STUDY OF MINERALS IN THE WATER AND SOURCE ROCKS OF RURII SPRING IN MERU COUNTY, KENYA

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ABSTRACT

This study was aimed at investigating the minerals in the water and surrounding rocks of Rurii spring which is located in Meru County, Kenya. The spring is well known for discharging highly carbonated and salty water for many years, but no research has been done previously with regard to this phenomenon. The sampling was done twice during the dry and rainy seasons, that is, months of September and November 2012, respectively. Ten samples or replicates of the mineral water, rocks and sediments were collected and analysed in each case. The analytical methods used were AAS, XRF, UV/VIS and Titrimetry. The mineral water was found to be very rich in free CO_2 and HCO_3^-, with almost two to three litres of carbon dioxide per litre of mineral water at room temperature. The CO_2 most likely originates from the earth's crust and rises to the surface through a volcanic vent where it gets mixed with the water to form H_2CO_3. Sodium level was 1,043±35.0 mg/l and 954.4±20.3 mg/l, while chloride was 950.9±13.1 mg/l and 853.6±10.0 mg/l, during the dry and rainy periods, respectively. The high NaCl content contributed to the salty taste in the water. Basically, the water had somewhat high level of mineral ions content which in turn was responsible for the large TDS (5,056.7±51.2 mg/l and 4,923.1±40.7 mg/l) as well as very high electrical conductivity (6,014.0±41.0 µS/cm and 5,986.0±40.0 µS/cm), in dry and rainy seasons, respectively. The overall mineral analysis of the water, rocks and sediments revealed possibility of having dolomite, $CaMg(CO_3)_2$ and feldspar, $(K,Na,Ca)Al_2Si_2O_8$ containing rocks in the studied area. The *F*-test showed no significant difference between the results obtained for the dry and rainy seasons.

Keywords: ***carbon dioxide, earth's crust, volcanic vent, mineral ions, dolomite and feldspar rocks***

INTRODUCTION

In a geologically active environment like Rift Valley, groundwater frequently has higher salt content. High temperatures increase solubility of many compounds in water, which explains the high level of salinity. Water that comes from a natural spring and contains minerals is called mineral water [1]. The most abundant cationic constituents in groundwater are the more soluble alkali elements (Na^+, K^+) and the alkaline earth elements (Ca^{2+}, Mg^{2+}), while the most common anions are bicarbonate (HCO_3^-), Chloride (Cl^-) and Sulphate (SO_4^{2-}). However, other less common (trace) cations and anions are dissolved in small quantities. The quality of water is also greatly influenced by human activities such as disposal of domestic, urban, industrial and agricultural wastes [1].

CO_2-rich springs have been reported from all over the world. The occurrence of these springs is related to major faults and volcanoes. In South Korea, many CO_2-springs are found in Mesozoic granitoids and the surrounding rocks. The CO_2-rich water can be classified into three-chemical-water types; Ca-HCO_3 water, Ca(Na)-HCO_3 water, and Na-HCO_3 water. Most of the soda waters show a high CO_2 concentration (P_{CO2} 0.12 atm to 5.21 atm), slightly acidic, pH (4.8-6.76) and high ion concentration [2]. CO_2-rich cold springs occur near the active volcanoes at Wudalianchi, North East China. The springs are rich in CO_2, with HCO_3 as the predominant anion and have elevated contents of total dissolved solids >1000 mg/l [3].

A study of CO_2-rich (up to 3000mg/l), mineral (up to 460 meq/l) and cold (2 ^{0}C–9 ^{0}C) springs of the lower Engadine region in the Swiss Alps, indicate the existence of Ca-HCO_3 water, Na-HCO_3, Cl^- water and $NaMgHCO_3$, SO_4^{2-} water [4]. By the close of the 19th Century, CO_2 gas was found in free state in many of Saratoga Springs in New Yolk. The springs discharge carbonated mineral water along Saratoga fault which is bottled and sold commercially [5].

The CO_2 in mineral springs may be derived from a variety of sources, including liberation of CO_2 by metamorphic processes, magmatic degassing, oxidation of organic matter, and interaction of water with sedimentary carbonate rocks. The origin of the CO_2 gas can be determined by isotopic analysis of ^{13}C, which indicates whether it is derived from the mantle, biogenic activity in the soil, metamorphic devolatilization or carbonate rocks [6].

In Kenya, CO_2-rich mineral springs occur at Mount Margaret in Kedong Valley, Lake Magadi, Esageri near Eldama Ravine and Kireita near Uplands [7]. Free carbon dioxide is currently being mined in Kenya at Kireita springs in Kiambu County. The amount of CO_2 mined in year 2011 was 16,275 tones which earned the Government of Kenya Kshs 105 million in foreign exchange [8].

Rurii Spring in Meru County is characterized by discharge of highly carbonated water which has a mixture of bitter and salty taste. It is consumed by the local community and is said to have therapeutic effects such as relief for heart-burn and other indigestion related problems. The water is liked by livestock due to its salty taste. Carbon dioxide is most probably discharged naturally from the earth's crust since the area has numerous volcanic hills. Interaction of CO_2-rich water with the rocks containing calcium, magnesium, potassium and sodium salts can result in enrichment of minerals in the spring water.

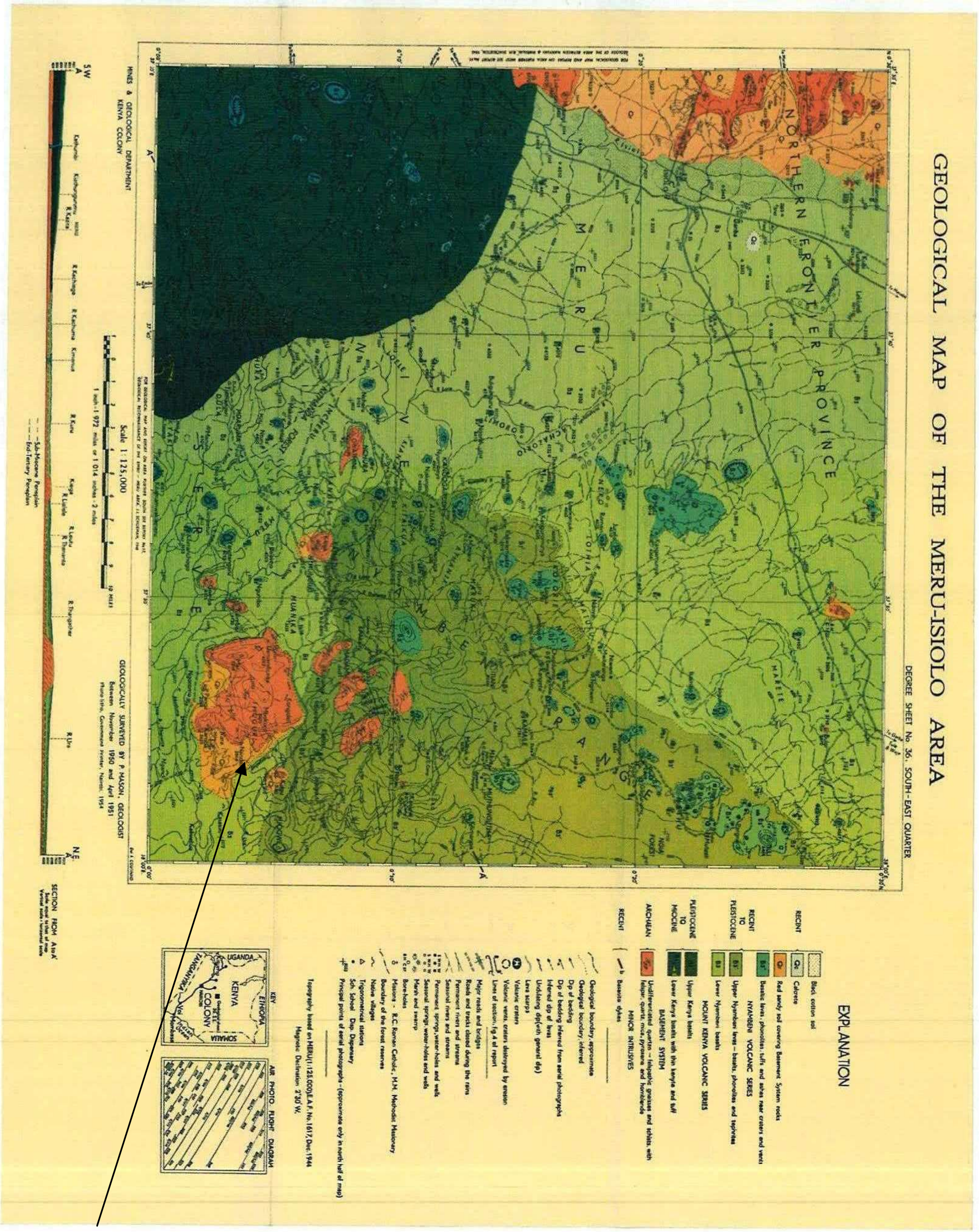
MATERIALS AND METHODS

Sampling site

The Rurii spring is within Meru-Isiolo area which lies in the South-Eastern quarter of degree sheet 36 (Kenya) and is bounded by the latitudes 0^o and 0^o 30'N and by longitudes 37^o 30' and 38^o E. It is approximately 35 KM East of Meru Town in Igarii location, Tigania East Sub-County, Meru County, Kenya [9]. The place is semi-arid and sparsely populated. The spring is in a valley at the floor of Nyambene range on the southern end, adjacent to Thuguri and Panga hills. There is a marshy ground at a short distance from the spring and sand is mined from the nearby Mukongoro River. The exact GPS location for Rurii spring is 0^o 01' 47.88" N, 37^o 53' 22.96" E and an elevation of 2,943 ft. above sea level (Figures 1 and 2).

Sampling procedure

The samples were collected from the study area in the months of September and November 2012, representing the dry and rainy seasons, respectively. The materials sampled included mineral water, sediments and rocks from the Rurii spring (An area approximately 50 M^2). Ten samples (replicates) of each material were collected at random per season. Water samples were collected straight from the spring in thoroughly cleaned and sterilized polypropylene bottles and carried in an ice box. The surface rock and sediment samples were collected in clean polythene bags at intervals of 5 metres distance away from the spring.



RURII SPRING (GPS: 0° 01’ 47.88” N, 37° 53’ 22.96” E, elevation 2943 feet above sea level)

Figure 1: Geological map of the Meru-isiolo area [9].

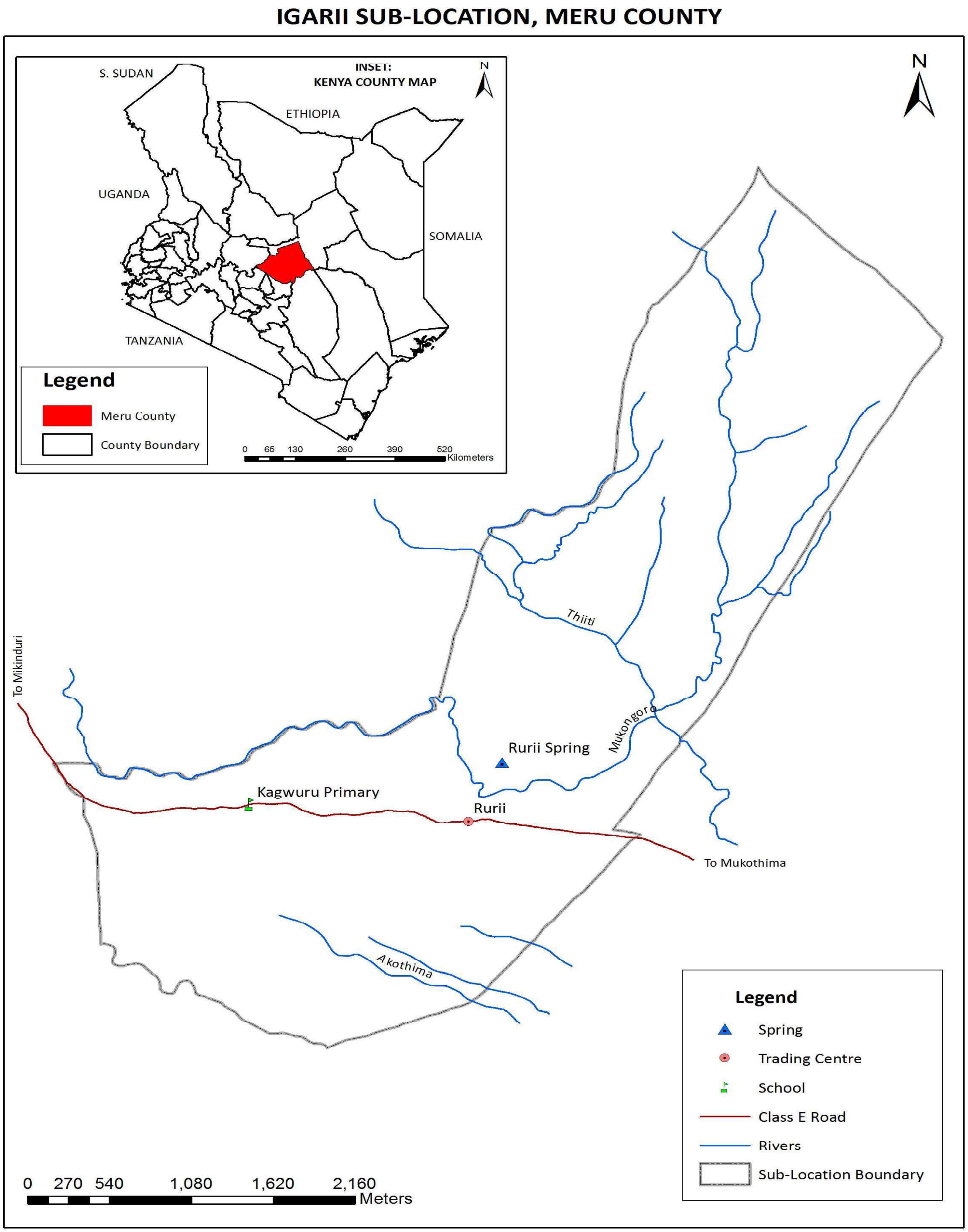


Figure 2: The Physical Map of Igarii sub-location showing Rurii spring [9].

Sample treatment

Water samples intended for AAS analysis were filtered after sampling and then preserved immediately to pH <2 by adding 1.5 ml concentrated nitric acid per litre to minimize precipitation and adsorption of cations on the container walls. The acidified samples were stored in a refrigerator at approximately 4 °C to prevent change in volume due to evaporation [10]. The containers and caps used had been thoroughly cleaned with non-ionic detergent solution, rinsed with tap water, soaked in 50% HNO_3 (v/v) for 24 hours at 70 °C, and then rinsed with de-ionized water. The preserved water samples were digested in order to reduce interference by organic matter and convert metals associated with particulates into free form that could be analyzed by atomic absorption spectrometer (AAS). The rock and sediment samples were dried, grinded and then digested before being analyzed with AAS [11].

Analysis of water

Field measurements like temperature, pH and electrical conductivity were carried out in situ. The CO_2 and various anions such as sulphate, nitrate, nitrite, ammonia-nitrogen, total phosphorus, chloride and fluoride were determined using the standard methods for examination of water [10]. Digested water samples were analysed for various metals using atomic absorption spectrometer (VARIAN SPECTRA A-10) after calibrating the instrument with the respective standards [12].

Analysis of rocks and sediments

Digested rock and sediment samples were analysed to determine the percentage of the major oxides (SiO_2, Na_2O, K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, MnO and TiO_2), using AAS method after calibrating the instrument with the respective standards. For comparison purpose, samples for both rocks and sediments were scanned with XRF instrument (MINIPAL 2), using a current of 2 μA and a potential of 25 keV to obtain the percentage of the major oxides stated above [10].

RESULTS AND DISCUSSION

Two sets of data were obtained representing the dry and rainy seasons. Ten replicates were analyzed for each parameter. Table 1 indicates results for the physical and chemical analysis of the mineral water. The tabulated literature F values for N-1=9 (95% confidence level) is 3.18; hence, the results indicated no significant difference between the variance of the dry and rainy seasons.

Table 1: Physical and Chemical analysis of mineral water.

Parameters	Dry Season*	Rainy Season**	*F* Values
PHYSICAL			
Temperature (^{0}C)	20.8±0.1	19.8±0.3	2.2
pH (pH scale)	7.5±0.1	7.5±0.1	1.0
conductivity(µS/cm)	6,014±41.0	5,986±40.0	1.0
TDS (mg/l)	5,056±51.2	4,923±40.7	1.6
CHEMICAL (mg/l)			
Free carbon dioxide	931.3±2.0	1,015.0±2.9	2.1
Carbonate	16.7±0.2	17.1±0.2	1.0
Hydrogen Carbonate (HCO_3^-)	5,511.4±67.2	5,632.6±64.2	1.0
Sulphate	492.5±17.7	420.1±25.3	1.4
Nitrate	2.8±0.3	2.0±0.2	2.2
Nitrite	0.0055±0.0	0.0037±0.0	-
Ammonia-Nitrogen	Not detected	Not detected	-
Phosphorus	115.68±1.5	96.42±1.7	1.3
Chloride	950.9±13.1	853.6±10.0	1.7
Fluoride	0.73±0.1	0.67±0.1	1.0
Bromide	0.97±0.1	0.59±0.1	1.0
Sodium	1,043±35.0	954.4±20.3	3.0
Potassium	121.6±2.1	116.7±2.2	1.1
Calcium	124.2±1.8	94.2±1.6	1.1
Magnesium	73.6±0.5	70.4±0.3	2.8
Iron	0.82±0.1	0.49±0.1	1.5
Manganese	0.097±0.0	0.075±0.0	-
Lead	<0.05	<0.05	-
Barium	0.677±0.1	0.537±0.1	1.0
Strontium	1.469±0.1	1.304±0.1	1.0
Cadmium	<0.002	<0.002	-
Copper	<0.01	<0.01	-
Aluminium	0.290±0.0	0.205±0.0	-
Chromium	0.056±0.0	0.055±0.0	-
Zinc	<0.005	<0.005	-

*September 2012, **November 2012, < Below AAS detection limit.

The water was characterized by remarkably high Total Dissolved Solids (5,056±51.2 mg/l and 4,923±40.7 mg/l, in dry and rainy seasons, respectively) and electrical conductivity (6,014±41.0 µS/cm and 5,986±40.0 µS/cm, in dry and rainy seasons, respectively). The high electrical conductivity and Total Dissolved Solids (TDS) were as a result of the excessive mineral content. The total alkalinity of water was very high due to the presence of large amount of bicarbonate. This was confirmed by the huge mineral content found in the water especially HCO_3^-, free CO_2, Cl^- and Na^+. The CO_2 gas possibly comes from the earth's crust and rises through volcanic vent to the surface where it mixes with water to form H_2CO_3 [3]. Other important minerals found in fairly large quantities were potassium, calcium, magnesium, sulphates and total phosphorus. The pH was slightly alkaline which was mainly contributed by HCO_3^- ion.

Sodium bicarbonate and sodium chloride were apparently the most abundant salts in the water. These mineral salts found in the water originated from neighbouring rocks which contained substantial oxide percentages of calcium, sodium, magnesium, and potassium (Tables 2). In other words, the rocks largely comprised of bicarbonates, carbonates, chlorides and sulphates which were the major anions present in the water.

Dissolution of carbonate and feldspar rocks could be the main source of Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- in the water as shown in reactions 1, 2 and 3 [2].

$$\mathbf{CaCO_{3v} + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-} \quad \mathbf{(1)}$$

$$\mathbf{MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^-} \quad \mathbf{(2)}$$

$$\mathbf{(K,Na,Ca)Al_2Si_2O_8 + H_2O + 2H^+ \rightarrow Al_2Si_2O_5(OH)_4 + (K^+,Na^+,Ca^{2+})} \quad \mathbf{(3)}$$

Table 2 represents results for rocks analysis (%) of the major oxides which included SiO_2, Na_2O, K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, MnO and TiO_2. Loss on ignition (LOI) was also determined. The highest three percentages were $SiO_2 > Fe_2O_3 > Al_2O_3$. The least was MnO.

Table 2: AAS and XRF percentage oxide analysis of rocks.

Oxides (%)	**AAS Results**		**XRF Results**		***F* Values**	
	Dry season	**Rainy season**	**Dry season**	**Rainy season**	**AAS**	**XRF**
SiO_2	38.773±2.818	36.344±1.613	39.00±2.60	38.40±2.30	3.05	1.28
$A1_2O_3$	13.534±1.009	13.074±1.518	21.80±2.20	21.41±1.93	2.26	1.30
CaO	9.264±1.019	10.360±1.241	11.043±0.85	10.982±0.90	1.48	1.12
MgO	3.261±0.265	3.084±0.228	-	-	1.35	-
Na_2O	4.203±0.640	4.593±0.558	-	-	1.32	-
K_2O	1.770±0.495	1.683±0.305	1.83±0.39	1.747±0.36	2.63	1.17
TiO_2	2.355±0.381	2.461±0.249	1.95±0.22	1.94±0.19	2.34	1.34
MnO	0.340±0.052	0.360±0.040	0.452±0.05	0.417±0.06	1.69	1.44
Fe_2O_3	18.420±0.970	19.080±1.100	23.10±2.70	22.94±2.04	1.29	1.75
LOI	6.38±2.190	7.042±1.866	-	-	1.38	-
Total (%)	98.3±9.839	98.081±8.718	99.175±9.01	97.836±7.78	1.27	1.34

-Not analysed.

Table 3 indicates results for sediment analysis (%) of the major oxides stated above and loss on ignition (LOI). The top three percentages were SiO_2 > Fe_2O_3 > Al_2O_3. Na_2O and K_2O were moderately high which can be attributed to salt deposits left behind after the mineral water evaporates.

Table 3: AAS and XRF percentage oxide analysis of sediments.

Oxides (%)	**AAS Results**		**XRF Results**		***F* Values**	
	Dry season	**Rainy season**	**Dry season**	**Rainy season**	**AAS**	**XRF**
SiO_2	57.515±2.116	57.165±2.410	56.100±2.80	56.320±2.42	1.30	1.34
Al_2O_3	12.537±1.806	11.804±1.675	20.030±1.34	19.700±1.20	1.16	1.25
CaO	1.598±0.344	1.742±0.462	1.785±0.24	1.594±0.22	1.80	1.19
MgO	0.671±0.107	0.497±0.093	-	-	1.32	-
Na_2O	2.659±0.080	2.349±0.102	-	-	1.62	-
K_2O	2.229±0.454	2.185±0.317	3.020±0.99	2.893±0.80	2.05	1.53
TiO_2	1.346±0.248	1.008±0.294	1.745±0.26	1.768±0.24	1.40	1.17
MnO	0.193±0.024	0.121±0.026	0.285±0.01	0.234 ±0.01	1.17	1.00
Fe_2O_3	11.331±0.762	11.836±1.214	16.756±1.16	15.661±1.47	2.54	1.60
LOI	8.947±2.097	8.707±1.746	-	-	1.44	-
Total (%)	99.026±8.038	97.414±8.339	99.721±6.80	98.170±6.36	1.08	1.14

-Not analysed.

The comparison between the results (Tables 2) for AAS and XRF analysis of rocks, indicate that both analysis were in agreement to a large extent, looking at the order of percentages from the highest to the lowest (SiO_2 > Fe_2O_3 > Al_2O_3 > CaO > Na_2O > MgO > TiO_2 > K_2O > MnO). Absence of Na_2O and MgO in the case of XRF analysis could have resulted in the increase of Al_2O_3 and Fe_2O_3 due to interference. The XRF technique was used for a general survey of most elements, except for lighter elements like sodium and magnesium. The total percentage was slightly below 100 since there may be other minor metal oxides that were not accounted for. Loss on Ignition (LOI) was higher in the sediments as compared to rocks indicating that the former had more volatile matter. The tabulated literature *F* values for *N*-1=9 (95% confidence level) is 3.18; hence, the results indicated no much difference between the variance of the dry and rainy seasons (Tables 2 and 3).

According to the literature values, silicon, aluminium and iron are the most abundant metals in the earth's crust with the following percentages, 28%, 8% and 4.6% in that order. They are followed by calcium (3.5%), sodium (2.8%), magnesium (2.7%) and potassium (1.84%) [13]. Thus, the results obtained did not deviate very much from the distribution of these elements in the earth's crust. However, the percentage of Fe_2O_3 in the rocks was more than that of Al_2O_3; hence, iron minerals are more prevalent in this area compared to aluminium minerals. TiO_2 in the rocks was also significantly high; however, titanium species are usually insoluble in water. This accounts for the absence of titanium metal in the water. The average abundance of manganese in the earth's crust is only 1060 mg/l and that is why MnO is quite low [10]. The percentage of Na_2O, K_2O and CaO were reasonably high and this could explain why these metals were present in the spring water and sediments in large amounts especially sodium which is more soluble (Tables 1 and 3).

CONCLUSION

From the results obtained, crucial minerals especially carbon dioxide are available at the Rurii spring. These minerals can be utilized commercially in the production of mineral water, salt licks for livestock, baking powder, pharmaceutical products, cement, laboratory chemicals, fertilizers, carbonated drinks, dry ice for refrigeration and fire extinguishers. Moreover, the spring can be developed into a modern Spa Park. Mining of such minerals can create employment, generate additional foreign exchange and accelerate the Country's economic growth in tandem with the Kenya Vision 2030.

This research should be advanced further to cover other similar springs within the region and determine the full extent of commercial worth of the minerals found there. It is also necessary to analyse further for the ^{13}C isotope of the CO_2-rich water to determine the external source of the CO_2 and know whether it is derived from the mantle, metamorphic processes, biogenic activity or from the surrounding carbonate rocks.

ACKNOWLEDGEMENT

We would like to sincerely thank Edward Mwangi of Mines and Geology Department and Mercy Muthoni of Central Water Testing Laboratories in Nairobi, for offering excellent additional technical assistance in the laboratory work.

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