg/kg (Table 4.11). The highest occurring major element is silicon with the highest concentration of 448,332.5 mg/kg (Table 4.11) in rock SR3 due to the high abundance of quartz (97.73 wt.%) in the total rock mass.

The lowest occurring major element is manganese (Mn) with a concentration of 41.82 mg/kg (Table 4.11). It is important to note that fluorine is regarded as a trace element rather than a major rock forming element, except for the exception of minerals like fluorite which sometimes occur independently in veins and dykes. Low concentration of K occurs at surface rock SR2 (Table 4.11) while the high concentration of 43580.25 mg/kg occurs in borehole BH1 at 30 m depth (Table 4.11). Figure 4.21 below shows the relationship between total rock fluoride and total rock potassium. The relationship is an inverse relationship because at Y5, K has low concentration where F is at its highest concentration (Figure 4.21), while at X30, K is at its highest concentration whereas, F is at its lowest concentration of 10 mg/kg although a rare case occurs at SR3. The low value of K in SR2 may be as a result of absence of orthoclase feldspar and muscovite ($KAlSi_3O_8$ and $KAl_2(AlSi_3O_{10})(F, OH)_2$). Fluorine content of SR2 is quite high at a concentration of 1400 mg/kg and it is attributed to the presence of chlorite. High fluoride concentration of about 30 mg/L can result from ion exchange/ replacement between OH and F in chlorite minerals (Smedley et al., 2002). The low fluoride concentration and very high concentration of K at depth X30 despite the presence of smectite, muscovite and chlorite could be caused by an alkaline pH condition which deters the adsorption of fluoride to clay surface but instead promote fluoride desorption and migration into groundwater (Saxena and Ahmed, 2001;2003). The X30 layer is the regolith layer directly above the saturated zone. This explains why it has easy desorption properties. However, the high concentration of K is as a result of the heavy presence of muscovite which has not been weathered out by frequent contact with groundwater. The average concentration of K would supersede that of fluoride because K is a primary mineral forming element. It is found in the primary rock forming minerals like feldspar and mica as a major element unlike fluorine which occurs as a trace element. Fluorine is a common trace element with an average crustal concentration of 700 mg/kg (Mason, 1965).

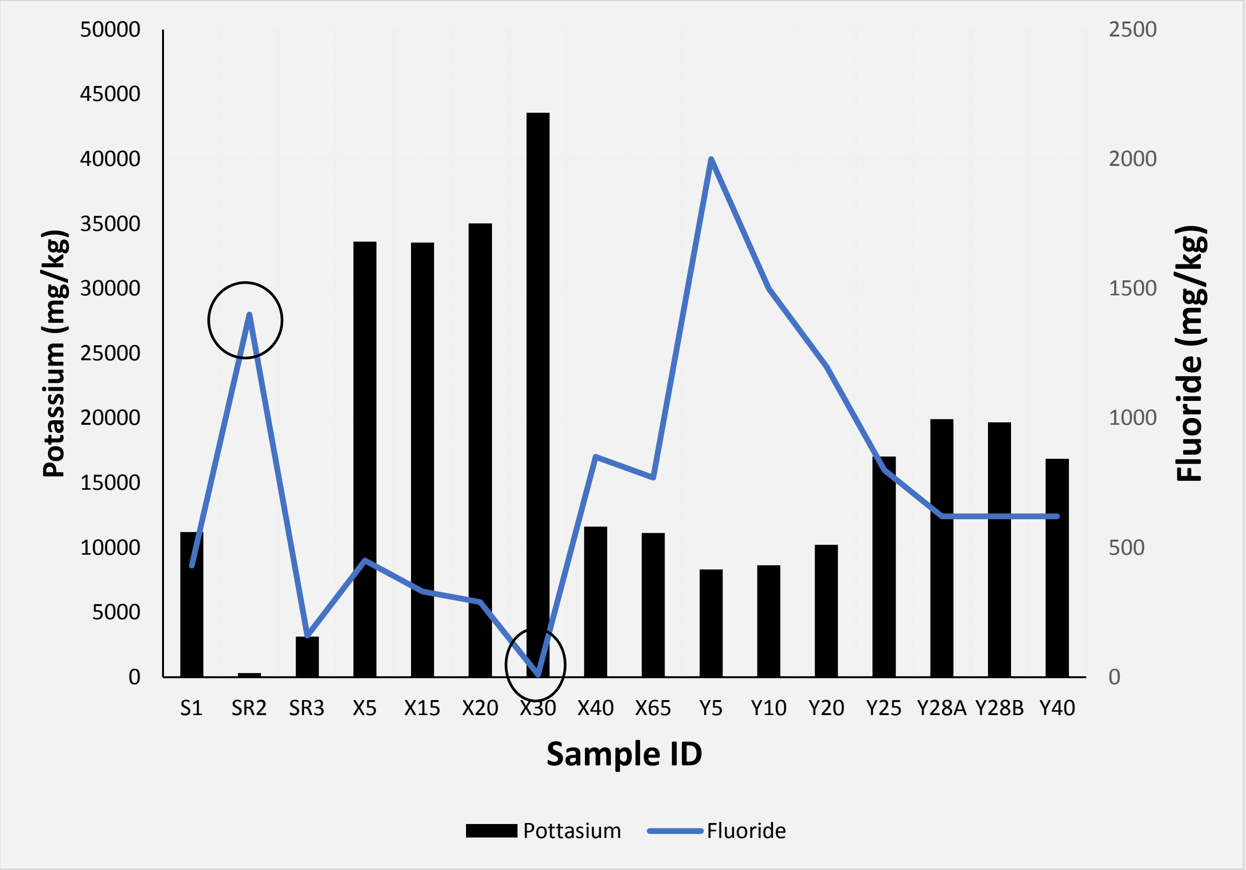

Figure 4.21: Relationship between K and F in rocks and Soils

At point Y5, the high concentration of fluorine is due to the high abundance of smectite clay. The slightly high K concentration, however, is due to the presence of orthoclase feldspar of K-feldspar.

The correlation coefficient is a way of determining the relationship between two values if they are dependent on each other in a positive or negative way or if they do not relate at all. The correlation between fluorine and major elements in the whole rock and soil mass is presented in Table 4.12.

Table 4.12: Correlation of major elements in rock and soils

	Ca	***Na***	***Mg***	***Al***	***Si***	***P***	***K***	***Mn***	***Fe***	***F***
Ca	1									
Na	**0.861**	1								
Mg	0.449	0.374	1							
Al	-0.033	0.068	0.473	1						
Si	-0.547	-0.614	-0.708	-0.793	1					
P	0.683	0.779	-0.005	-0.052	-0.387	1				
K	-0.403	-0.466	-0.275	0.494	-0.074	-0.234	1			
Mn	0.535	0.645	0.832	0.490	-0.798	0.308	-0.415	1		
Fe	0.295	0.445	0.688	0.825	-0.915	0.135	-0.004	0.795	1	
F	**0.251**	0.337	0.407	0.120	-0.332	0.180	**-0.621**	0.516	0.483	1

The relationship between fluoride and potassium as predicted is an inverse relationship. This is evident by the significant negative correlation of -0.621 between fluoride and Potassium (Table 4.12). However, there seem to be a weak correlation between Calcium and Fluoride in the rock as the correlation is 0.250. The dominance of Plagioclase is evident by the strong positive correlation of 0.860 between Calcium (Ca) and Sodium (Na). Ca and Na can substitute for each other in different forms of plagioclase feldspar's mineral crystal lattice structure. In Siloam village, Plagioclase end-member occurred in the form of Albite, Oligoclase and Andesine in the order of decreasing abundance, respectively (Appendices 1 - 17). The dissolution of fluorine into groundwater from a fluorine bearing rock does not depend alone on the fluorine concentration of such rock but rather on different environmental factors like temperature, residence time, hydrochemistry of the water and the geochemistry of the rock. The influence of temperature will be discussed in the next section on leaching experiment.

4.6 Hydrochemistry of Leachate

Leaching experiment was carried out using de-ionised water to determine the influence of the rocks and soils at Siloam village over the chemistry of groundwater. The methodology of the hydrogeochemical setup has been discussed in Chapter 3. Table 4.13 shows the result obtained.

Table 4.13: Physico-chemical parameters in the leachate obtained from leaching experiment

Sample	**K**	**EC**	**pH**	**Ca**	**Mg**	**Cl**	**NO_3**	**NO_2**	**PO_4**	**Na**	**B**	**F**
	mg/kg	µs/cm		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
S 1	62.50	24.00	7.57	135.00	891.00	36,03	1,65	0.00	1,89	**929.00**	1.75	10,52
SR 2	11.60	3.00	7.17	BDL	40.00	2,75	0,12	0.00	0,67	36.10	0.05	0,27
SR 3	27.80	3.00	6.83	BDL	BDL	2,77	0,21	0.00	3,17	2.26	0.04	0,44
X 5	379.00	42.00	7.10	19.80	773.00	**114,43**	24,66	0.00	1,55	**1020.00**	2.07	3,85
X 15	125.00	7.00	6.91	2.26	172.00	10,59	2,41	0.00	0,78	110.00	0.46	2,29
X 20	118.00	3.00	6.95	1.88	150.00	2,15	0,60	0.00	0,65	52.40	0.28	1,10
X 30	164.00	3.00	7.03	11.90	183.00	1,61	0,72	0,03	0,59	35.90	0.38	0,78
X 40	33.40	4.00	7.16	18.20	179.00	1,43	0,58	0,13	0,30	72.00	0.26	0,68
X 65	31.90	9.00	7.37	36.30	41.20	2,34	0,56	0,71	0,50	82.40	0.02	0,53
Y 5	31.90	32.00	8.00	186.00	675.00	11,57	0,78	0.00	0,39	**886.00**	0.93	14,88
Y 10	45.60	76.00	7.97	145.00	438.00	**171,79**	8,10	0.00	1,00	**1620.00**	1.11	9,51
Y 20	26.00	6.00	7.16	68.00	178.00	2,12	0,85	0.00	0,39	129.00	0.26	3,79
Y 28	61.90	9.00	7.43	94.80	97.90	1,93	0,29	0,33	0,90	151.00	0.15	1,02
Y 25	25.30	5.00	7.10	19.30	61.60	1,59	0,15	0,01	0,70	84.20	0.14	2,60
Y 40	54.50	10.00	7.50	110.00	104.00	2,46	0,27	0,49	0,80	166.00	0.17	0,72

BDL: Below detection Limit

The fluoride concentration emigrating out of the rock and soil samples of Siloam village ranges from 0.27 mg/L to 14.88 mg/L. Leachate with the lowest fluoride concentration occurs at surface rock SR2 and the leachate with the highest fluoride concentration occurs at depth 5 m of borehole BH2 (Table 4.13). Fluoride concentration shows a decreasing trend from the surface down to the aquifer. Figure 4.22 shows the fluoride concentration trend in the borehole BH1 leachates.

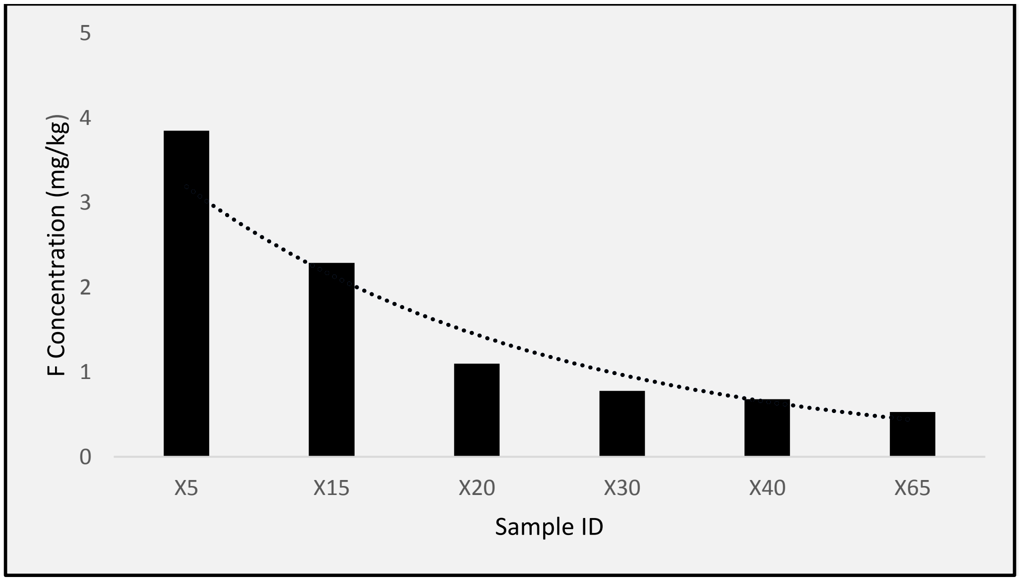

Figure 4.22: Fluoride trend in borehole BH1

The same trend as for BH1 can be seen for borehole BH2 (Figure 4.23). The fluoride trend also decreases with depth.

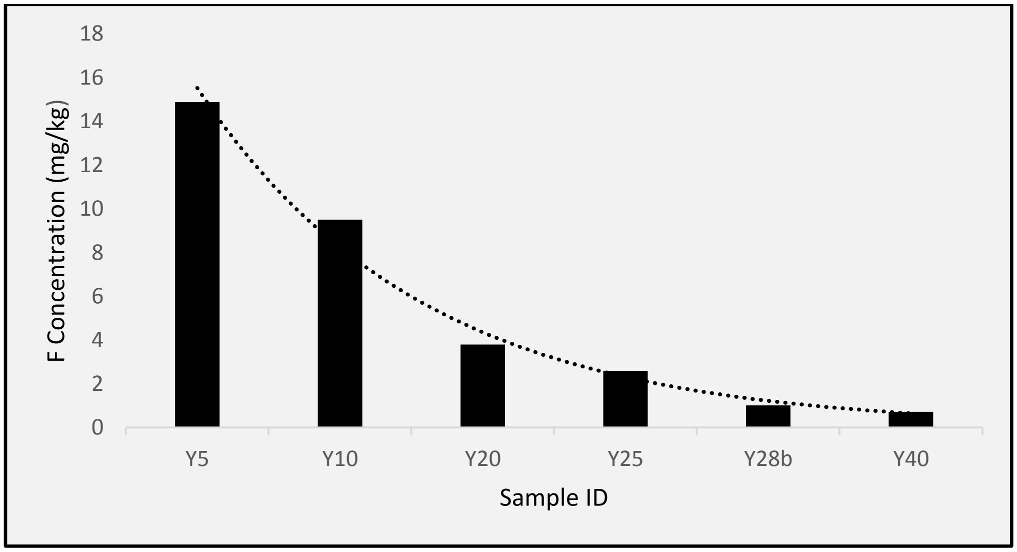

Figure 4.23: Fluoride trend in borehole BH2

The fact that from boreholes BH1 and BH2, the sub-surface rocks and soils of Siloam village show decreasing trends in fluoride concentrations, means that the aquifer rocks release less fluorine into the groundwater compared to the regolith and overburden soils and clays. This may partially be due to the loose state of the overburden. The highest ion release is 1620 mg/kg (Table 4.13) from

Sodium and it occurs at point Y10. This coincides with high occurrence of Chloride. This shows the dominating factor of Na and Cl and explains the source of Na and Cl in groundwater at Siloam village. The Ca concentration in SR2 and SR3 were below detection limit. Magnesium concentration in SR3 was also below detection limit. This is due to the total absence of Mg bearing minerals like chlorite, pyroxene and smectites (Table 4.8) and the high presence of silicate minerals like quartz.

The ions in the leachate were correlated against each other to determine the relationship between them in relation to the release of fluoride. Table 4.14 shows the correlation coefficients in the leachate at Siloam village.

Table 4.14: Correlation of physico-chemical constituent of leachates

	K	*EC*	*pH*	*Ca*	*Mg*	*Cl*	NO_3	NO_2	PO_4	*Na*	*B*	*F*
K	1.000											
EC	0.250	1.000										
pH	-0.273	0.690	1.000									
Ca	-0.257	0.596	0.936	1.000								
Mg	0.443	0.641	0.501	0.563	1.000							
Cl	0.411	0.942	0.437	0.327	0.546	1.000						
NO_3	0.849	0.601	0.020	-0.032	0.564	0.736	1.000					
NO_2	-0.196	-0.188	0.174	0.092	-0.349	-0.244	-0.205	1.000				
PO_4	0.146	0.106	-0.218	-0.088	0.171	0.194	0.219	-0.221	1.000			
Na	0.264	0.969	0.715	0.666	0.800	0.885	0.586	-0.265	0.152	1.000		
B	0.622	0.699	0.356	0.393	0.953	0.695	0.755	-0.367	0.267	0.818	1.000	
F	-0.058	**0.673**	**0.769**	**0.815**	**0.796**	0.439	**0.161**	-0.348	0.011	**0.790**	0.642	1.000

From Table 4.14, fluoride concentrations in groundwater of boreholes BH1 and BH2 show a high positive correlation to pH, Ca, Na. This means that at an increasing F concentration, pH, Ca and Na increases. The concentrations of these highlighted parameters (pH, Ca, Na) are directly proportional to each other. EC is also positively correlated to F, which means that increase in fluoride results in an increase in pH, Ca and Na which in turn increases the conductivity of the groundwater of boreholes BH1 and BH2. The very weak correlation between fluoride and nitrate confirms that the possible source of high nitrate in groundwater of BH2 is not from a natural source rather it is from an anthropogenic source. The negative weak correlation between fluoride and potassium connotes that most of the occurrence does not originate from K bearing minerals like muscovite. This simply means that a large percentage of the groundwater fluoride does not come from muscovite minerals in the sandstone of Siloam village. The strong correlation between fluoride and Na, Ca and Mg denotes that the more the release of these minerals into the groundwater, the more fluoride concentration increases. This goes to show that the groundwater fluoride is controlled by the desorption and adsorption properties of smectite clay and partly by chlorite. This is why the groundwater hydrochemistry is dominated by Na-Cl water type signifying the importance of Na weathering and dissolution to investigating groundwater fluoride source. The process is simplified by the equation below:

$$\mathbf{2NaAlSi_3O_8} + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(\mathbf{OH})_4 + 4H_4SiO_4 + \mathbf{2Na} \text{ ………….(4.9)}$$

The hydroxl ion in the clay is displaced by fluoride in the structure lattice of the kaolin-smectite clay due to the similarity in their charge and radius. The resultant Na in the equation explains the abundance of Na in groundwater at Siloam village.

4.7 Effect of Temperature on Fluoride Release

Siloam village is located on Siloam fault which acts as a channel of transport of heated groundwater up to some near surface aquifer. This gives Siloam village a very high geothermal gradient. Therefore, the effect of temperature is very important when investigating the source of fluoride from the dissolution of minerals irrespective of the temperature of the water at present. The effect of temperature in the dissolution of fluoride from the mineral constituents in the rocks and soil into the groundwater was experimented in the laboratory. The average water temperature of 42°C from past literatures focusing on Siloam Village was used as the base temperature. Although, the effect of temperature was simulated for less than 10 hrs., the general effect of temperature still plays an important role by increasing the fluoride concentration in the leachates. This difference can be observed in Figure 4.24 where the comparison can be seen between fluoride release at room temperature and fluoride release at 40°C.

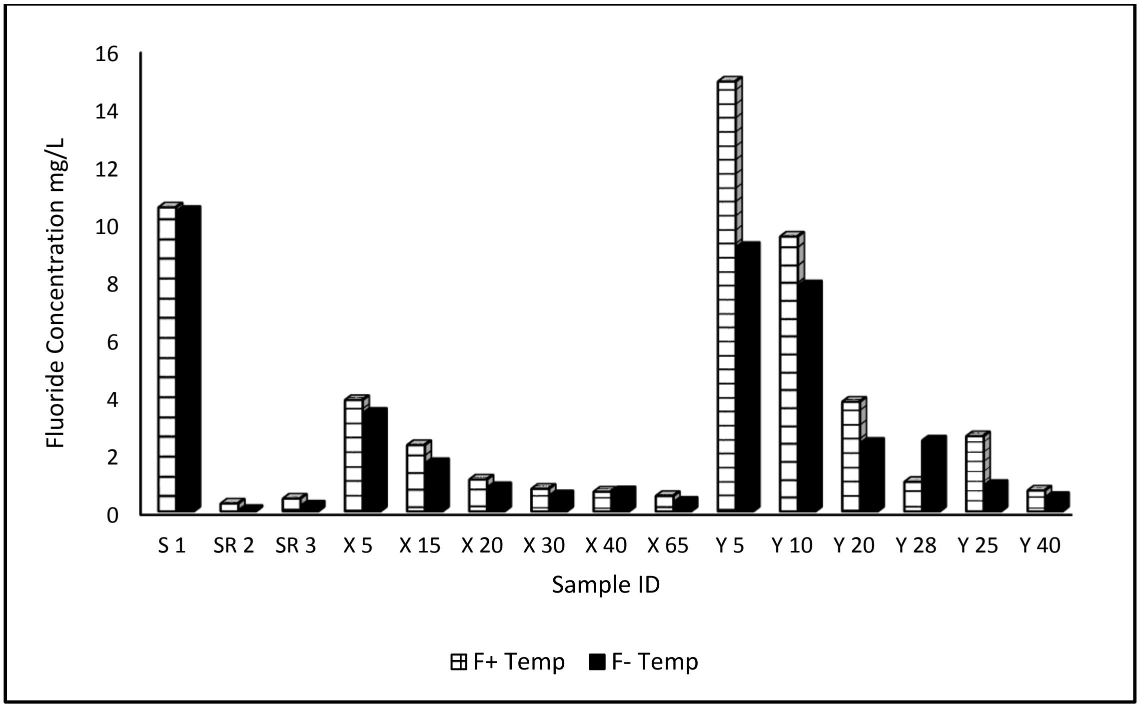

Figure 4.24: Plot showing fluoride leachate behaviour at room temperature and at 40°C

The temperature effect can be seen at almost all sampling points except for Y28 (Figure 4.24). The sampling point Y5 shows a distinct effect of temperature by a concentration difference of almost 5 mg/L. The temperature effect of Siloam is evident to be one of the driving factor favouring the dissolution of fluorine from the rocks and soils at Siloam, into the groundwater as fluoride.

5. CONCLUSION AND RECOMMENDATION

5.1 Preamble

This chapter summarises the whole study and gives a recommendation based on the outcome of the study. This chapter also includes the shortcomings of this study and suggestion on how to improve on it on a larger level.

5.2 General Conclusion

A regional study carried out on the distribution of F in the groundwater of Northern South Africa, reported that the source of F is from F-bearing minerals in rocks of aquifer materials. Although Siloam was left out in their study. The geology of the area is such that there is evidence of major paleo-tectonic activities in the village. This is evident by the presence of a large Siloam fault in the village. This fault and many other smaller faults play a major role in the geohydrology of the village. The following conclusions were made based on the main and specific objectives of this study:

From this study, the groundwater of the village was classified based on temperature as tepid and hot groundwater. The study also elucidated on the hydrochemistry in an attempt to understand the process or processes governing the transfer of fluoride from the host rocks and soils into the groundwater at Siloam village. The water is dominated by Na and Cl ions which makes the groundwater type Na-Cl water type according to Piper. This denotes that the water is brine and alkaline in nature and originates from deeper aquifer. From the study, the geological process or processes responsible for the enrichment of groundwater was inferred to be rock-water interaction and weathering. The chemical processes caused by the rock-water interaction were identified as ion exchange and reverse ion exchange.

The host minerals are the muscovite, chlorite and smectite clay. Smectite clay is the major contributor of fluoride to Siloam groundwater, followed by chlorite and then lastly by muscovite. The study also revealed a decreasing trend in the fluoride concentrations across the village from the surface down to the aquifer unlike previous studies that suggest that fluoride increases in concentration downwards. The geothermal temperature of Siloam is high due to radioactive decay and various tectonic activities deep within the earth. This prompted a controlled experiment to check if geothermal temperature influences the release of fluoride into the groundwater. The leaching experiment confirms that the geothermal temperature of the village plays an important role in the migration of fluoride from soils and rock into the groundwater.

RECOMMENDATIONS

Objective 1: To identify the mineral phases, present in the surface rock unnits, subsurface rock units and aquifer rock unit of the study area in relation to fluoride in the groundwater

Recommendation: More drilling sites is needed for good sampling representation. Furthermore, different subsurface geological structures need to be explored e.g groundwater associated with diabase dykes and faults in the area to see the association between their mineralogy.

Objective 2: To determine the relationship among the different rock units, soil and groundwater and how they influence the groundwater fluoride

Recommendation: Longer time based leaching experiment should be carried out and dissolution factors like pH should be taken into consideration. The experiment should be carried out in acidic, neutral and basic pH concentrations to note how dissolution of fluoride would behave in different pH environment. Radioactive dating should be carried out to address the relationship and formation of these aquifers in relation to the age of the groundwater recharge

Objective 3: To establish if Siloam has one regional aquifer or different smaller aquifer units in relation to the sources of fluoride

Recommendations: Radioactive dating should be carried out to determine if the aquifers are linked or have different properties to denote different recharge time and source. Therefore their age should be determined. Also this will help confirm the inference of long residence time drawn from this study.

Charge balance should be calculated for water quality data.

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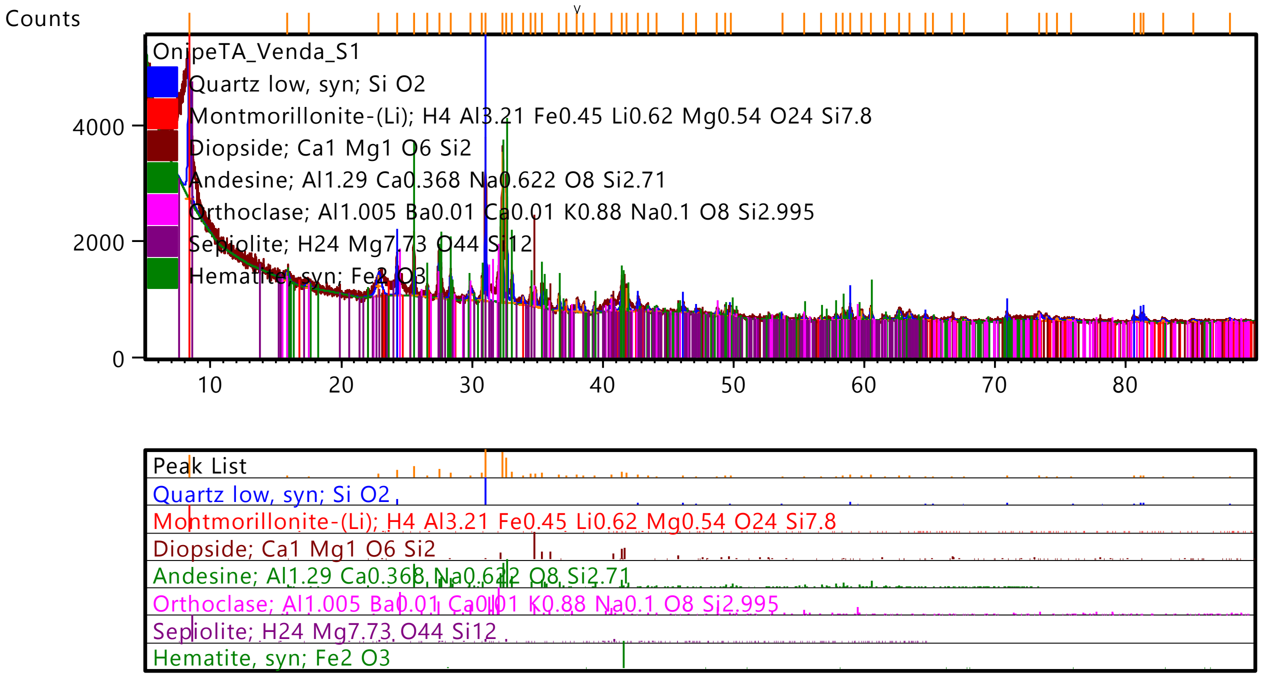
APPENDICES

Appendix 1



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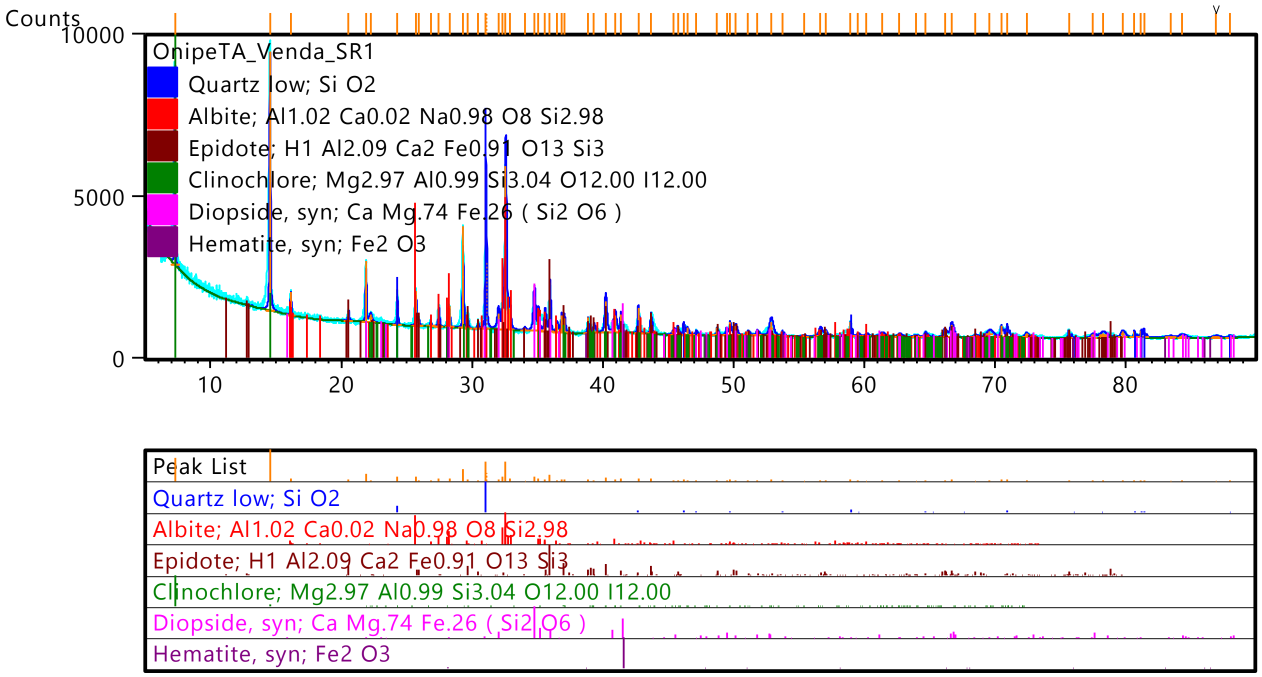
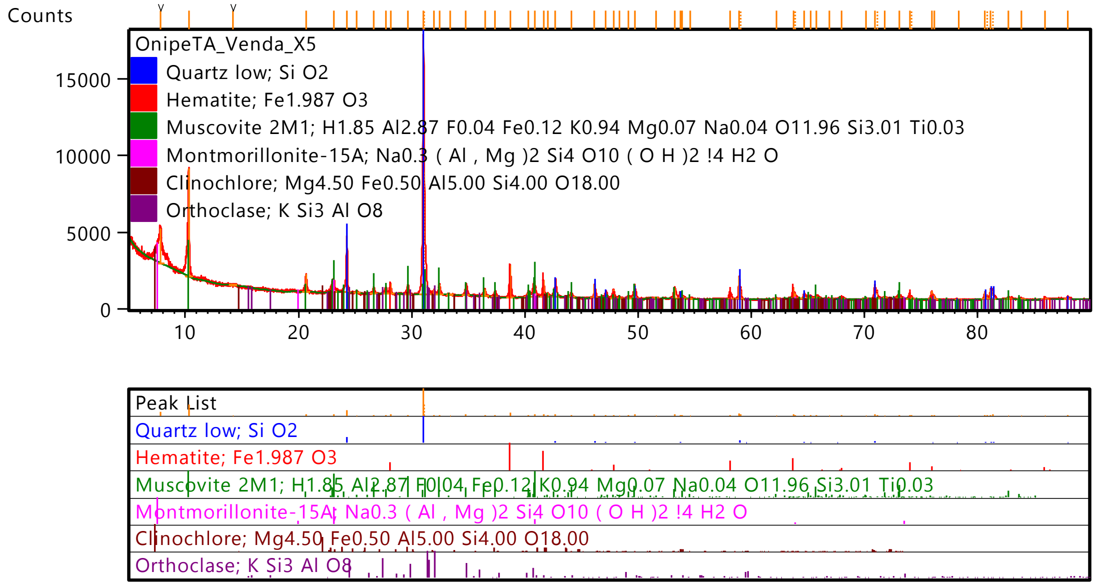


Appendix 3

The major oxides in the sampled rocks and soils

	CaO	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	MnO	Fe_2O_3
S1	3.56	3.22	3.58	17.17	51.64	0.80	1.35	0.20	13.67
SR2	8.16	2.73	8.00	16.60	48.18	0.22	0.04	0.21	14.58
SR3	0.0582	0.03	0.16	2.39	95.90	0.11	0.38	0.01	0.91
X5	0.0922	0.78	3.32	18.98	58.07	0.06	4.05	0.07	13.09
X15	0.283	0.35	3.76	19.29	58.10	0.11	4.04	0.09	12.31
X20	0.353	0.19	3.55	17.90	63.45	0.11	4.22	0.10	8.98
X30	0.568	0.20	3.85	20.57	56.52	0.15	5.25	0.11	11.43
X40	1.98	1.45	9.80	19.62	49.61	0.27	1.40	0.23	13.97
X65	5.04	1.61	9.01	16.69	49.80	0.23	1.34	0.21	14.31
Y5	1.89	1.47	4.89	16.42	57.14	0.53	1.00	0.15	13.09
Y10	1.93	1.67	4.54	16.17	56.72	0.48	1.04	0.16	13.61
Y20	2.4	1.14	4.47	18.41	55.65	0.58	1.23	0.16	12.85
Y25	4.37	1.89	4.08	16.40	54.64	0.85	2.05	0.18	12.46
Y28	7.22	2.81	4.83	15.50	51.25	1.13	2.40	0.13	10.68
Y40	7.62	2.62	5.30	14.54	50.52	0.97	2.03	0.15	11.63

Appendix 4



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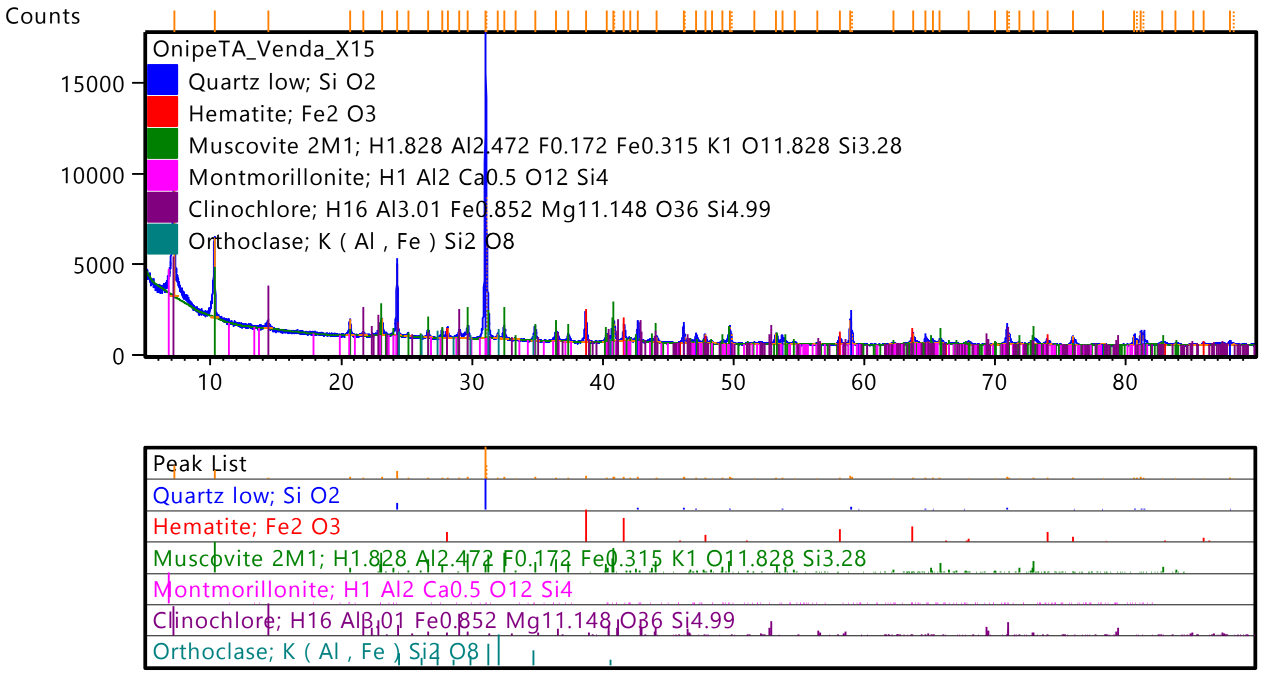

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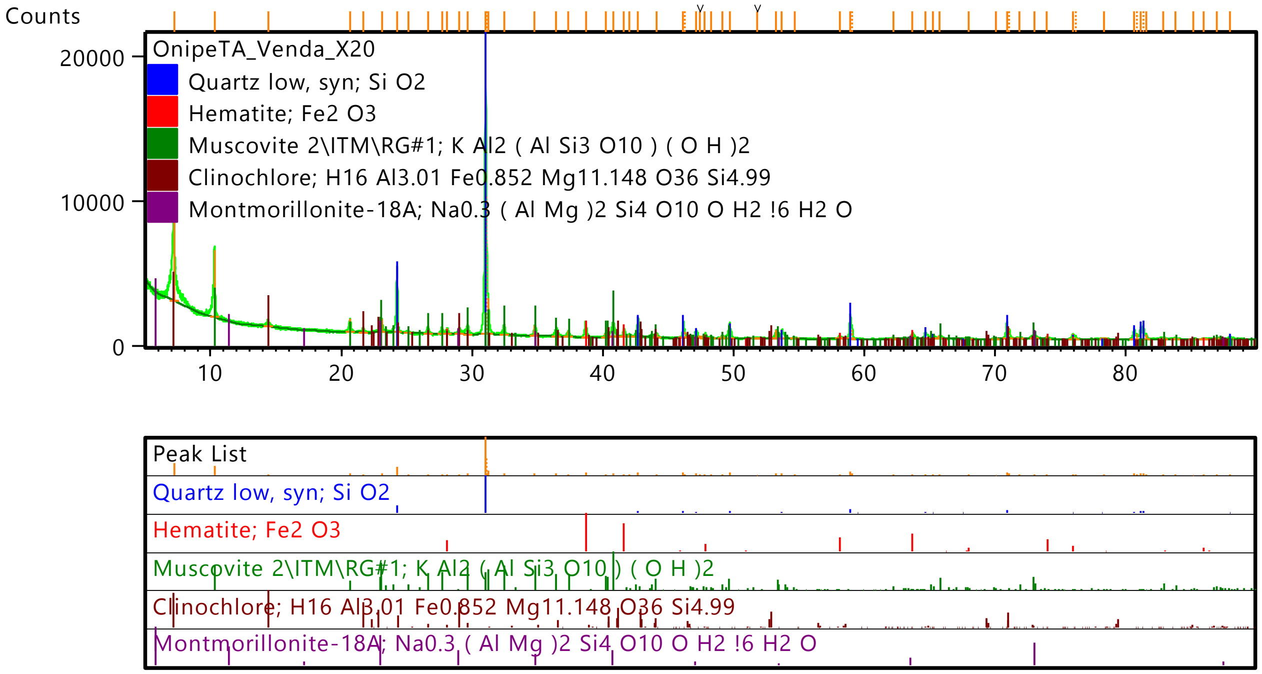

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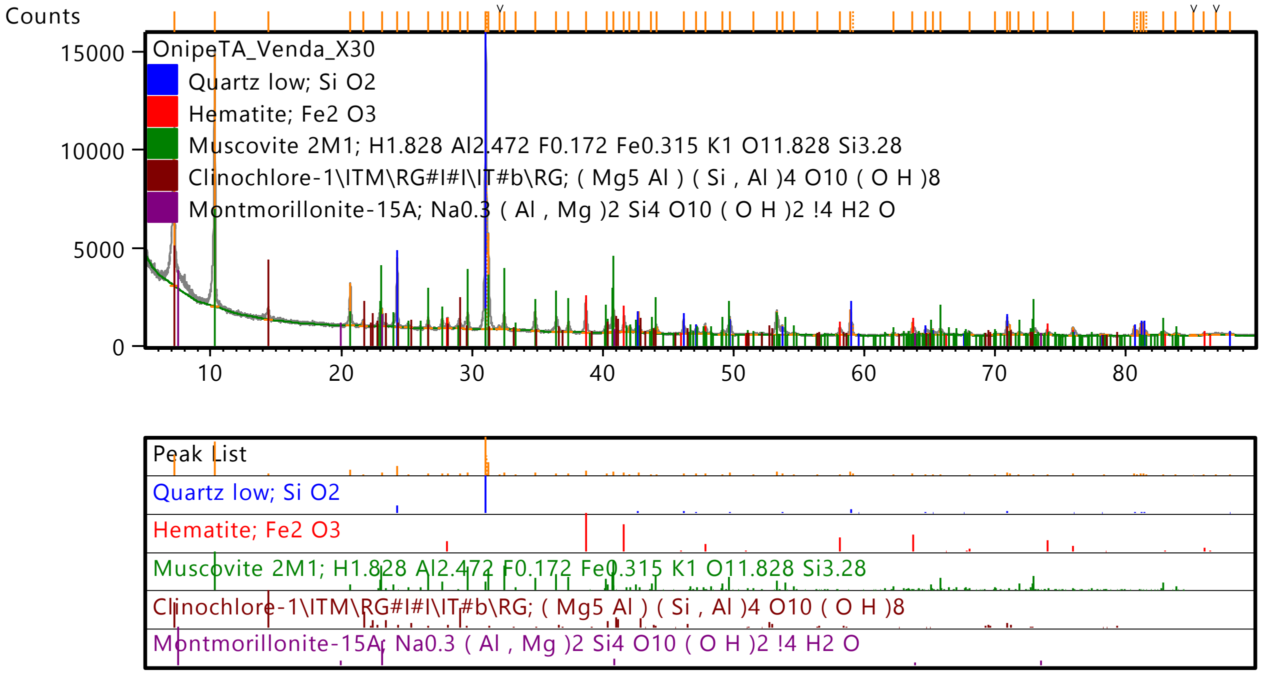

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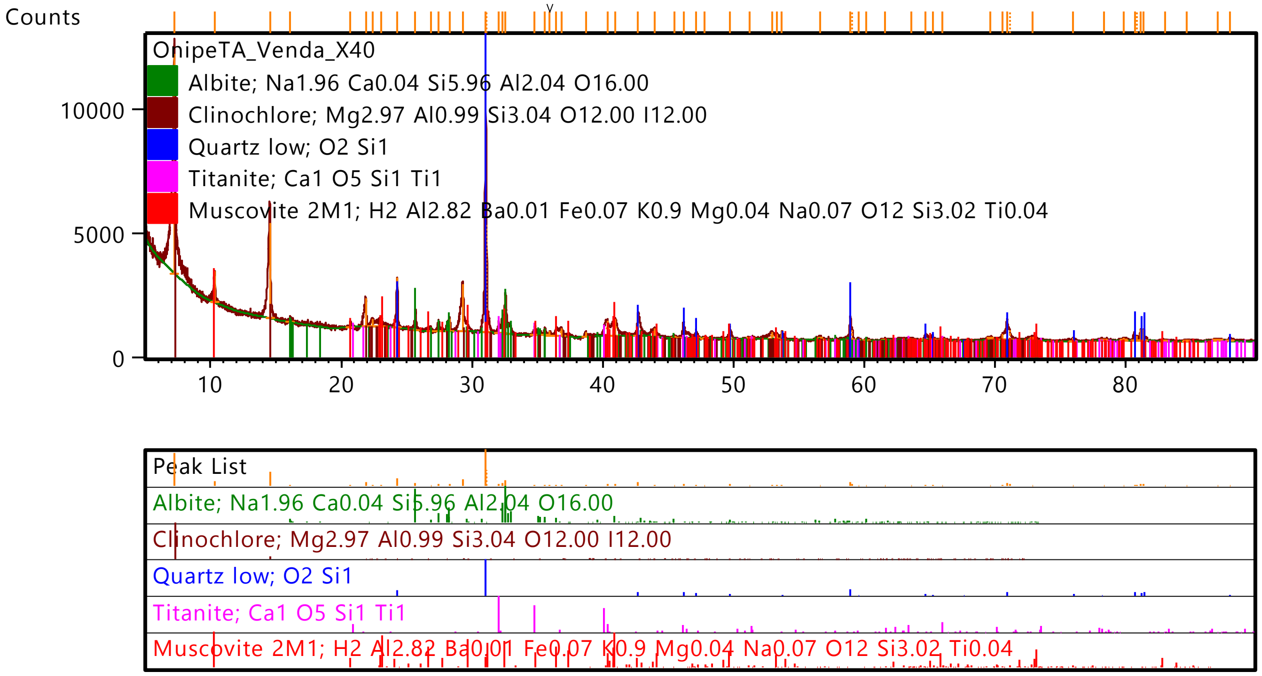

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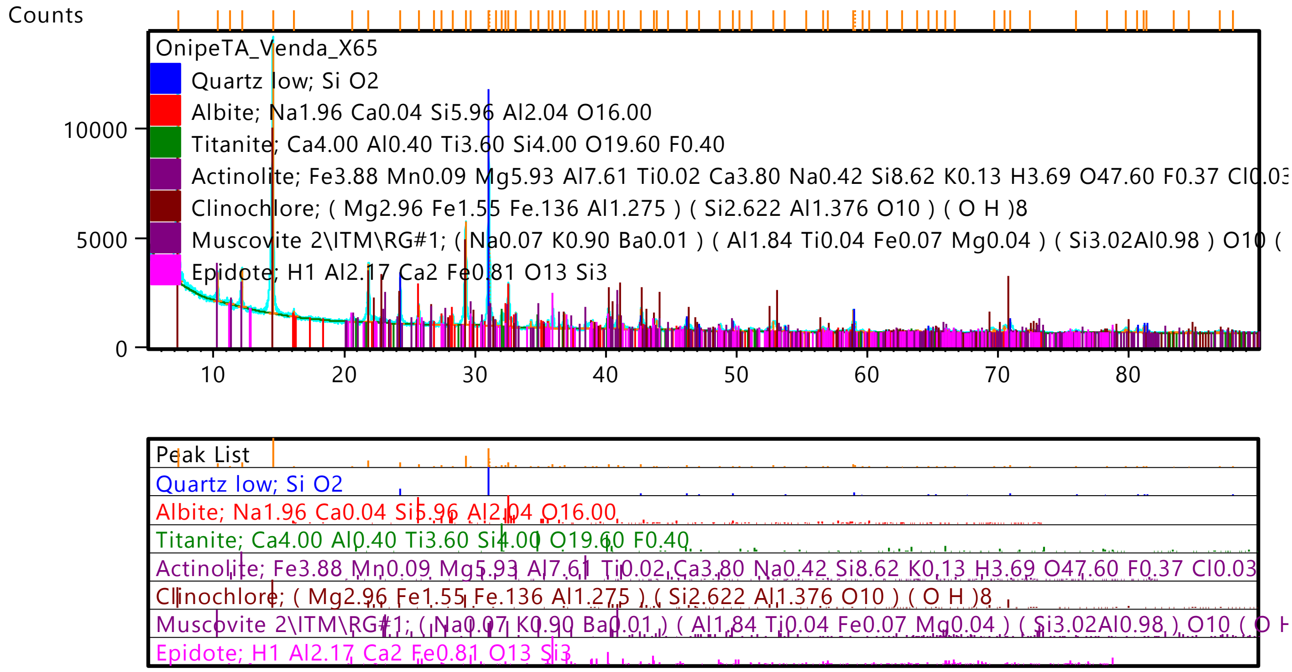

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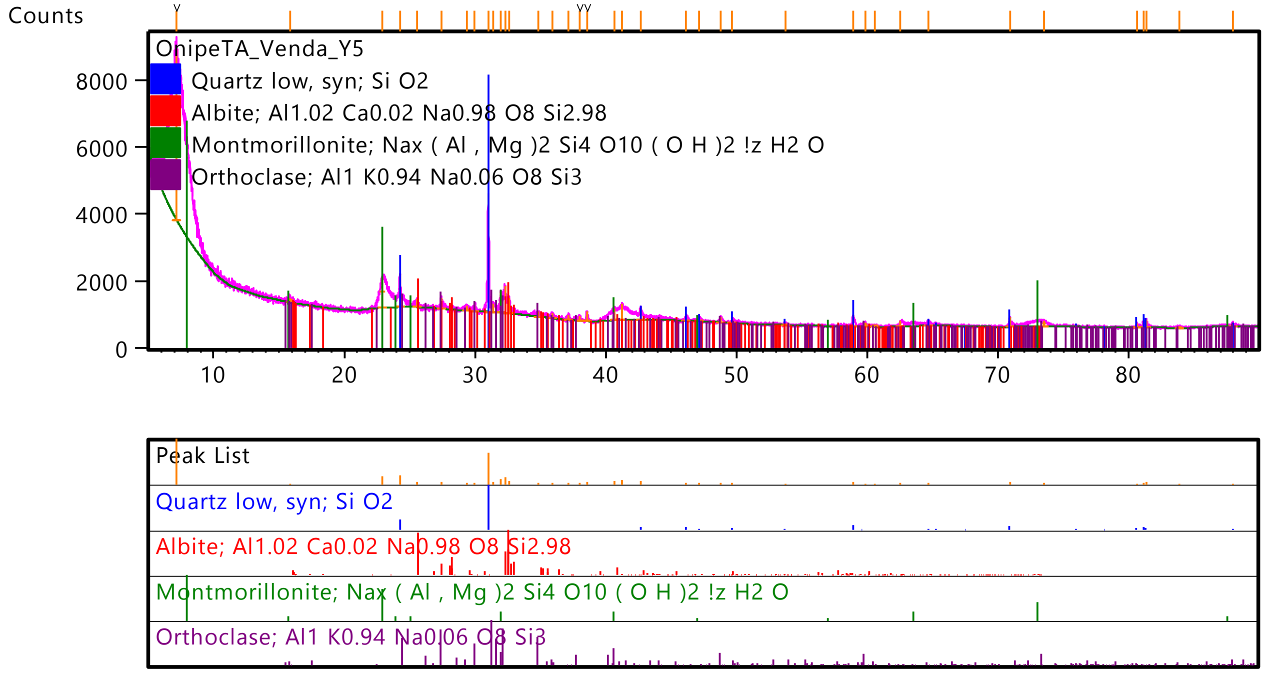

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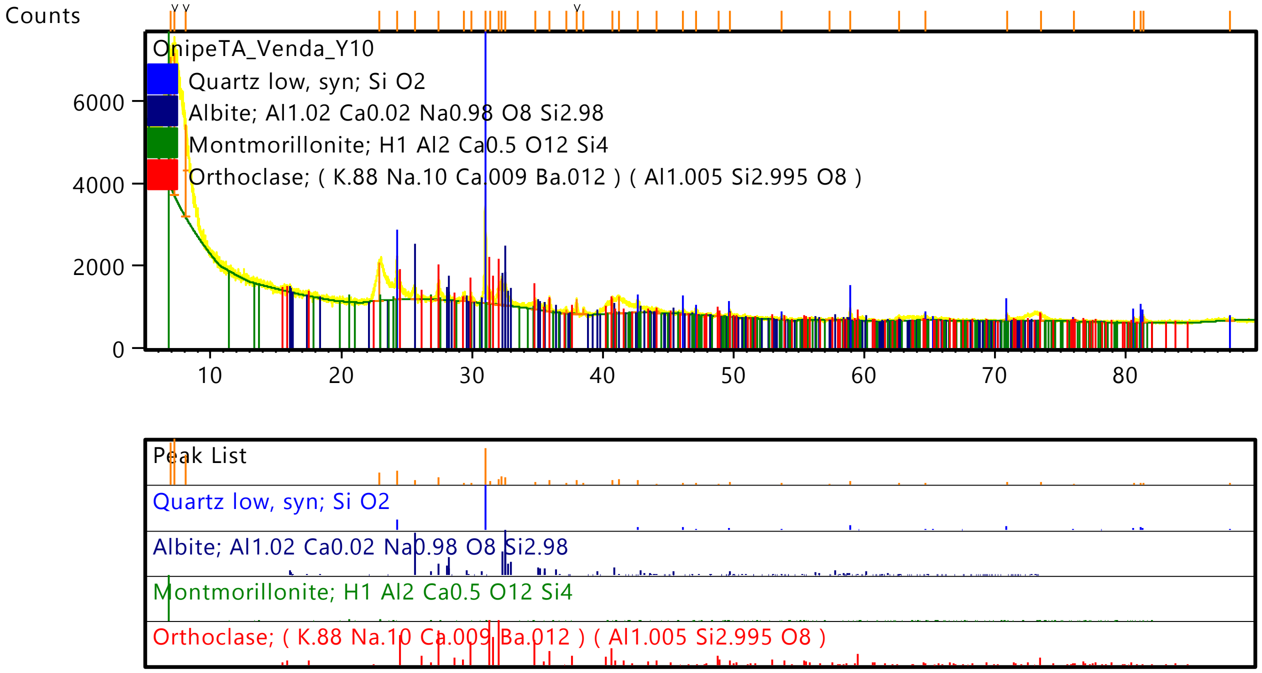

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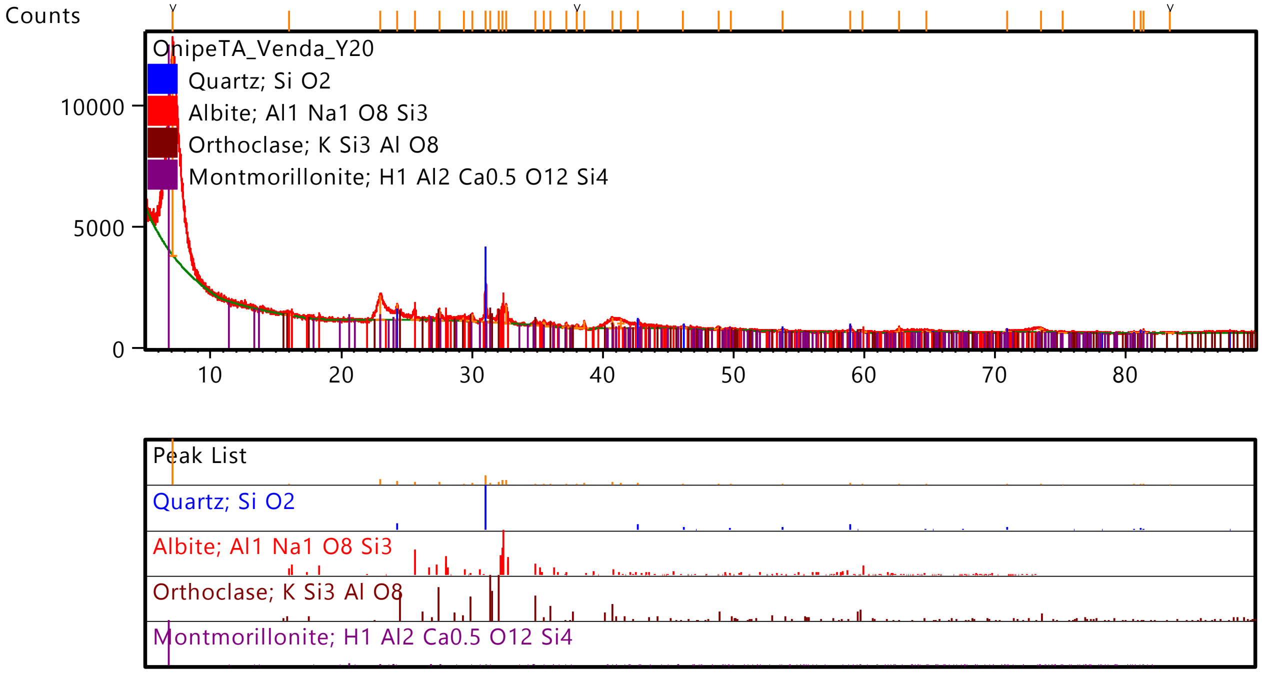

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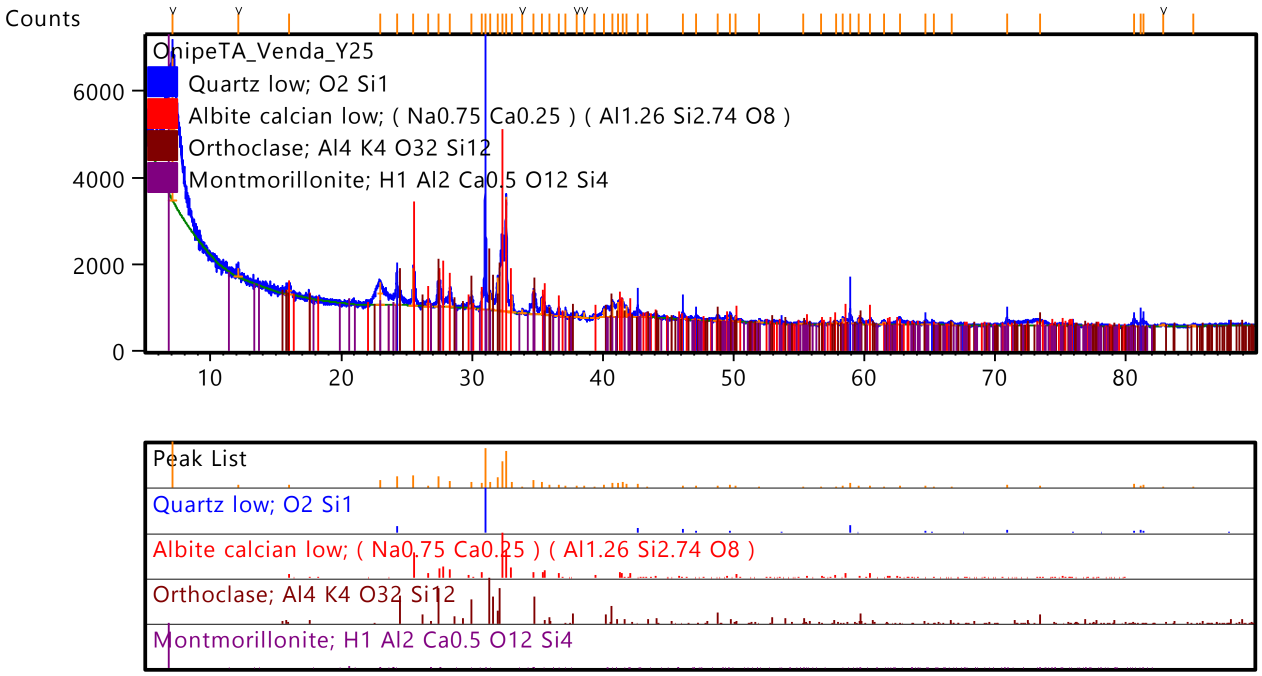

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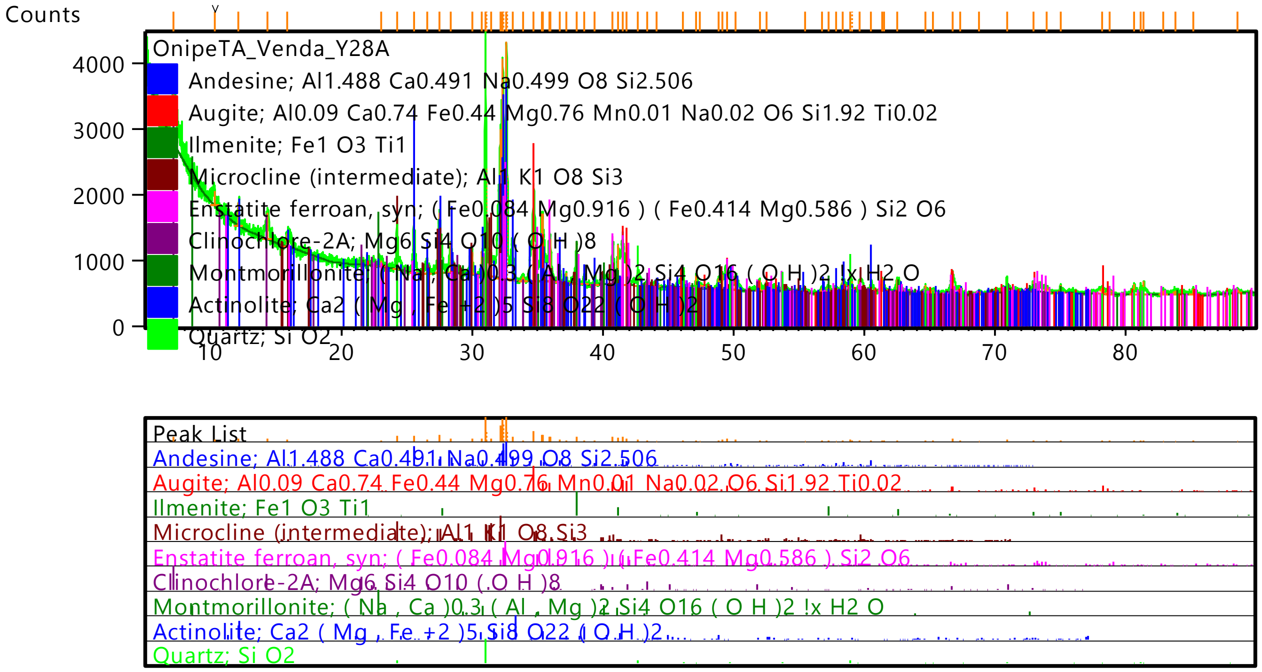

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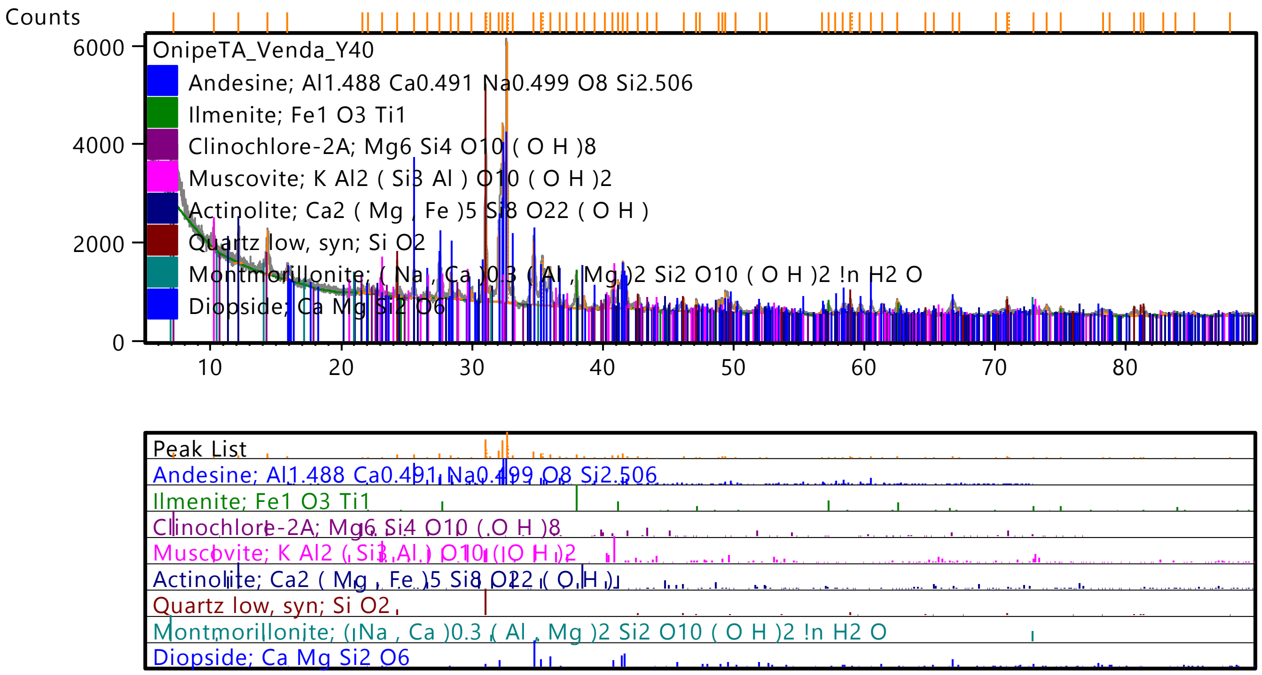

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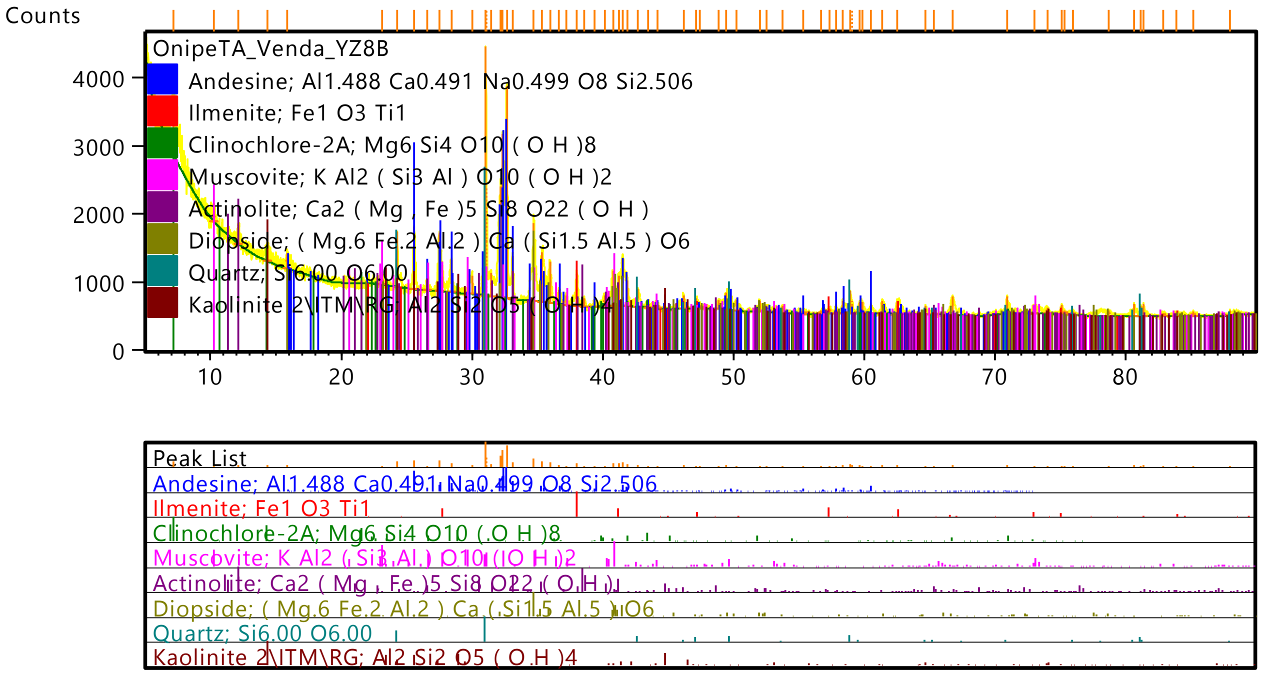

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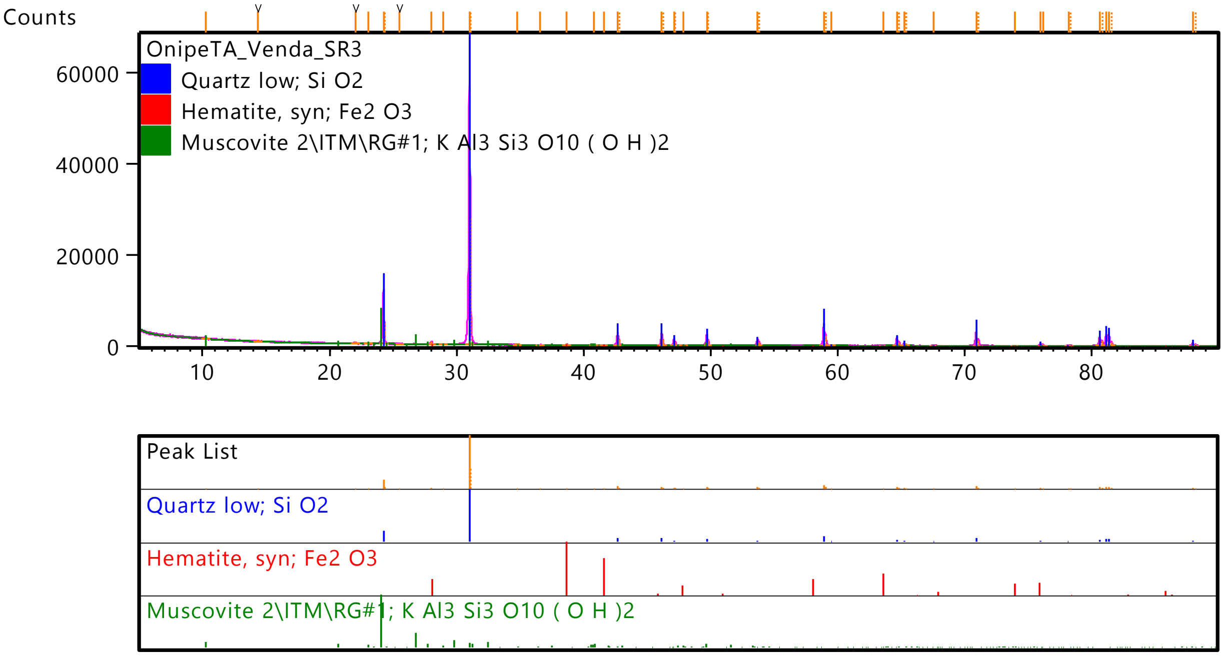

Appendix 18

Fluoride concentration in leachate with and without temperature

Sample ID	*F concentration at 25°C(mg/L)*	*F concentration at 42°C (mg/L)*
S1	10.52	10.40
SR2	0.27	0.05
SR3	0.44	0.20
X5	3.85	3.41
X15	2.29	1.67
X20	1.10	0.84
X30	0.78	0.55
X40	0.68	0.69
X65	0.53	0.33
Y5	14.88	9.15
Y10	9.51	7.82
Y20	3.79	2.37
Y25	1.02	2.45

Y28	2.60	0.91
Y40	0.72	0.50