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ABSTRACT

Available online: Rock geochemistry influences groundwater quality and the aquifer processes 30th June, 2021 of an area. The geology of the study area comprises quartzo-feldspathic gneiss Keywords: and biotite gneiss of the Precambrian basement, sedimentary Turkana Grits Petrography and Holocene sediments, Tertiary volcanics comprising nepheline phonolites Groundwater and augite basalts, alluvial deposits along the banks of major streams and chemistry laggas (ephemeral streams), and Quaternary sands that blanket much of the Geochemistry area. This paper evaluates the influence of rock chemistry on groundwater Lodwar town quality in Lodwar area. Conventional petrography and geochemistry Groundwater techniques involving measurement of major elements using X-ray fluorescence quality (XRF) and trace elements using and X-ray diffraction (XRD) in 69 rock samples to evaluate their mineralogical compositions. The major rock-forming in rocks of the study area include pyroxenes, olivine, kaolinite, siderite, fluorite calcite and dolomite. These minerals release major ions to groundwater through weathering, leaching, oxidation, dissolution and precipitation, and ion exchange reactions during rock-water interactions. The rocks in study area have generally low amounts of Na and K with modal values < 2.00 wt%, suggesting other sources of Na⁺ and K⁺ ions in groundwater. In contrast, Ca, Mg, Al, Fe and Mn are released to groundwater from rocks, as shown by high modal compositions of individual elements and associated oxides. The higher concentrations of Na⁺, K⁺, Ca²⁺ and Mg²⁺ in the groundwater of the Turkana Grit aquifer relative to the grit rock samples suggest a long history of dissolution and recycling of the groundwater. The ratio $SiO_2:Al_2O_3$ was found to be greater than 8.0 implying a high degree of maturity of the grits. The results presented by this study show that geological factors and processes have location-specific influence on groundwater quality and should be considered in aquifer water guality studies and supply development across Africa's vast ASAL regions. ©2021 Africa Journal of Physical Sciences (AJPS). All rights reserved. ISSN 2313-3317

1. Introduction

Groundwater is a vital resource for the sustainability of economic and social development in arid and semi-arid areas. Effective use of groundwater depends on its overall water quality. Groundwater quality has significant implications for drinking water and other groundwater uses, such as agriculture. Its chemical composition is a function of aquifer processes and the formation through which it flows due to rock-water interaction [1]. Evaporation, concentration, precipitation and dilution can also alter the chemical composition of groundwater and aquifer chemistry. Particularly, rock-water interaction processes are the primary sources and sinks of dissolved groundwater constituents[1]. Thus, the nature of the geological formations, flow patterns and retention period influence the groundwater quality and its geochemistry [2]. Rock types are broadly classified as igneous, metamorphic, and sedimentary. Minerals in these rocks partially or fully dissolve in water, depending on the chemical weathering sensitivity[3]. The resultant weathering minerals reflect the interaction and mineral exchange between groundwater and aquifer chemistry. The frequency and strength of these chemical reactions depend on the initial instability of the water in contact with rocks [1]. During rock–water interaction, various chemical processes occur, such as weathering and dissolution, ion exchange processes, oxidation, and reduction [1,2,4]. These geochemical processes are responsible for seasonal and spatial variations in groundwater quality parameters[5]. Oxidation of elements such as iron, silica and calcium occur due to oxidation and precipitation processes during the lowering of the water table [4].

Lodwar depends almost exclusively on groundwater [6–8], but the geology, petrography, and rock compositions and how this influences groundwater quality are unknown. The water quality and aquifer hydrogeochemistry has been investigated by Tanui *et al* (2020). This paper investigates the mineralogical composition of the rock types in Lodwar and evaluates their influence on groundwater quality. The study presents mineralogy and geochemistry data of rocks in Lodwar, determine their mineral evolution and weathering processes governing the groundwater chemistry in the region. The study will contribute to determining areas with better quality groundwater for targeted groundwater exploration and use.

2. Geological setting of the study area

2.1 Geology of Turkwel River Basin

The geological formations in the Turkwel River basin (Fig. 1) comprise; (1) Precambrian basement system rocks (gneisses, granulites, quartzites and limestones with metamorphosed/non-metamorphosed/anatectic intrusive rocks such as granites, aplites, pegmatites, norites and gabbros); (2) Cretaceous-Palaeogene-Neogene sediments (Cretaceous sandstones and conglomerates of the Lapur Formation, and Turkana Grits series; (3) Tertiary volcanics (basalts, pyroclastic volcanic rocks, phonolites, trachy-andesites and nephelinites with numerous intrusive rocks of nephelinite, dolerite, teschenite, lamprophyre and microfoyaite compositions), and (4) Superficial deposits of Plio-Pleistocene to Recent age comprising Aeolian sands, alluvial soils and gravels, lacustrine shales, shelly limestones and coarse grits [9–13]. The dominant rock formations within the study area (Fig. 2) comprise quartzo-feldspathic gneiss and biotite gneiss of the Precambrian basement, sedimentary rocks with predominantly the Turkana Grits and Holocene sediments, Tertiary volcanic rocks including the nepheline phonolites and augite basalts, and alluvial deposits along streams and major *laggas (ephemeral streams)*.



Figure 1: Geological map of the Turkwel River Basin (Ministry of Energy and Regional Development 1987)



Figure 2. Geological map of the study area published by [6] showing the designated boundary of the Lodwar Alluvial Aquifer System (LAAS) - the majority of of the boreholes and handpumps are along the Turkwel River and are mainly concentrated within Lodwar town

2.2. Hydrogeological setting and groundwater chemistry

A water quality and aquifer geochemistry study in the current study area [8] revealed three distinct aquifers collectively referred to as the Lodwar Alluvial Aquifer System; the shallow alluvial aquifer (SAA), intermediate aquifer (IA), and deep aquifer (DA) aquifers are the primary source of fresh water. The Turkana Grit Shallow Aquifer (TGSA) is exceptionally saline and has high fluoride levels. The shallow aquifers are classified as shallow at depth < 30 m, intermediate aquifer at 31-100 m and deep aquifer at depth > 100 [7]. The average yield in the SAA is 16.87 m³/h, 8.28 m³/hr in the IA, and 6.25 m³/h in the deep aquifer with one outlier of 100 m³/hr in the Napuu. The yield of wells in the TGSA was not available during this study. Weathering minerals during the groundwater flow leads to the release of alkali and alkaline earth elements and trace elements into the waters [4,14]. In 2020, Tanui and co-workers indicated that the SAA is dominated by Ca-HCO₃ water type because of the recharge influence of Turkwel River, which has the same water type. The intermediate aquifer (IA) is Na-HCO₃ water type, while pockets of Mg-HCO₃ water occurs in the shallow alluvial and

intermediate aquifers. The TGSA is dominated by Na-Cl water type, but NaHCO₃ water type is dominant near its contact with the Holocene sediments.

3. Materials and Methods

In February and May 2018, 69 rock samples were collected during a comprehensive geological mapping and water sampling exercise within the study area. Ten of the 69 rock samples were petrographically analyzed after preparation of thin sections at the Department of Mines and Geology laboratory using standard mounting techniques. All the 69 rock samples were analyzed for major oxides such as SiO₂, Al₂O₃, CaO, MgO, Na₂O, K₂O, TiO₂, MnO, Fe₂O, and Loss on ignition (LOI), using X-ray fluorescence (XRF) at the Department of Mines and Geology, Kenya. Samples were prepared for analysis using the lithium metaborate fusion procedure [15] and replicated analyses for each sample. The LOI was determined by weight loss measurement upon heating one-gram split sample at 95 °C for 90 minutes. Fifty-four of the samples were ground and analyzed for major elements including Na, Mg, Al, P, S, K, Ca, Fe, and Mn and for trace elements such as Ti, Cr, Co, Ni, Cu, Zn, As, Se, Mo, and Pb. elements at International Centre of Agriculture and Forestry (ICRAF) lab by X-ray diffraction (XRD) Tracer 5*i* and vacuum technology were used in quantitative analysis of lighter elements [16]. The acquired data was filtered using R Knime Application in parts per million (ppm) and subsequently uploaded into the database for analysis. The results in ppm were divided by 10,000 to convert to a weight per cent. K means clustering algorithm using XLSTAT Microsoft Add-in was applied to the varied chemistry of the Turkana Grit samples to create clusters with similar geochemistry.

4. Results

4.1 Petrography

(i) Nepheline-phonolite

The nepheline-phonolite collected at Lodwar town has anhedral prismatic nepheline crystals (Figure 3) that assume hexagonal crystal symmetry and are sometimes partly altered sodalite and turbid anorthoclase feldspar. Euhedral haematite grains are contained in the fine-grained groundmass of green aegirine-augite, anorthoclase, and nepheline. Under PPL and XPL, cataclastic deformation of plagioclase was observed as a result of a later, lower-temperature phase of strain localization in plutonic rocks. Deformation bands form, which are most likely linked to the shear strain trend. The hematite grains are larger in the deformation zone. In a thin fragment, rare nepheline microphenocrysts, partially modified to sodalite, and turbid anorthoclase feldspar are also present in the fine-grained groundmass.



Figure 3: Microphotograph of the nepheline-phonolite (sample 1650) observed under XPL (a) and PPL (b) showing the prismatic nepheline crystals and euhedral hematite grains. Cataclastic deformation of plagioclase was observed in the thin section

(ii) Dolerite

Dolerite is a dark grey to black intrusive volcanic rock and with fine to medium-grained groundmass. It was identified as occurring as a dyke that outcrops in the Turkana Grits. The dolerite rock (Figure 4 a, and b) had numerous colourless grains of quartz and feldspars as observed under the PPL (Figure 4 b), where the feldspars assume a prismatic habit. Primary minerals identified include plagioclase, pyroxene, and amphiboles. The plagioclase crystals are acicular, and the pyroxene grains are subhedral with chloritised outlines. Secondary minerals included chlorite and quartz. The accessory minerals are orthoclase, chlorite and magnetite. Cleavages and twinning features are observed on the specimen within the quartzo-feldspathic gneiss (Figure 4 c & d).



Figure 4. Microphotograph of the dolerite dyke rock within the Turkana grits under PPL (a) and XPL (b) for sample 1656 and that of a mafic dyke (3845) observed under PPL (c) and XPL (d) showing plagioclase feldspars and twinning features

(iii) Conglomerate

Specimen 3857 of conglomerate capping the Turkana Grit at its contact zone with the nepheline phonolite revealed angular quartz and feldspar fragments cemented by clay and some calcite. Colourless sub-rounded quartz minerals are observed in both PPL (a) and XPL (b), and prismatic nepheline crystals are present in the rock sample (Figure 5). Poorly defined sedimentary banding is present with angular altered volcanic rock fragments. Also present are altered biotite grains that suggest alkalic or acidic volcanism. The conglomerate is cemented with coarse-grained sparry calcite cement, which fills the clasts in cracks as well. The feldspars present are andesite and deep brown sodic amphibole similar to that described by [13] and [9].



Figure 5: Microphotograph of the conglomerate sample (3857) under PPL (a) and XPL (b) showing a prismatic nepheline crystal and distinct cleavages and sub-rounded quartz grains

(iv) Sandstone

Three sandstone samples in Fig. 6 a & b have medium-sized grains comprising quartz, feldspars, and biotite. The fined grained compact sandstone sample (Figure 6 c & d) show dominant feldspar grains under XPL (d). Fluid inclusion features had diameters ranging from less than 20.00 μ m to 130.47 μ m, indicating that temperatures >100 °C were not reached during the sandstone's burial history. The sandstone was highly fractured, with some of the fractures filled by brown minerals, possibly iron and oxyhydroxides. The poorly sorted sand and gravels in the coarse-grained sandstone and the existence of fractures in the fine-grained counterpart suggest the high permeability of sandstone in the study area. The coarse-grained sandstone (Figure 6e & f) comprised mainly of subrounded to well-rounded quartz pebbles cemented by calcite and carbonate. Cryptocrystalline chert, micro-micaceous mudstone, siltstone and stretched quartz grains dominate the mineral framework. Fewer feldspars grains were present in the coarse-grained sandstone as compared to those present in the fine-grained specimens.



Figure 6. Microphotographs for the medium-grained gravelly sandstone (sample 1659) under PPL (a) and XPL (b) for sample 1659, PPL (c) and XPL (d) for the compact altered sandstone and PPL (e) and XPL (f) microphotographs for coarse-grained gravelly-sandstone from sample 3858

(v) Turkana Grits

The Turkana Grit samples (Fig. 7) predominantly consists of fine to coarse arkosic sandstone suggesting fluvial deposition and comprise 25-45 % quartz and feldspar cemented by calcite. The yellow crystals observed under XPL were regarded as staurolite, and green are hornblende minerals. The Turkana Grit in contact with the dolerite dyke (Figure 7 a & b) had zoning features and altered minerals probably caused by contact metasomatism. The quartz and feldspars are anhedral-shaped and are poorly sorted within the calcite matrix with grains ranging from 0.25 to 1.00 mm (Figure 7 c & d).

Figure 7: Microphotographs of the Turkana grit samples showing (a and b) zoning features and (b & c) calcite cemented matrix on quartz and feldspars minerals

(vi) Quartzo-feldspathic gneiss

Two samples of the quartzo-feldspathic gneiss collected at the same location indicate different mineralogical characteristics. The sample attached to the igneous intrusion (Figure 8 a & b) showed highly deformed minerals caused by high-grade metamorphism. Quartz and feldspars are the dominant minerals observed in Figure 8 c & d, and biotite comprises 5% of the mineralogy occurring as an accessory mineral. The feldspars present include altered orthoclase, microcline, and plagioclase. The majority of the orthoclase grains have been converted to small flakes of sericite while the initial biotite grain has reacted to oxides, orthopyroxene, and (inferred) melt during

contact metamorphism. The partly replaced biotite grains are surrounded by relict plagioclase in sieve texture with spaces filled with quartz and feldspars.

Figure 8. Microphotographs of the quartzo-feldspathic collected at the same locality where the one in contact with the igneous intrusion (a& b) showed deformed surfaces while the one not attached to the intrusion (c & d) shows fine-grained quartz and feldspars

4.2 Geochemistry

The geochemistry of the rock samples has been described based on the results of the major elements and the concentration of major metals oxides and trace elements using XRF and XRD, respectively. The major elements were expressed as oxides of SiO₂, Al₂O₃, CaO, MgO, Na₂O, K₂O, TiO₂, MnO, Fe₂O, and moisture content. The trace elements comprised Ti, Cr, Co, Ni, Cu, Zn, As, Se, Mo, and Pb and are expressed as percentages.

4.2.1 Metamorphic rocks

The XRF results indicated that the dominant minerals in the quartzo-feldspathic gneiss are SiO_2 ;53.25 wt %, Al_2O_3 ; 9.35 wt %, K_2O ; 5.96 wt %, and Na_2O ; 4.66 wt %. The abundance of these minerals suggests the dominance of aluminosilicate weathering in the study area (Table 1). The K_2O/Na_2O ratios exceeded 1.0, indicating high-temperature recrystallization. The rock samples are poor in ferromagnesian elements - MnO, TiO₂ and MgO. The lack of Na in all the rocks samples suggests that the quartzo-feldspathic gneiss is rich in anorthite, a characteristic of the granulite

facies of metamorphic rocks [17]. The major elements compositions are in the order of Ca>Fe>Mg>Mg>Al>K (Table 1b), indicating that these are the elements that would likely characterize the type of groundwater hosted in these rocks. The trace elements concentrations indicate that the groundwater in these rocks is unlikely to have high and undesirable concentrations of the measured trace elements.

(a) Major element oxides [weight %]												
Quartzo- feldspathic gneiss	SIO2	Al ₂ O ₃	CaO	MgO	Na₂O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	LOI		
3841- Nabuelpus	53.71	18.2	1.52	1.07	4.03	6.52	0.19	0.27	3.92	9.63		
3843 - Nabuelpus	52.83	19.95	2.15	0.01	4.93	5.87	0.18	0.25	4.31	8.66		
3846 - Nabuelpus	53.21	19.89	2.49	0.09	5.01	5.5	0.23	0.24	4.49	8.84		
Average	53.25	19.35	2.05	0.39	4.66	5.96	0.20	0.25	4.24	9.04		
		(b) Major elements [weight %]										
	S	Al	Са	Mg	Na	к	Р	Mn	Fe			
3841 - Nabuelpus	0.07	1.71	12.63	1.96	nd	0.37	0.03	0.07	1.12			
3843 - Nabuelpus	nd	1.82	5.34	2.89	nd	0.17	0.05	0.18	4.26			
3846 - Nabuelpus	0.01	3.38	7.82	2.42	nd	0.14	0.03	0.20	6.32			
Average	0.04	2.30	8.60	2.42		0.22	0.04	0.15	3.90			
			Т	race eleme	ents							
	Ti	Cr	Со	Ni	Cu	Zn	As	Se	Мо	Pb		
3841 - Nabuelpus	0.01	0.01	nd	0.00	0.03	0.01	nd	nd	nd	nd		
3843 - Nabuelpus	0.01	0.08	0.00	0.02	nd	0.01	nd	nd	nd	nd		
3846 - Nabuelpus	nd	0.08	0.00	0.01	nd	0.01	nd	0.00	nd	nd		
Average	0.01	0.06	0.00	0.01	0.03	0.01	nd	0.00	nd	nd		

Table 1. Results for the major oxides, major elements and trace metals in the quartzo-feldspathic gneiss.

4.2.2 Sedimentary rocks

(a) Turkana Grits

Generally, the chemical and mineralogical compositions of the sediments and sedimentary rocks are diverse due to the varied origin of sediments and resulting end-members. Application of the K means clustering algorithm revealed four unique clusters of the Turkana Grits in the study area (Fig. 10; Table 3). The clusters differed in the compositions of the major oxides; Cluster 1 and 2 were in the order of SIO₂>CaO>Al₂O₃>MgO, where cluster 2 was richer in CaO and MgO than in cluster 1, indicating more plagioclase minerals. Cluster 3 differed from the first two clusters with relatively higher SIO₂ content and higher levels of Al₂O₃ and Fe₂O₃ than CaO and MgO changing the order to SIO₂ >Al₂O₃>Fe₂O₃. Cluster 4 exceptionally had higher levels of CaO than SiO₂, indicating dominates of carbonate minerals over silicates with the order CaO>SIO₂>MgO>Al₂O₃>Fe₂O₃. Ca, Al and Fe are the dominant minerals in all four clusters, suggesting that these minerals can be leached into the groundwater hosted in these rocks. The concentration of trace elements < 0.01 wt % to 0.002 wt % indicates that they are unlikely to have high and undesirable concentrations in groundwater hosted in the Turkana Grits.

Figure 9. Variations of the chemical compositions of the major elements among the clusters of Turkana Grits

Table 2. Description of the major oxides, major and trace elements of the four clusters of the Turkana Grits

Cluster	Description	Major Oxides	Major elements	Trace elements
Cluster 1: Fine- grained Turkana Grits	Cluster 1 had seven rock samples representing specimens of the Turkana Grits in Lodwar town and at Nakutan area.	 Characterized by high MgO, Na₂O, K₂O and MnO than in clusters 2 &3. Has the least composition of Na₂O (Table 3; Cluster 1) 	 Ca, Al, and Fe are the most abundant major elements with median values of 8.83%, 2.80 % and Fe 2.42 %, respectively K, Mg, Mn, Na had median concentrations <0.50%. 	 Ti, Cr, Co, Ni, Cu, Zn, Se and Mo had median values <0.01% while As, and Pb was not within detectable limits in this cluster
Cluster 2: Gravelly Turkana Grits	Two rock samples comprised Cluster 2 and were collected north- east of Lodwar town at Kakwanyang and to the east of Talent High school	 Characterized by very high CaO and low Fe₂O₃ SiO₂ levels between are relatively lower than that of Clusters 1 and 3 (Table 3. Cluster 3) 	 Like in cluster 1, Ca and Fe were the most abundant major elements Mg, P, S, and K were < 0.05%, while Na was not detected in specimens of this cluster. 	 Cu, As, and Pb were below detectable limits while Ti was 0.07%. Cr, Ni, Co, Zn, Se and Mo was <0.01%
Cluster 3: Semi- consolidated sandy Turkana Grits	Cluster 3 comprised six rock samples of the Turkana Grits that occurred adjacent to the Holocene sediments. The rock specimens were mainly sandy and semi- consolidated and often capped by a highly consolidated gravelly layer.	 Highest compositions of SiO₂, Al₂O₃, K₂O, TiO, Fe₂O₃, CaO with the lowest levels of MgO and Na₂O than in Clusters 1, 2 and 4 (Tale 3: Cluster 4) 	 Ca content of 9.08%, Al; 2.62%, and Fe; 2.22% were most abundant than the rest of the trace elements. Mg was 0.74%, while P, S, and K were below 0.05%. Na was not detected like cluster 2 	 Ti was 0.05% As, Se and Pb were below detectable limits in this cluster. The rest of the elements;Ti, Cr, Co, Ni, Cu, Zn, and Mo were <0.01%
Cluster 4: Consolidated Turkana Grits	Cluster 4 comprised three rock samples of the Turkana Grits from Nachomin, Nakadukui and Natir areas. Like Cluster 2 samples, these members were observed at isolated locations and often capped by calcareous material	 High concentration of CaO of 15.80 – 38.15 % after cluster 2 and highest moisture and volatile materials and MgO compositions and the least SiO₂ content of < 40.00%) among all the three clusters (Table 3; Cluster 4). 	 Major elements showed the highest Ca concentration of the four clusters with17.08% Al was 1.78%, Fe 1.53% and Mg 0.70%, K, P and S were below 0.05% 	 Concentration of all trace elements was <0.02%

Table 3. Descriptive statistics for the major elements of the different clusters of the Turkana Grits samples

Statistics	SIO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	LOI
Minimum	45.70	3.89	7.80	0.02	0.02	0.98	0.14	0.09	1.32	7.88
Maximum	60.48	16.40	18.24	9.21	1.98	4.03	2.40	2.01	7.90	17.37
Range	14.78	12.51	10.44	9.19	1.96	3.05	2.26	1.92	6.58	9.49
Median	56.92	9.12	14.01	6.10	0.87	1.51	0.17	0.19	1.95	9.89
Mean	53.86	8.53	13.58	4.82	0.77	2.06	0.59	0.45	2.83	11.76
Variance	43.48	19.51	12.38	14.78	0.58	1.21	0.69	0.48	5.53	15.44
Standard	6.59	4.42	3.52	3.84	0.76	1.10	0.83	0.69	2.35	3.93
Deviation										

Cluster 1: Fine-Grained Turkana Grits

Cluster 2: Gravelly Turkana Grits

Statistic	SIO ₂	Al ₂ O ₃	CaO	MgO	Na₂O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	LOI
Minimum	48.36	4.03	30.14	1.06	0.20	0.61	0.19	0.13	1.17	1.88
Maximum	53.70	4.21	37.00	6.01	0.58	0.65	0.23	0.15	1.81	6.81
Range	5.34	0.18	6.86	4.95	0.38	0.04	0.04	0.02	0.64	4.93
Median	51.03	4.12	33.57	3.54	0.39	0.63	0.21	0.14	1.49	4.35
Mean	51.03	4.12	33.57	3.54	0.39	0.63	0.21	0.14	1.49	4.35
Variance	14.26	0.02	23.53	12.25	0.07	0.00	0.00	0.00	0.20	12.15
Standard	3.78	0.13	4.85	3.50	0.27	0.03	0.03	0.01	0.45	3.49
Deviation										

Cluster 3: Semi-Consolidated Sandy Turkana Grits

Statistic	SIO ₂	AI_2O_3	CaO	MgO	Na₂O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	LOI
Minimum	60.80	4.81	2.76	0.03	0.09	0.94	0.32	0.08	2.40	5.47
Maximum	71.06	15.87	9.80	3.02	0.21	2.51	0.89	0.32	4.90	24.91
Range	10.26	11.06	7.04	2.99	0.12	1.57	0.57	0.24	2.50	19.44
Median	64.05	11.29	3.73	1.92	0.13	2.06	0.46	0.11	3.31	7.77
Mean	65.60	11.00	5.03	1.57	0.14	1.92	0.53	0.17	3.43	10.24
Variance	19.29	12.78	8.11	1.59	0.00	0.28	0.04	0.01	0.81	53.83
Standard	4.39	3.57	2.85	1.26	0.04	0.53	0.21	0.12	0.90	7.34
Deviation										

Cluster 4: Consolidated Turkana Grits

Statistic	SIO ₂	AI_2O_3	CaO	MgO	Na₂O	K ₂ O	TiO ₂	MnO	Fe_2O_3	LOI
Minimum	21.83	3.41	15.80	0.05	0.03	0.54	0.18	0.15	1.65	25.87
Maximum	40.09	4.21	38.15	9.15	0.57	1.12	0.23	0.71	2.73	34.27
Range	18.26	0.80	22.35	9.10	0.54	0.58	0.05	0.56	1.08	8.40
Median	24.51	4.20	30.14	6.01	0.20	0.61	0.19	0.19	1.81	29.49
Mean	28.81	3.94	28.03	5.07	0.27	0.76	0.20	0.35	2.06	29.88
Variance	97.22	0.21	128.22	21.37	0.08	0.10	0.00	0.10	0.34	17.75
Standard	9.86	0.46	11.32	4.62	0.28	0.32	0.03	0.31	0.58	4.21
Deviation										

|GEOLOGY

(a) Holocene Sediments

The geochemistry of the Holocene sediments collected on selected profiles in the east of Lodwar town, Napuu / Lolupe area, and Turkwel River at Kakwanyang (Table 5). The mineralogical compositions of the major oxides East of Lodwar town and Napuu and Lolupe areas showed that SiO₂>Al₂O₃> Fe₂O₃>CaO, suggesting an abundance of silicate and clay minerals. In the Natir and Kankanyang areas, the sequence was CaO>SiO₂>Al₂O₃>MgO>Fe₂O₃, showing more predominant carbonate minerals than in Napuu and Lolupe. In the case of major elements' compositions, Al, Fe, Ca, and Mg dominated the Holocene sediments East of Lodwar. Within Napuu / Lolupe areas, Ca dominated the deposits of Turkwel River near Kakwanyang and at Natir. These results indicate the minerals that can be released into the groundwater during weathering and dissolution processes. The low concentrations of trace elements in Holocene Sediments suggest they may not be found in undesirable quantities in its groundwater.

The ratio of SiO₂ / Al₂O₃ is used as an indicator of the maturity of sedimentary rocks, a geochemical criterion that reflects the presence of clays, feldspars and quartz [18]. Values of SiO₂/Al₂O₃ ratio >5.0 (low clay content) indicate the progressive maturity of the sediments [29]. The Holocene sediments in Natir, Napuu and Lolupe range in maturity from moderate (2.3 to 4.7) to high (5.1 to 7.4) (Table 4). The sediments at Turkwel River at Kakwanyang have an average ratio of 3.9, suggesting they are moderately mature and are derived from mixed sources (Obasi, 2015). Mature Holocene sediments in the study represent the 10,000 yr BP sedimentation, while the immature samples of Holocene sediments with medium to moderate SiO₂/Al₂O₃ ratio represent the 4, 000 yr BP deposits. The K₂O / Al₂O₃ ratio for clay minerals and feldspars is used to indicate the source composition of pelitic sedimentary rocks. Pelitic sedimentary rocks with a K₂O / Al₂O₃ ratio > 0.5 indicate a significant concentration of alkali feldspar relative to other minerals in the original rock, while those with a K₂O / Al₂O₃ was ≤ 0.2 in all the samples of the Holocene sedimentary rocks are recycled [30]. The ratio of K₂O / Al₂O₃ was ≤ 0.2 in all the samples of the

Table 4: Ratio of SiO_2 / Al_2O_3 showing the maturity of Holocene sediments in the study area while the ratio of K_2O / Al_2O_3 indicating the pelitic origin of the sediments

No.	Description	Lab No.	SIO ₂ / Al ₂ O ₃	K2O / Al ₂ O ₃
1	East of Lodwar	3824 (A)	3.5	0.1
2	East of Lodwar	3825 (B)	5.9	0.2
3	Napuu/Lolupe	3820 (A)	4.2	0.2
4	Napuu/Lolupe	3821 (B)	3.7	0.1
5	Napuu/Lolupe	3822 (C)	3.2	0.1
6	Napuu/Lolupe	3823 (D)	7.4	0.2
7	Turkwel River at Kakwanyang	3852 (A)	2.6	0.2
8	Turkwel River at Kakwanyang	3853 (B)	2.3	0.2
9	Turkwel River at Kakwanyang	3854 (C)	3.3	0.2
10	Turkwel River at Kakwanyang	3855 (D)	4.7	0.2
11	Natir	3829 (A)	6.8	0.2
12	Natir	3827 (B)	6.4	0.0
13	Natir	3826 (C)	5.1	0.1

Table 5: Results and summary statistics of the major elements and trace elements in the Holocene Sediments of the study area

Description	Lodwa	ar East	nst Napuu/Lolupe			Turkwel I	Riverbank		Natir			Statistics					
								near Kak	wanyang								
Lab No.	3824	3825	3820	3821	3822	3823	3852	3853	3854	3855	3829	3827	3826	Min	Max	Median	SD
	(A)	(B)	(A)	(B)	(C)	(D)	(A)	(B)	(C)	(D)	(A)	(B)	(C)				
SIO ₂	57.97	69.97	66.90	55.10	51.80	80.85	48.79	43.69	46.51	46.07	68.97	12.89	24.91	12.89	80.85	51.80	18.53
Al ₂ O ₃	16.52	11.89	16.05	14.70	16.42	10.92	18.90	18.70	13.95	9.87	10.21	2.01	4.89	2.01	18.90	13.95	5.11
CaO	2.06	5.34	2.74	2.55	2.62	2.61	1.25	1.01	8.15	19.50	1.82	45.78	27.15	1.01	45.78	2.62	13.51
MgO	1.37	1.97	1.50	1.47	0.11	0.12	1.93	0.08	3.05	2.87	2.67	0.07	7.01	0.07	7.01	1.50	1.88
Na₂O	0.14	0.09	0.15	0.10	0.17	0.12	1.30	1.96	0.99	0.87	0.05	0.04	0.08	0.04	1.96	0.14	0.62
K ₂ O	1.39	2.02	2.43	1.87	1.84	1.68	3.24	3.41	2.41	1.57	1.81	0.06	0.72	0.06	3.41	1.84	0.91
TiO ₂	0.94	0.43	0.76	1.34	1.24	0.14	1.20	1.41	0.14	0.75	0.62	0.14	0.27	0.14	1.41	0.75	0.48
MnO	0.12	0.08	0.10	0.19	0.20	0.17	0.14	0.17	0.15	0.60	0.09	0.52	0.30	0.08	0.60	0.17	0.16
Fe ₂ O ₃	7.97	3.14	3.78	7.70	7.71	1.11	9.53	13.15	6.51	3.90	4.73	1.99	2.14	1.11	13.15	4.73	3.49
LOI	11.26	4.10	5.50	14.16	17.09	2.07	13.16	15.97	16.72	12.91	8.48	36.31	32.00	2.07	36.31	13.16	9.96
Na	nd	nd	nd	nd	nd	0.11	0.00	nd	0.00	0.19	nd	nd	0.00	0.00	0.19	0.00	0.09
Mg	1.18	0.84	0.64	0.73	0.69	0.09	1.80	0.75	4.53	0.37	1.36	0.34	2.83	0.09	4.53	0.75	1.22
AI	5.32	3.01	3.76	4.87	4.69	1.72	4.23	1.79	2.06	1.31	4.04	1.13	1.62	1.13	5.32	3.01	1.50
Р	0.04	0.05	0.07	0.07	0.06	0.03	0.06	0.09	0.03	0.08	0.02	nd	0.03	0.02	0.09	0.06	0.02
S	0.18	0.00	0.01	0.00	nd	0.01	0.06	0.07	0.08	0.02	nd	0.02	0.02	0.00	0.18	0.02	0.05
К	0.69	0.26	0.39	0.64	0.62	0.11	0.36	0.26	0.12	0.40	0.27	0.07	0.09	0.07	0.69	0.27	0.21
Са	1.49	4.93	2.51	1.88	1.88	2.50	5.22	14.79	13.32	9.36	1.25	25.23	18.98	1.25	25.23	4.93	7.82
Ті	0.13	0.05	0.14	0.19	0.19	0.02	0.10	0.10	0.01	0.01	0.06	nd	0.02	0.01	0.19	0.08	0.07
Cr	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00
Mn	0.09	0.07	0.09	0.14	0.14	0.03	0.12	0.71	0.13	0.26	0.05	0.87	0.23	0.03	0.87	0.13	0.26
Fe	5.67	2.40	3.03	5.16	4.80	1.23	3.96	2.29	1.17	1.84	3.32	0.88	1.18	0.88	5.67	2.40	1.64
Со	0.00	0.00	0.00	0.00	0.00	nd	0.00	0.00	nd	0.00	0.00	nd	nd	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.00
Cu	0.01	nd	0.00	0.00	0.00	0.00	0.02	0.00	nd	0.00	0.00	nd	nd	0.00	0.02	0.00	0.01
Zn	0.02	0.01	0.01	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.00
As	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	N/A	N/A	N/A	N/A
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00	nd	0.00	0.00	N/A	N/A
Мо	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	N/A	N/A	N/A	N/A

(b) Sandstone

Sandstones are classified variously based on the chemical compositions of their three major oxide groups: silica and alumina, alkali oxide, and iron oxide plus magnesia using a bivariate diagram plot. Sandstone classification (Figure 10) showed that the sandstone formation comprises five distinct groups; Fe-sand, Fe-shale, wacke, litharenite, and arkose. The majority of the coarse sandstone falls within the wacke category, while the fine-grained sandstone comprised mainly the litharenite and wacke categories. In the coarse-grained unconsolidated sandstone, the occurrence of major oxides was more abundant than in the fine-grained consolidated counterpart (Table 6). SiO₂, CaO, Al₂O₃, and Fe₂O₃ are the most abundant major oxides in both samples but with higher proportions of Al₂O₃ than CaO in the consolidated sandstone, indicating an abundance of clay minerals over that of carbonates. Ca, Al, Fe and Mg are the most abundant major elements with higher compositions observed in coarse and fine-grained sandstone. Generally, the sandstone in the study area has low trace elements compositions of <0.05%, indicating that they are not present in undesirable quantities in the groundwater hosted in the sandstone.

(a) Major oxides - fine-grained sandstone												
Location	SiO ₂	AI_2O_3	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	LOI		
1645 (Nadapal)	40.01	7.7	25.15	1.81	0.89	1.13	0.40	0.31	3.4	18.19		
1659 (Lodwar town)	47.61	9.03	24.42	0.04	0.37	1.32	0.50	0.38	6.15	10.11		
1668 (Turkwel River at Natir)	49.4	5.87	18.61	4.13	0.65	1.12	0.30	0.12	1.9	17.49		
1669 (Turkwel River at Natir)	52.6	5.15	24.91	4.70	0.53	0.84	0.19	0.07	1.6	9.25		
3832 (Nachomin)	47.84	5.92	25.01	0.02	0.06	1.32	0.17	0.50	1.50	17.2		
3833 (Nachomin)	48.09	5.32	24.91	0.03	0.13	1.51	0.16	0.18	1.18	18.47		
3850 (Natir)	30.91	6.51	27.9	0.10	0.21	1.35	0.64	1.21	8.53	22.59		
3858 (Natir)	40.01	7.50	26.2	0.05	0.87	1.09	0.41	0.32	3.61	18.86		
Minimum	30.91	5.15	18.61	0.02	0.06	0.84	0.16	0.07	1.18	9.25		
Maximum	52.6	9.03	27.9	4.70	0.89	1.51	0.64	1.21	8.53	22.59		
Median	47.73	6.22	24.96	0.08	0.45	1.23	0.35	0.32	2.65	17.84		
SD	7.05	1.35	2.67	1.99	0.32	0.21	0.17	0.36	2.62	4.54		
(b) major oxides - coarse-grained sandstone												
	SiO ₂	AI_2O_3	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Fe_2O_3	LOI		
1658 (Lodwar town)	55.8	13.41	7.60	3.15	1.55	2.61	0.92	0.13	5.15	9.08		
1670 (Turkwel River at Natir)	64.02	11.87	4.87	4.31	0.72	1.51	0.7	0.06	3.92	8.01		
1675 (Turkwel River at Natir)	62.07	10.92	10.91	0.02	1.86	2.14	0.42	0.17	2.40	8.99		
1676 (Turkwel River at Natir)	72.00	10.93	4.60	1.41	0.80	2.30	0.39	0.09	2.40	5.06		
1678 (Turkwel River at Nati)	65.10	13.69	1.72	2.82	0.49	1.95	0.64	0.09	4.05	9.44		
3842 (Nabuelpus)	26.67	12.31	8.05	21.01	5.04	6.31	0.17	0.05	0.92	19.03		
3847 (Natir)	57.5	20.15	8.59	6.79	0.12	0.43	0.13	0.09	5.47	0.46		
Minimum	26.67	10.92	1.72	0.02	0.12	0.43	0.13	0.05	0.92	0.46		
Maximum	72.00	20.15	10.91	21.01	5.04	6.31	0.92	0.17	5.47	19.03		
Median	62.07	12.31	7.60	3.15	0.80	2.14	0.42	0.09	3.92	8.99		
SD	14.63	3.20	3.07	7.11	1.67	1.84	0.29	0.04	1.64	5.61		

Table 6. Results and summary statistics for the Major oxides in the (a) fine-grained sandstone and (b) coarse-grained sandstone in the study area

(a) Major elements - fine-grained sandstone													
Sample	Na	Mg	Al	Р	S	К	Ca	Mn	Fe				
3832 (Nachomin)	0.19	0.24	0.95	0.04	0.03	0.22	19.13	0.22	0.99				
3833 (Nachomin)	0.22	0.24	0.94	0.03	0.04	0.21	18.21	0.22	0.97				
3850 (Natir)	nd	1.26	5.89	0.07	0.02	0.88	0.62	0.09	6.88				
3858 (Natir)	0.00	3.91	2.04	0.05	0.02	0.12	12.65	0.11	0.97				
Minimum	0.00	0.24	0.94	0.03	0.02	0.12	0.62	0.09	0.97				
Maximum	0.22	3.91	5.89	0.07	0.04	0.88	19.13	0.22	6.88				
Median	0.19	0.75	1.50	0.04	0.03	0.22	15.43	0.17	0.98				
SD	0.12	1.74	2.34	0.02	0.01	0.35	8.52	0.07	2.95				
		(b) maj	or eleme	nts - coars	e-grained	sandsto	ne						
1675 (Turkwel River at Natir)	nd	1.09	2.68	0.04	0.03	0.15	11.09	0.15	1.7				
1676 (Turkwel River at Natir)	nd	1.07	2.63	0.06	0.01	0.22	7.74	0.11	1.91				
1678 (Turkwel River at Natir)	nd	1.09	4.37	0.03	nd	0.3	1.18	0.05	3.68				
3842 (Nabuelpus)	0.27	0.29	4.73	0.03	0.01	0.74	1.37	0.19	3.41				
3847 (Nabuelpus)	0.00	2.67	1.49	0.01	0.08	0.07	19.7	0.15	0.97				
Minimum	0.00	0.29	1.49	0.01	0.01	0.07	1.18	0.05	0.97				
Maximum	0.27	2.67	4.73	0.06	0.08	0.74	19.7	0.19	3.68				
Median	0.13	1.09	2.68	0.03	0.02	0.22	7.74	0.15	1.91				
SD	0.19	0.87	1.34	0.01	0.03	0.26	7.69	0.05	1.16				

Table 7. Results and summary statistics for the Major elements in the (a) fine-grained sandstone and (b) coarse-grained sandstone in the study area

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(b) Conglomerate

The mineralogical compositions of two specimens of conglomerate collected at Lodwar town and Natir area indicated variations in mineralogical compositions based on major element oxides (Table 8). Al, Ca, and Mg are the major elements in the conglomerate showing the presence of aluminosilicates, carbonates and ferromagnesian minerals; the conglomerate in Natir was more Ca-enriched than the one in Lodwar. The occurrence of Mn between 0.05 and 0.22 wt % and Fe of 0.99 to 2.06 wt % in both the conglomerate samples present undesirable values in groundwater. The trace elements occurred in concentrations < 0.01 wt %.

Table 8. Compositions of major element oxides, major and trace elements in the conglomerate samples

Major element oxides											
Location	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	SIO ₂	LOI	
1677 Lodwar)	9.72	4.99	2.25	0.79	2.13	0.31	0.09	2.03	71.6	5.99	
3857 (Natir)	9.20	12.00	0.00	1.70	3.50	0.30	0.70	2.51	60.00	8.70	
Major elements											
	Al	Ca	Mg	Na	К	Ti	Mn	Fe	Р	S	
1677 (Lodwar)	3.98	2.63	1.08	nd	0.19	0.04	0.05	2.06	0.02	0.01	
3857 (Natir)	1.45	14.86	2.20	0.00	0.16	nd	0.22	0.99	0.04	0.02	
Trace elements											
	Cr	Со	Ni	Cu	Zn	As	Se	Мо	Pb		
1677 (Lodwar)	0.00	nd	0.00	0.00	0.01	nd	nd	0.00	nd		
3857 (Natir)	0.01	nd	0.00	nd	0.01	nd	nd	0.00	nd		

(c) Grainstone

Table 9 indicates, slight variations in the compositions of major elements oxides with $SiO_2 > CaO > Al_2O_3 > Fe_2O_3$. CaO of 23.00 wt % was relatively higher in the fine-grained sample than in the coarsegrained specimen with 7.84 wt %. Ca, Al, and Fe are the major elements in the grainstone, with Mn and Fe occurring in undesirable levels for groundwater. The abundance of trace elements ranged from <0.01 to 0.05 wt %, suggesting that they would be low concentrations in groundwater in contact with the grainstone.

Table 9.	Compositions	of major	element	oxides,	major	and	trace	elem	nents	in the	grains	tone	samp	les

	Major element oxídes									
Description	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	Fe ₂ O ₃	SIO ₂	LOI
1657 (medium-grained)-	5.8	23.00	0.02	0.20	1.06	0.18	0.32	1.50	58.1	9.83
Natir east										
1667 (Coarse-grained) –	8.3	7.84	5.19	0.73	2.95	0.15	0.13	1.13	64.3	9.13
Natir east										
	Major elements									
	AI	Са	Mg	Na	К	Ti	Mn	Fe	Р	S
1657 (medium-grained) –	1.37	17.18	0.43	0.05	0.14	nd	0.41	1.22	0.03	0.02
Natir east										
	Trace elements									
	Cr	Со	Ni	Cu	Zn	As	Se	Мо	Pb	

1657 (medium-grained)-	0.01	nd	0.00	nd	0.01	nd	0.00	0.00	nd
Natir east									

4.2.3 Volcanic rocks

(a) Nepheline-phonolites

SiO₂ in the nepheline-phonolite ranged from 48.24 to 54.81 %, with specimen 1653 that formed a contact with the Turkana Grit having the highest silica content (Fig 11). The nepheline-phonolite at the contact zone also had high compositions of Al₂O₃; 15.31 %, CaO; 8.20 % and K₂O; 2.50 %. Slight variations in the Fe₂O₃ content were observed with values ranging from 9.61 to 10.08%. Low compositions of Na₂O ranging from 0.90 to 1.28 % and MnO between 0.16 and 0.70 % was observed across the nepheline-phonolite rock samples (Figure 11). The occurrence of the minor and trace elements was determined for specimen 1650 of the nepheline-phonolite and the Turkana Grit sample at the contact zone, as seen in specimen 1653. As a result, S, As, and Pb were undetectable, while Mg was determined to be 1.37% at the contact zone. The occurrence of minor elements was as follows; Fe; 3.62 - 6.01 %, Al; 3.87 - 5.46 %, and Ca; 1.69 - 6.80 %, K; 0.52 - 0.87 %, Ti; 0.10 - 0.71 %, P; 0.08 - 0.33 % and Mn; 0.13 - 0.20%. Concentrations of trace elements ranged from < 0.01 to 0.02%, implying the nepheline-phonolite would not contribute these elements in undesirable quantities to groundwater.

Figure 11. Distribution of the major elements in the rock samples of the nepheline-phonolite at Lodwar town, grit contact and at Kanamkemer

(a) Augite basalts

The analysis of the distribution of the major elements oxides in the augite basalt was as follows; SiO₂; 53.79 %, Al₂O₃; 18.00%, moisture and volatile materials; 9.22%, Fe₂O₃; 6.08%, CaO; 5.69%, MgO; 3.22%, K₂O; 2.06%, and TiO₂; 1.09%. The major elements (Table 10) occurred in the order of Fe>Ca>Al>Mg>Mn, indicating that they can be released into groundwater in substantial quantities. The occurrence of trace elements is not at the levels of great concern in groundwater.

(b) Dolerite dyke

Variations in the mineral compositions of the major elements for two igneous intrusions; specimen 1656 for the dolerite dyke in the Turkana Grits, and sample 3845 of the quartzo-feldspathic gneiss were observed (Table 10). The dolerite in the basement system had higher levels of SiO₂; 74.09 % and MgO; 7.31 % than that in the Turkana Grits where SiO₂ was 50.59% while MgO was 1.71%. No significant variations in the compositions of CaO were observed; specimen 1656 had 4.70% and 4.99% in sample 3845. The compositions of Al₂O₃, K₂O, TiO₂, Fe₂O₃ and LOI were higher in the dolerite in the Turkana Grits where since the quartzo-feldspathic gneiss. Minor and trace elements were not measured in the dolerite within the Turkana Grits.

Figure 12. Compositions of major elements in the dolerite dyke in the Turkana Grits and in the Basement system

Table 10.	Compositions of	of major oxide	s, major and trac	e elements in the	volcanic rocks of	the study area
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Rock Type	Augite	Np - Lodwar	NP at Grit	Dyke -	NP -	Dyke –
	Basalt	area	Contact	Turkana	Kanamkemer	Basement
	(1648)	(1650)	(1653)	Grit (1656)	area	(3845)
					(1674)	
SIO ₂	53.79	48.24	54.81	50.59	52.30	74.09
Al ₂ O ₃	18.00	12.81	15.31	15.87	13.79	4.98
CaO	5.69	8.01	8.20	4.70	7.09	4.99
MgO	3.22	3.50	2.30	1.71	2.41	7.31
Na ₂ O	0.64	1.28	0.90	0.27	1.12	0.15
K ₂ O	2.06	2.01	2.50	7.01	1.31	0.94
TiO2	1.09	4.11	3.03	1.89	2.60	0.35
MnO	0.12	0.16	0.28	0.28	0.70	0.16
Fe ₂ O ₃	6.08	10.08	10.01	8.12	9.61	5.01
LOI	9.22	8.80	2.09	8.62	9.06	1.46
Na	nd	0.22	0.00	nm	nm	0.00
Mg	1.26	nd	1.37	nm	nm	2.32
Al	4.70	5.46	3.87	nm	nm	3.71
Р	0.18	0.08	0.33	nm	nm	0.02
S	nd	nd	nd	nm	nm	0.01
K	0.48	0.52	0.87	nm	nm	0.02

Rock Type	Augite	Np - Lodwar	NP at Grit	Dyke -	NP -	Dyke –
	Basalt	area	Contact	Turkana	Kanamkemer	Basement
	(1648)	(1650)	(1653)	Grit (1656)	area	(3845)
					(1674)	
Са	4.99	1.69	6.80	nm	nm	8.56
Ti	0.26	0.10	0.71	nm	nm	nd
Cr	0.01	0.00	0.01	nm	nm	0.03
Mn	0.17	0.13	0.20	nm	nm	0.14
Fe	5.09	3.62	6.01	nm	nm	4.12
Со	0.00	0.00	0.00	nm	nm	0.00
Ni	0.00	0.00	0.00	nm	nm	0.00
Cu	0.00	nd	0.02	nm	nm	nd
Zn	0.01	0.02	0.02	nm	nm	0.01
As	nd	nd	nd	nm	nm	nd
Se	0.00	0.00	0.00	nm	nm	nd
Мо	nd	0.00	nd	nm	nm	0.00
Pb	nd	nd	nd	nm	nm	nd

Classification of Volcanic rocks

The TAS classification diagram after Le Bas (1986) (Figure 13) revealed that the nepheline phonolite at Lodwar town and that forming contact with the Turkana Grits belonged to the basaltic-andesite group. In contrast, augite basalt and the nepheline phonolite at the Kanamkemer area is volcanic andesite. The volcanic intrusions identified as dolerite rock were of distinct volcanic origins; the dolerite rock dyke in the Turkana Grit was determined to be basaltic trachyandesite in nature, while the volcanic intrusion in the basement system identified to be dacite rock grading into rhyolite. The AFM classification [20] of the volcanic rocks in the study area showed that augite basalt and dolerite in the Turkana grit are calc-alkaline nepheline-phonolite and the dolerite in the Basement system as tholeiitic in nature Figure 14.

Figure 13. TAS classification diagram after Le Bas. (1986)

Figure 14. AFM classification diagram after Le Bas (1986) showing augite basalt and dolerite in the Turkana grit being calc-alkaline while the nepheline-phonolite, and the dolerite in the Basement system as tholeiitic

5. Discussion

5.1 Mineralogical compositions

The major rock-forming minerals in the rocks in the study area included olivine, pyroxenes, amphiboles, plagioclase and orthoclase feldspars, aluminosilicates, ferromagnesian minerals, quartz, micas and carbonates. Sedimentary formations mainly comprise quartz, clay minerals, aluminous oxy-hydroxides, or reprecipitated soluble phases such as calcite, gypsum, and other salts. In the Turkana Grits, thin section microscopy, trace amounts of plagioclase feldspars were observed with various stages of replacement by calcite, resulting in decreased secondary intragranular porosity created by the dissolution of feldspars [21]. The composition of Mg in the Basement system rocks was smaller than that of Fe. Due to Mg²⁺ being slightly smaller than Fe²⁺, there is a tendency for iron to dissolve and leave with the fluids. The increasing amounts of Mg/Fe ratios selectively drive off Na and K alkalis, resulting in anorthite formation [22]. Olivine and anorthite, the first formed minerals in the discontinuous and continuous reaction series, are the most susceptible to weathering. At the same time, quartz, muscovite, and K-feldspar are particularly resistant. Water acts as a chemical weathering agent by hydrating the surface of minerals, hydrolysing minerals and replacing some of their exposed surface cations with hydrogen ions, and dissolving minerals to remove mineral matter as solutes. Ferrous iron in minerals, including ferromagnesian silicates, carbonates, and magnetite, is preferentially soluble [22]. Weathering of carbonate rocks proceeds more rapidly than weathering of silicate rocks. Despite a

low relative abundance of carbonates in metamorphic and igneous rocks, their higher weathering rate allows that carbonates have the dominant effect on watershed geochemistry.

5.2 Sources of major cations and anions in groundwater

5.2.1 Carbonate weathering

Kunkar carbonates were identified in the Turkana Grits, Holocene sediments and alluvial deposits. Dissolution of carbonates and reaction of silicates with carbonic acid accounts for the addition of HCO_3^- to the groundwater [5]. Carbonate weathering involving gypsum, dolomite and calcite is a major source of Ca^{2+} , Mg^{2+} and HCO_3^- in groundwater. In the case of dolomite weathering (Eq. 1) by carbonic acid, the Ca: HCO_3 ratio in groundwater is 1:4, while calcite weathering (Eq. 2) by sulphuric acid contributes Ca: SO_4 of 1:1. Mg^{2+} ion is derived from calcite or dolomites and silicates. The low SO_4^{2-} in the groundwater of the study area suggests that calcite dissolution by sulphuric acid is not predominant than calcite dissolution by carbonic acid (Eq. 3). The presence of carbonates in alluvial sediments in arid areas [5] and the occurrence of metamorphosed sediments upstream of the study area favours dolomite weathering by carbonic acid, resulting in Ca-HCO₃ type water (Eq. 2).

$$CaMg(CO_3)_{dolomite} + 2H_2CO_3 = Ca^{2+} + Mg^{2+} + 4HCO_3^{-}$$
(1)

$$CaCO_{3_{calcilte}} + H_2SO_4 = CaSO_4 + H_2O + CO_2$$
⁽²⁾

$$2CaCO_{3 \ calcite} + H_2CO_3 = 2Ca^{2+} + 2HCO_3^- \tag{3}$$

5.2.2 Silicate weathering

(a) Weathering of aluminium silicates

The rocks in the area are rich in silica with $SiO_2 >40$ wt %, indicating a high potential of silicate weathering and leaching of ions into the aquifers. Silicate weathering involves hydrolysis reactions that consume primary minerals such as K, Ca, Fe and Mg and protons to form silicate minerals [23]. Kaolinite was identified to be present in the Cretaceous Turkana Grits, suggesting weathering of plagioclase feldspar like albite - NaAlSi₃O₈ to form kaolinite by consuming H⁺ ions and water, releasing Na⁺ and SiO₂ (Eq. 4). The higher compositions of K₂O; average =1.88 wt % and K; average = 0.35 wt % in the Holocene sediments of the study area than Na₂O; average = 0.47 wt % and Na; average = 0.06 wt % suggest hydrolytic reaction in favour of orthoclase feldspar (KAl₃SiO₈) releasing K⁺ and soluble silica (H₄SiO₄) (Eq. 5). Weathering of anorthite – CaAl₂SiO₈ also contributes Ca²⁺ ions in groundwater (Eq. 6). The occurrence of silicate weathering in the study area is subject to spatial and temporal variations. The shallow alluvial aquifer had high compositions of K⁺ ions than Na⁺ ions for most wells, indicating the dominance of orthoclase weathering [8]. The reverse was observed in the intermediate sub-system of the LAAS.

$$2NaAlSi_{3}O_{8\ albite} + 2H^{+} + H_{2}O \rightarrow Al_{2}Si_{2}O_{5}(OH)_{4_{Kaolinite}} + 2Na^{+} + 4SiO_{2}$$
⁽⁴⁾

$$2KaAlSi_{3}O_{8 orthoclase} + 2H^{+} + 9H_{2}O \rightarrow Al_{2}Si_{2}O_{5}(OH)_{4_{Kaolinite}} + 2K^{+} + 4H_{4}SiO_{2}$$
(5)

$$CaAlSi_3O_{8 anorthite} + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_{4_{Kaolinite}} + Ca^{2+}$$
(6)

(b) Weathering of ferromagnesian silicates

Pyroxenes and olivine are ferromagnesian silicates identified in the volcanic rocks of the study area. Weathering of these minerals release silica, ferrous Fe²⁺ and Mg²⁺ to the solution. However, pyroxene and olivine minerals do not usually form in an aquifer environment, even though they are considered primary minerals [24]. Therefore, they may not control the concentrations in groundwater as a result of disequilibrium.

$$Ca(Mg, Fe)Si_{2}O_{6}_{pyroxene} + 4H^{+} + H_{2}O \rightarrow Ca^{2+} + Mg^{2+}/Fe^{2+} + 2H_{4}SiO_{4}$$
(7)
$$(Mg, Fe)_{2}SiO_{4}_{olivine} + 4H^{+} \rightarrow 2Mg^{2+}/Fe^{2+} + 2H_{4}SiO_{4}$$
(8)

Phase relations in silicate systems [25] indicate that low concentrations of Ca²⁺, Na⁺ and Mg ²⁺ in all the LAAS sub-systems [8] is associated with the presence of quartz and kaolinite [26]. Like in the Turkana Grit shallow aquifer [6], the abundance of these ions is associated with montmorillonite, illite and chlorites [26].

5.2.3 Oxidation Reactions

Haematite and magnetite in the basement system rock and alluvial deposits are susceptible to oxidation because they have high iron content. Fe^{2+} and Mn^{2+} are considered the dominant oxidation products in the groundwater of the study area. Shallow groundwater removes magnetite from rocks during weathering, transport, and diagenesis [22]. The mineral saturation indices of groundwater of the LAAS and the Turkana Grit aquifer indicated siderite (FeCO₃) and melanterite (FeSO₄: 7H₂O) are the ferrous compounds present. Oxidation reaction for siderite (Eq. 9) and melanterite is written as:

$$4FeCO_{3 \ siderite} + O_2 + 10H_2O \rightarrow 4Fe\ (OH)_3 + 4HCO_3^- + 4H^+ \qquad (9)$$

The H⁺ ion produced is then neutralized by calcite according to Equation 10, reducing the activity of the free hydrogen and thus moderating the pH of the system:

$$CaCO_3 + H^+ \to Ca^{2+} + HCO_3^-$$
 (10)

As oxidizing conditions become dominant, the iron reprecipitates to ferrihydrite [Fe (OH)₃], leaving Mg^{2+} as the dominant, redox-sensitive species [24]. According to the mineral SI for the groundwater in the area, rhodochrosite (MnCO₃), pyrolusite (MnO₂: H₂O), pyrochroite [Mn (OH)₂], manganite (MnOOH) and hausmanite (Mn₃O₄) [8]. The manganese carbonate (MnCO₃) form in zones with elevated Mn²⁺ concentrations.

5.2.4 Fluoride Enrichment

Fluoride is a crucial element for forming bone and enamel of teeth; a daily intake of 0.5 mg is essential for a healthy diet [27]. However, concentrations above 1.5 mg/L adversely affect human health [28]. Elevated fluoride concentration in the intermediate aquifer was recorded in the dry season, while the TGSA had F⁻ levels exceeding 1.5 mg/L in all the wells throughout the wet and dry seasons [8]. Dissolution of CaF₂ contributes F- in groundwater of the study area. In arid and semi-arid regions, less rain and high evaporation play an essential role in the dissolution of fluorite in groundwater [27]. The hydrolysis of aluminosilicate in aquifers produces bicarbonate ion, which enhances the dissolution of fluorite in groundwater. In alkaline environments, hydroxyl ions replace F- from fluorite-bearing minerals, and high TDS enhances the ionic strength for CaF₂ dissolution [29]. Along with alkaline pH, high Na⁺ and HCO₃⁻ make it favourable for fluorite dissolution [27] and simultaneous precipitation of CaCO₃ [23] (Eq. 11; 12).

$$CaF_{2 fluorite} + 2HCO_3^- \leftrightarrow CaCO_3 + 2F^- + H_2O + CO_2 \tag{11}$$

$$CaF_{2 fluorite} + 2Na_2HCO_3 \leftrightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$$
(12)

5.2.5 Expected composition of groundwater

Rock geochemistry in the study area revealed that Ca, Fe, Mg and Al are dominant elements in the metamorphic, sedimentary and volcanic rocks of the study area. Here, these are evaluated against reported groundwater chemistry in co-located sites [6]. The chemical composition of water is controlled by weathering the rock's primary minerals in the secondary phase, where the composition of the solutions determines the secondary phase formation. Chemical weathering is selective because minerals do not contribute to their modal abundance in the rocks to the water composition [4]. Generally, the study area rocks have low amounts of Na and K than in the groundwater, suggesting other sources of Na⁺ and K⁺ ions in groundwater. Rainfall, streams and aquifer weathering processes contribute additional ions to the groundwater hosted in alluvial and Holocene sediments. The groundwater hosted in volcanic rocks showed undetectable Ca levels, corresponding to its low modal compositions (< 2.00 wt %) in the nepheline-phonolite. The Ca²⁺ in the groundwater at Natir reflects that of the calcium-rich Holocene sediments (10,000 Yr BP) in the area. The high Fe concentrations in the alluvial aquifer [8] reflects that of the Fe-rich alluvial deposits. The groundwater chemistry at Nabuelpus reflects that of the adjacent augite basalts rather than for the adjoining Basement system rocks occurring to the east of the community handpump. This suggests the recharge water originates from the streams draining the volcanic Ngapoi Hills.

6. Conclusions

Conventional petrographic and rock geochemistry data from XRD and XRF techniques help to understand the major rock-forming minerals in rocks that can influence groundwater quality. The major rock-forming in rocks of the study area include pyroxenes, olivine, kaolinite, montmorillonite siderite, fluorite calcite and dolomite as determined from elemental analysis results. Low amounts of Na and K with modal values <2.00 wt% was observed across all rock samples, suggesting other

sources of Na⁺ and K⁺ ions in groundwater. Generally, Ca, Mg, Al, Fe and Mn are released to groundwater from rocks in the region as shown by high modal compositions of individual elements and their oxides. Metamorphic and volcanic rocks contain Fe and Mn of up to 6.32 wt % and 0.20 wt %, respectively, indicating potential groundwater contamination. Ti, Cr, Zn, P, Cu, Se, and Mo can occur in traceable quantities with values between >0.01 and 1.18 wt % in groundwater hosted in Holocene Sediments and in the Turkana Grits. The higher concentrations of Na⁺, K⁺, Ca²⁺ and Mg²⁺ in the groundwater of the Turkana Grit aquifer relative to the grit rock samples suggest a long history of dissolution and recycling of the groundwater. The ratio SiO₂/Al₂O₃ was found to be greater than 8.0 implying a high degree of maturity of the grits. The findings obtained by this study reflect possible processes and sources of major chemical components in groundwater of similar regions in sub-Saharan Africa.

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