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Origin of Carbon dioxide in Selected Mofette Springs in the Eastern Mt. Kenya Region and Associated Characteristics

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ABSTRACT

The Eastern Mt. Kenya region has a significant number of mofette springs containing high content of dissolved carbon dioxide. They include Gikumene, Kathathantu, Kiambogo, Mbwinjeru, Mulathankari, Nthungu, Rwarera-A, Rwarera-B, Tharu and Ukuu. The origin of carbon dioxide and their geochemistry has not been understood. This work was aimed at establishing the origin of carbon dioxide and thereof the chemistry of the mofette springs as a significant contributor of carbon dioxide in the environment. The source of carbon dioxide was determined by measuring the $\delta^{13}C$ for dissolved inorganic carbon using cavity ring-down spectroscopy. The $\delta^{13}C$ which ranged from -3.394 to +0.283 ‰ Vienna Pee Dee Belemnite was above the mantle signatures of -6 ± 2.5 ‰. This indicated that the CO_2 was mantle or deep crust derived probably due to post volcanic degassing with a minor contribution from carbonate minerals. The springs had low temperatures between 21.9-29.7 °C and slightly acidic pH of 5.83-6.57. Dissolved inorganic carbon ranged between 39,184-89,013 µmol/kg, total alkalinity 14,925-61,810 µmol/L and electrical conductivity 1,375-5,195 µS/cm. The predominant cation in the waters was Na^+ at 5,261-55,348 µmol/L which was largely counterbalanced by HCO_3^-. Other ions found in lesser amounts included Mg^{2+}, Ca^{2+}, K^+, Cl^- and SO_4^{2-}. The apparent carbon dioxide degassing phenomenon would be of interest in terms of understanding the geoscience of this region, climate change monitoring and harnessing the potential socio-economic benefits.

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Introduction

The occurrence of mofette or cold CO_2-rich springs is mainly linked to major faults and volcanoes. Deep CO_2 emissions may continue to be released from inactive volcanoes for a long period [1, 2, 3]. The apparent sources of CO_2 in mofette springs include the mantle, sedimentary carbonate rocks, metamorphic processes and breakdown of organic matter.

The continuous diffuse degassing of magmatic CO_2 through faults which is observed at various volcanoes is caused by unerupted magma [4, 5, 6]. The origin of the dissolved CO_2 gas can be determined by isotopic ratio analysis of $^{13}C/^{12}C$, which is expressed by delta notation in parts per thousand or per mil ($\delta^{13}C$ ‰). The $\delta^{13}C$ ‰ value of a sample is derived by comparison with a

Vienna Pee Dee Belemnite (VPDB) reference standard. The $\delta^{13}C$ value is negative, if a sample is more enriched with isotope ^{12}C than the standard and positive when the sample is enriched with ^{13}C [4, 7].

$$\delta^{13}_{\text{VPDB}} = 1000\frac{\left(R_{\text{sample}} - R_{\text{standard}}\right)}{R_{\text{standard}}} \qquad (1)$$

$$\delta^{13}_{\text{VPDB}} = 1000\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \qquad (2)$$

where R = $^{13}C/^{12}C$

Mofette springs have been investigated in different parts of the world. The cold 'mazuku' CO_2 vents at Rungwe Volcanic Province in South West Tanzanian which is part of the East African Rift System (EARS), are characterised by a narrow range of $\delta^{13}C$ from -2.8 to -6.5 ‰ VPDB indicating mantle-derived CO_2 fluxes [8].

The Bongwan CO_2 springs at KwaZulu-Natal in South Africa have $\delta^{13}C$ values varying from -0.6 to +0.9 ‰ VPDB. An indication that the source of the CO_2 is most likely due to the reaction of acid groundwater with carbonate rocks at depth. The issuing CO_2 is 97.5% pure and has been exploited commercially. The emission of CO_2 is linked to about 80 km long Bongwan gas fault trending North-South [9].

The chemistry of Lake Nyos waters in Cameroon showed an average of $\delta^{13}C$ of -3.4 ‰ VPDB and suggested deep magmatic origins. The cation content (Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+} and Fe^{2+}) corresponds to the dissolution of host rock and the waters are close to saturation with respect to siderite ($FeCO_3$) [10].

The $\delta\ ^{13}C$ isotope values for thermal springs (22 °C to 39 °C) at Choygan area of southern Siberia in Russia, varies from −0.3 to +1‰ which is consistent with metamorphism of carbonate rocks at depth. But inputs from other sources cannot be ruled out. Major ions such as Na^+, K^+, Ca^{2+}, Si^{4+} and Cl^- are associated with the dissolution of silicate phases in the subsurface [11].

A study highlighting isotope and chemical analysis of cold and thermal mineral waters at the Northern part of Portuguese Mainland found high contents of Na^+ (365-1246 mg/L), K^+ (28-105 mg/L), Ca^{2+} (22-203 mg/L), HCO_3^- (1,724-4,716 mg/L) and free CO_2 (350-4,670 mg/L). The $\delta^{13}C$ values for dissolved inorganic carbon (DIC) ranged from -6 to -1 ‰ VPDB which could be attributed to either deep-seated (mantle) origin or mixing of mantle and limestone CO_2. The chemistry of these mineral waters is a manifestation of water-rock interactions favoured by the enriched CO_2 at a low temperature [12].

A study of CO_2-rich springs of Jungapeo at the state of Michoacán in Mexico revealed high HCO_3^-, moderate Ca^{2+}, Mg^{2+}, Na^+, K^+, moderate to low Cl^- and low F^-.
The $\delta^{13}C$ values lied between -6.7 ‰ and -7.2 ‰, VPDB. Hence, most CO_2 probably originated from the mantle with some organic sources contribution from the underlying cretaceous rocks [13].

Carbon dioxide occurs in the Kenya Rift Valley (KRV) at mount Margaret Estate in Kedong Valley, Lake Magadi, Esageri and Kireita [14]. Beside the Rift System, the Eastern slopes of Mt. Kenya and the neighbouring Nyambene range is another important area of focus with numerous CO_2 degassing sites which have not been fully investigated [15]. Rurii spring located in Nyambene hills was found to be moderately cold (19.8 °C) and characterised by very high total dissolved solids (TDS = 5,056 mg/L), extremely high total alkalinity (5,528 mg/L) and was rich in free CO_2 (1,015 mg/L) [15].

Mt. Kenya is a stratovolcano with summit elevation of 5,199 m and lies outside the Kenya Rift Valley (KRV). It is the second tallest mountain in Africa after Mt. Kilimanjaro. The Eastern slope is dominated by basalt rocks and presence of many volcanic craters and vents. There are multiple lineaments which are expression of underlying buried faults [16]. Degassing in this region seems to occur in the form of point sources through small mofette springs trending North-South. This could indicate existence of fractures on the slopes of the volcano which act as conduits for the escaping CO_2 gas from shallow-level magma chamber [17, 18].

This investigation involved 10 mofette springs selected from Meru County in the Eastern part of Mt. Kenya, namely; Gikumene, Kathathantu, Kiambogo, Mbwinjeru, Mulathankari, Nthungu, Rwarera-A, Rwarera-B, Tharu and Ukuu. The springs are spread out over a distance of about 30 km across the mountain slope between Nkubu and Ruiri. They discharge high content CO_2 waters throughout the year and hence they could be considered as permanent point sources of CO_2. The nearby residents frequent the springs to draw water for drinking, cooking, feeding the livestock and selling.

The key objective of the study was to establish whether the release of CO_2 from the springs is due to magmatic degassing or from other sources such as carbonate rocks with respect to $\delta\ ^{13}C$ isotope values. The research findings could help to close some information gaps on the spatial distribution of the isotopic signature and understand the CO_2 degassing behaviour of solid Earth in a volcano setting. Also, there is need to consider these CO_2 sources and possibly include them in the global CO_2 budget estimates [19, 20, 21, 22]. For example, a study done in Slovak Republic, emissions of CO_2 from mineral springs is estimated at 4 Mt yr^{-1}. This may contribute to aggregated emissions from other countries with related geological and hydrogeological structures [23].

Moreover, the mofette springs can be exploited commercially for extraction of CO_2 which has wide applications in soft drinks, refrigeration, fire extinguishers, supercritical fluid chromatography, solvent extraction and lasers. The spring waters are naturally enriched with minerals and can be utilised for production of therapeutic healthy drinks as well as establishment of Spas [9, 24, 25]. Currently, Kenya has one commercial CO_2 mining plant at Kireita forest in Kiambu County which generated about US $ 29.5 million between the years 2013-2017 [26].

Fig. 1 and 2 represents the physical and geological maps of the study region, respectively. The springs are bound by latitudes 00° 13.401’ N and 00° 05.004’ S and longitudes 37° 35.620’ E and 37° 40.763’ E, with an elevation of 1410 m to 1938 m above sea level.

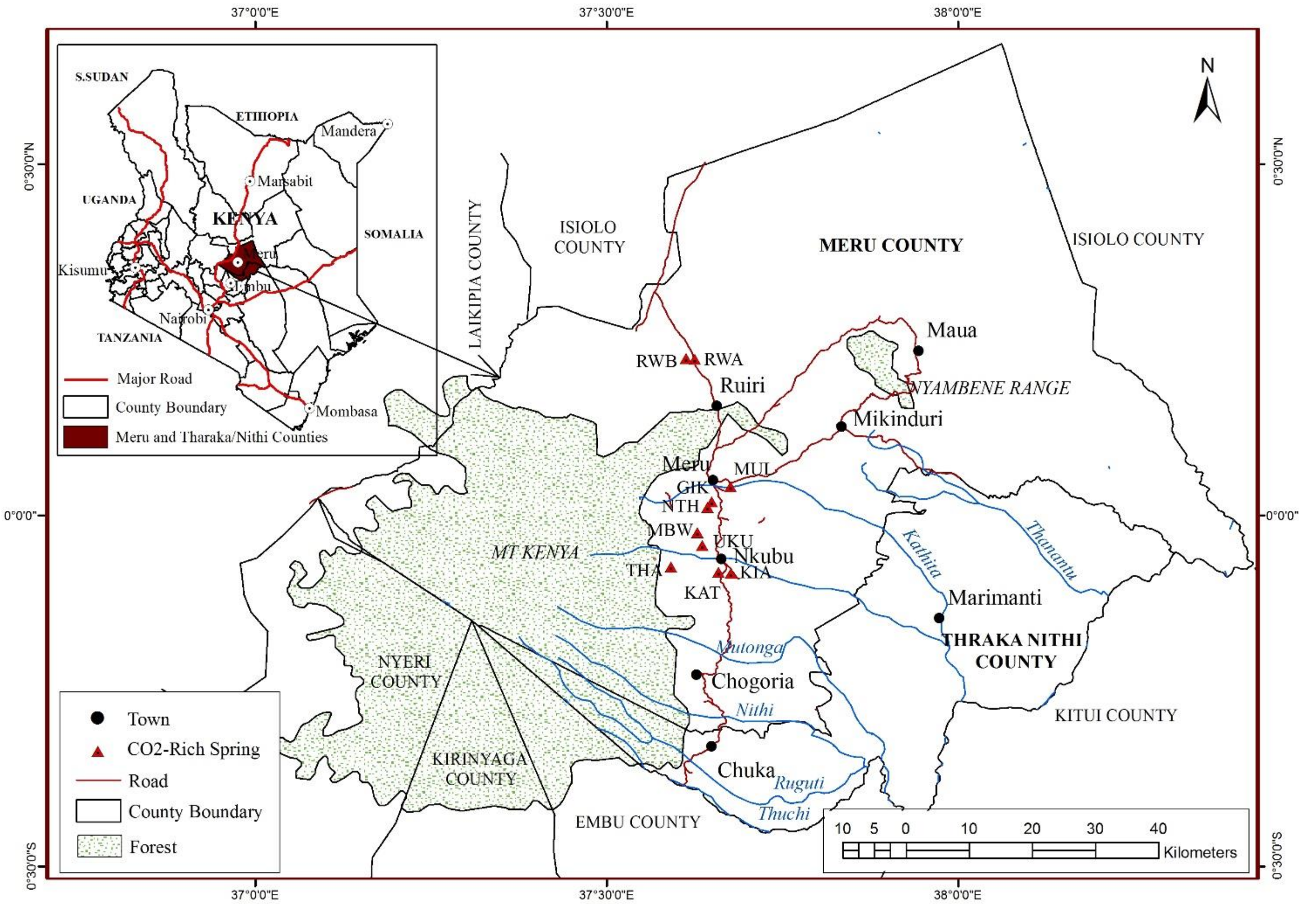

Figure 1. Physical map of Eastern Mt. Kenya, showing the sites of CO_2-rich springs. (*Courtesy of Department of Geography and Environmental Studies, University of Nairobi*)

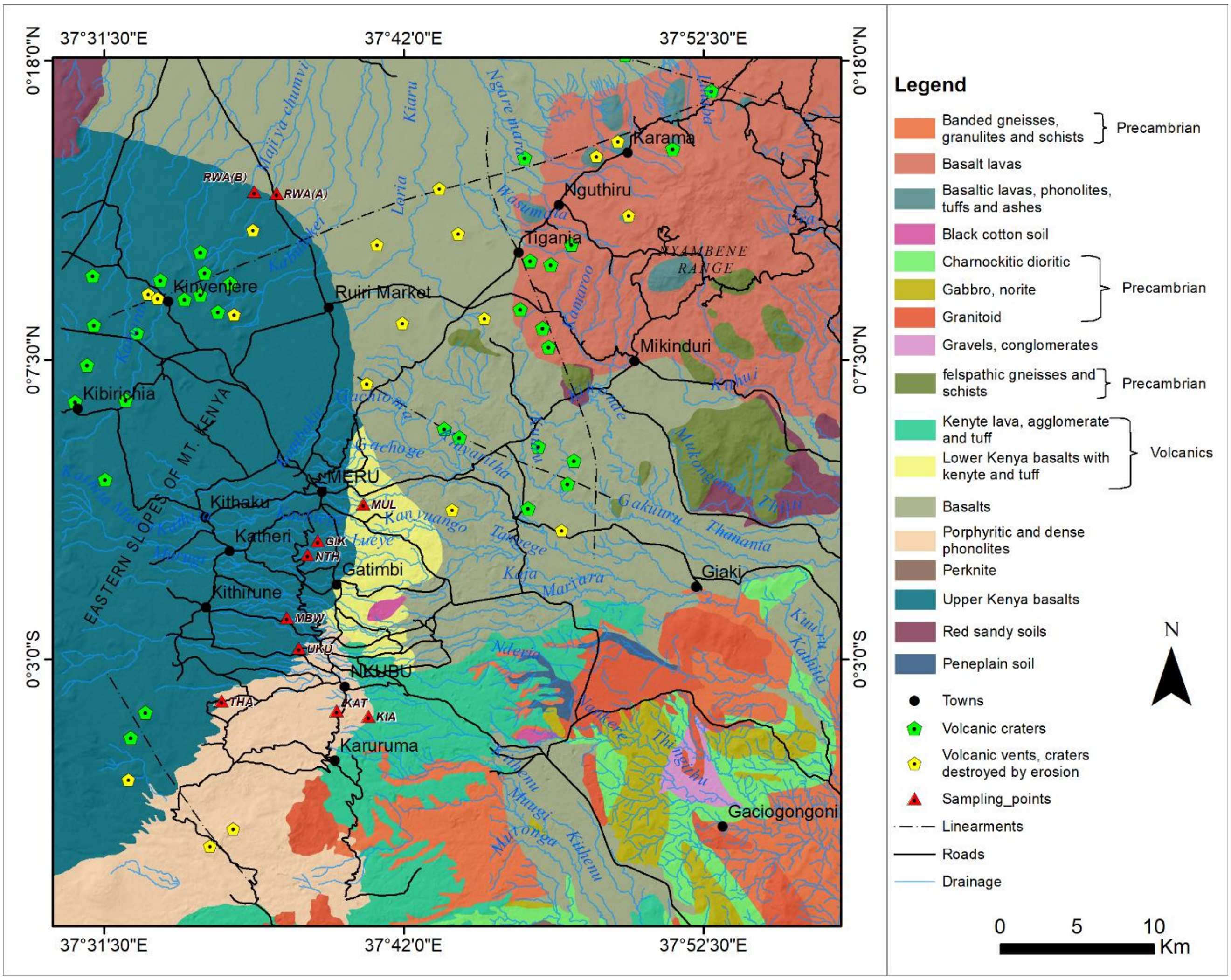

Figure 2. Geological map of Eastern Mt. Kenya region. The sites of sampling are shown. (*Courtesy of Department of Geology, University of Nairobi*)

Figure 3 shows one of the sampling sites.

Figure 3. Rwarera-A spring and some cattle drinking the CO_2-rich mineral water.

Materials and Methods

Sampling and field measurements

Sampling of the 10 springs was carried out during the dry season in February 2019 to avoid interference from runoff waters. Three water samples were obtained per spring using 13 mL glass vials, for the determination of $\delta^{13}C$ and DIC. One drop of saturated $HgCl_2$ solution was added to each vial to preserve the sample. Another set of untreated water samples were collected and filtered through 0.45 μm filters into clean 300 mL PET bottles for the determination of total alkalinity and major ions. Samples for silicon analysis were filtered and acidified with 1 mL of concentrated HNO_3. The samples were preserved at approximately 4°C in a refrigerator.
Temperature, pH and electrical conductivity (EC) of the water samples were measured in situ using a portable meter (HANNA Instruments: HI 98129).

Laboratory analysis

Cavity Ring-Down Spectroscopy (CRDS) method was used for $\delta^{13}C$ and DIC measurements after acid extraction of CO_2 from the water samples [27, 28, 29]. The instrument (Picarro CRDS G2101-i Isotopic CO_2 Analyzer) was calibrated using Certified Reference Materials, NBS 18 (-5.014 ‰), NBS 19 (1.95‰) traceable from the National Institute of Standards and Technology (NIST) and analytical grade $CaCO_3$ (-9.650 ‰). The mean absolute deviation due to isotopic drift was ±0.5‰. Six standards ranging between 0.3 – 2 mg $CaCO_3$, NBS 18 and NBS 19 were weighed separately into vials for DIC and $\delta^{13}C$ calibration. The vials were tightly closed and evacuated for five seconds with a vacuum pump. A volume of 2 mL of each sample was drawn with a syringe and sucked into previously weighed and evacuated vial. The vials containing the 2 mL samples were reweighed. Each standard and sample containing vial was treated with 2 mL of 25% H_3PO_4 to release CO_2 gas. An evacuated blank was also treated with 2 mL of 25% H_3PO_4. The gaseous CO_2 obtained was directed into the Picarro CRDS system for the $\delta^{13}C$ isotope and DIC determination. Total alkalinity (Talk) was determined by an automatic potentiometric titrator (Metrohm: 888 Titrando) using 0.02 N HCl to pH 4.5 endpoint.

The major anions and cations were analysed using ion chromatography (IC) system (Metrohm system: 881). The eluents were composed of 3.2 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$ for anions and 1.7 mmol/L HNO_3 and 0.7 mmol/L $C_7H_5NO_4$ (dipicolinic acid, DPA) for cations. Calibration stock solutions were made of TraceCERT®, 1000 mg/L multi-ion standards. A volume of 20 µL of standards and samples aliquots were injected into the IC system for analysis after filtration through 0.45 µm filters [30, 31]. Inductively coupled plasma-optical emission spectrometer, ICP-OES (Agilent Technologies: 5110) was used for silicon (Si) analysis [32, 33].

Results

Table 1 summarises the average $\delta^{13}C$ analytical data for dissolved inorganic carbon ($^{13}C_{DIC}$) and other characteristic physical parameters. The chemical composition of major cations and anions in the waters are shown in Table 2 and 3, respectively. In some cases, parameters such as Li^+, NH_4^+, Br^-, F^-, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}, were below the limits of quantitation (LOQ) whereby LOQ were equal to ten times the standard deviation of their respective Milli-Q calibration blanks. Three sample replicates were analysed in each spring and acceptable (< ±5%) relative standard deviations (RSD) were obtained.

Table 1: Average analytical data for $\delta^{13}C_{DIC}$ values and other physical parameters.

Spring	T (°C)	pH	$\delta^{13}C_{DIC}$ [‰ VPDB]	EC [µS/cm]	DIC [µmol/kg]	Talk [µmol/L]	DIC-Talk [µmol/L]
Gikumene	21.9 ±0.2	5.83 ±0.5	-2.168 ±0.6	1,375 ±1.8	39,184 ±2.7	14,925 ±3.6	24,259 ±2.6
Kathathantu	23.2 ±0.2	6.03 ±0.3	-3.394 ±0.4	2,753 ±1.2	54,008 ±3.1	23,926 ±3.9	30,082 ±3.2
Kiambogo	23.4 ±0.5	6.02 ±0.6	-3.341 ±0.7	2,590 ±2.7	47,569 ±3.6	24,433 ±1.4	23,136 ±1.8
Mbwinjeru	23.5 ±0.3	6.34 ±0.4	-1.730 ±0.5	3,858 ±1.6	81,268 ±2.9	48,421 ±3.2	32,847 ±2.0
Mulathankari	21.8 ±0.2	6.34 ±0.6	-2.369 ±0.9	3,505 ±3.2	66,799 ±3.5	41,531 ±1.7	25,268 ±2.4
Nthungu	24.8 ±0.7	6.34 ±0.3	+0.283 ±0.7	3,715 ±2.8	70,240 ±1.5	45,247 ±3.4	24,993 ±2.2
Rwarera-A	24.3 ±0.4	6.37 ±0.8	-0.065 ±1.4	4,980 ±2.5	89,013 ±3.2	57,385 ±2.5	31,628 ±3.1
Rwarera-B	25.6 ±0.5	6.47 ±0.6	+0.178 ±0.5	4,625 ±3.4	72,403 ±2.6	50,247 ±2.8	22,156 ±2.5
Tharu	29.7 ±0.2	6.57 ±0.5	-1.273 ±0.8	5,195 ±2.9	87,286 ±2.8	61,810 ±4.4	25,476 ±3.8
Ukuu	23.8 ±0.3	6.33 ±0.2	-1.838 ±1.1	3,990 ±2.6	72,653 ±3.5	44,562 ±3.2	28,091 ±2.4

Table 2: Major cations in µmol/L.

Spring	Li^+	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Si^{4+}
Gikumene	<14	5,261 ±1.4	<19	458 ±1.4	1,970 ±1.9	2,694 ±1.7	73 ±1.2
Kathathantu	50 ±1.1	21,683 ±1.4	<19	1,132 ±1.7	1,920 ±4.3	1,770 ±1.8	65 ±1.6
Kiambogo	48 ±3.8	20,032 ±1.4	<19	1,080 ±1.6	1,642 ±2.7	1,580 ±1.1	68 ±0.9
Mbwinjeru	99 ±1.1	34,947 ±1.4	<19	1,755 ±1.2	3,272 ±2.8	2,610 ±1.8	72 ±2.6
Mulathankari	<14	16,565 ±1.0	<19	882 ±2.0	4,576 ±1.9	7,161 ±1.3	61 ±1.9

Spring	Li^+	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Si^{4+}
Nthungu	88 ±1.4	35,240 ±3.7	<19	1,869 ±1.6	2,598 ±4.1	2,897 ±1.2	75 ±2.1
Rwarera-A	100 ±1.9	34,668 ±1.4	<19	1,801 ±1.6	2,596 ±3.0	6,877 ±1.7	78 ±2.4
Rwarera-B	96 ±2.12	31,665 ±1.4	<19	1,682 ±1.2	2,603 ±3.8	7,067 ±1.6	71 ±1.5
Tharu	157 ±1.8	55,348 ±1.5	<19	2,369 ±1.8	1,778 ±3.5	2,037 ±2.7	92 ±1.2
Ukuu	97 ±1.9	36,186 ±1.8	<19	1,855 ±1.6	1,967 ±4.3	1,662 ±1.3	58 ±0.7

Table 3: Major anions in µmol/L.

Spring	Br^-	Cl^-	F^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Gikumene	<0.05	459 ±0.7	<8.9	<2.8	<1.03	<33	16 ±3.4
Kathathantu	<0.05	4,686 ±0.1	66 ±0.3	<2.8	<1.03	<33	94 ±1.4
Kiambogo	<0.05	4,319 ±0.2	71 ±0.8	<2.8	<1.03	<33	79 ±1.3
Mbwinjeru	<0.05	2,349 ±0.1	46 ±0.5	<2.8	<1.03	<33	<3.4
Mulathankari	<0.05	1,511 ±0.4	<8.9	<2.8	<1.03	<33	85 ±1.1
Nthungu	<0.05	2,662 ±0.2	<8.9	<2.8	3 ±0.5	<33	52 ±1.4
Rwarera-A	12 ±1.7	5,612 ±0.3	<8.9	<2.8	2 ±0.4	<33	931 ±0.3
Rwarera-B	12 ±1.2	5,759 ±0.2	<8.9	12 ±0.3	<1.03	<33	912 ±0.4
Tharu	10 ±1.8	6,633 ±1.8	115 ±0.9	<2.8	<1.03	<33	<3.4
Ukuu	8 ±1.3	5,005 ±0.5	37 ±0.5	11 ±0.7	<1.03	<33	<3.4

Discussion

The springs were characterised by relatively low discharge temperature (21.9-29.7 °C) and were generally cold. The low temperature allows large volume of CO_2 to remain dissolved in the water [12]. The geochemistry of CO_2-rich waters in Iceland has an implication that lower subsurface temperatures increases the aqueous solubility of CO_2. The high concentrations of CO_2 gives the water a slightly acidic pH (6.4) which leads to increased dissolution of carbonate and silicate minerals [34]. This conclusion correlates with the reported results.

The slightly acidic pH (5.83-6.57) could be attributed to the dissolved CO_2 in form of weak carbonic acid (H_2CO_3). Given that the pH range of the springs was 5.83-6.57, the alkalinity of the waters was dominated by HCO_3^- rather than CO_3^{2-} [35].

The obtained $\delta^{13}C$ values from Eastern Mt. Kenya springs ranged from −3.394 to +0.283 ‰, VPDB, showing a deviation from the mantle signatures. This is apparently above the mantle range (-6 ± 2.5 ‰) or close to the upper levels [36]. Therefore, the ultimate source of CO_2 in the study region is likely to be mantle but could be variably enriched with ^{13}C from deep carbonate rocks especially the calcite precipitated in basalt as shown in Eq. 3 [34, 37].

$CaAl_2Si_2O_8 + CO_{2(g)} + 2H_2O_{(l)} \rightarrow Al_2Si_2O_5(OH)_{4(s)} + CaCO_{3(s)}$. (3)
Anorthite Kaolinite Calcite

The source of CO_2 (whether crust, limestone, organic or mantle) may be altered by carbon isotope fractionation in the process of magmatic degassing, assimilation of organic carbon near the surface and calcite precipitation in the subsurface geothermal or hydrothermal systems beneath volcanoes [36]. A study of groundwater in Iceland showed $\delta^{13}C_{DIC}$ range of -27.4 to +2.0 ‰, VPDB. This points to mixed sources such as atmosphere, dissolution of partially degassed basaltic rocks, upper mantle and lower crust [37].

The reported values of EC (1,375-5,195 µS/cm), DIC (39,184-89,013 µmol/kg) and total alkalinity (14,925-61,810 µmol/L) were high because of the large CO_2 content of the system which raises the dissolution of carbonate and silicate minerals from parent rocks [38]. This could be due to the acid hydrolysis reactions taking place as shown in Eq. 4, 5 and 6 [35].

$CaCO_{3(s)} + H_2CO_{3(aq)} \rightarrow Ca(HCO_3)_{2(aq)}$. (4)
Calcite

$2NaAlSi_3O_{8(s)} + 2H_2CO_{3(aq)} + 9H_2O_{(l)} \rightarrow 2NaHCO_{3(aq)} + Al_2Si_2O_5(OH)_{4(s)} + 4H_4SiO_{4(aq)}$.(5)
Albite Kaolinite Silicic acid

$Mg_2SiO_{4(s)} + 4H_2CO_{3(aq)} \rightarrow 2Mg(HCO_3)_{2(aq)} + H_4SiO_{4(aq)}$. (6)
(Forsterite)

The predominant cation in the waters was Na^+, followed by Mg^{2+}, Ca^{2+} and K^+, in that order while HCO_3^- was the predominant anion followed by Cl^- and then SO_4^{2-}. The high NaCl levels produces the slight salty taste in the waters. It is important to note that the F^- level at Tharu of 115 µmol/L, was above the maximum 79 µmol/L WHO permissible limit in drinking water [39]. Ingestion of excess F^- can lead to chronic dental and skeletal fluorosis especially in children below the age of seven years [40].

DIC-Talk values (24,259-32,847 µmol/L) represents the free CO_2 and/or undissociated H_2CO_3 which is at equilibrium with HCO_3^- and CO_3^{2-} in the system [35]. In general, the results depicts high concentration of DIC species or rather large content of dissolved CO_2, with RWA and THA springs being the highest. This is a sign of CO_2 degassing through buried faults in the region. The springs could therefore be harnessed for commercial extraction of CO_2 and production of mineral water healthy drinks [9, 24, 25].

Fig. 4 shows that $\delta^{13}C$ increases with DIC and total alkalinity (Talk) with a positive correlation (r) of +0.623 and +0.689, respectively. In Fig. 5, the data is showing a strong positive correlation of EC with DIC and Talk. This suggests that the more CO_2 in the system containing ^{13}C, the more dissolution of carbonate and/or silicate minerals leading to increase in conductivity levels [38].

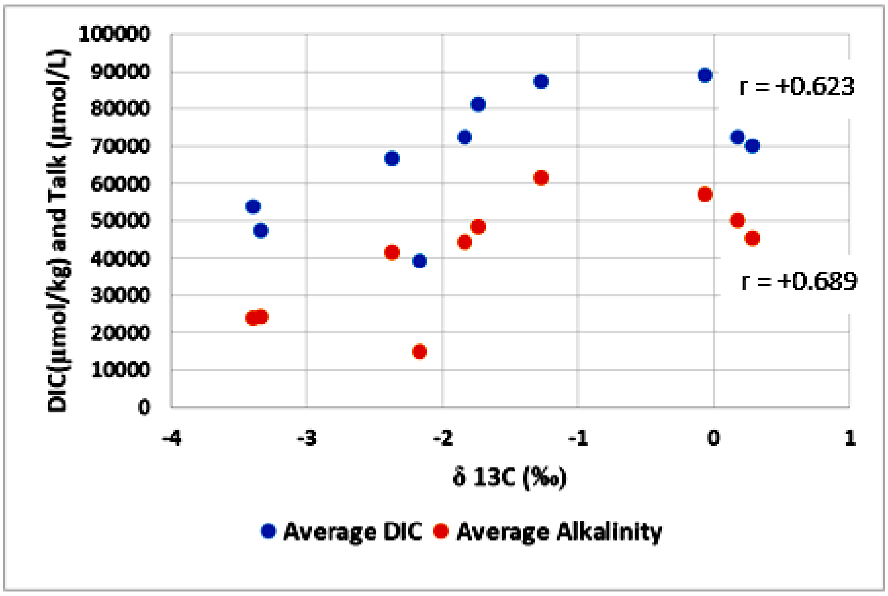

Figure 4. Correlation of $\delta^{13}C$ with DIC and Talk.

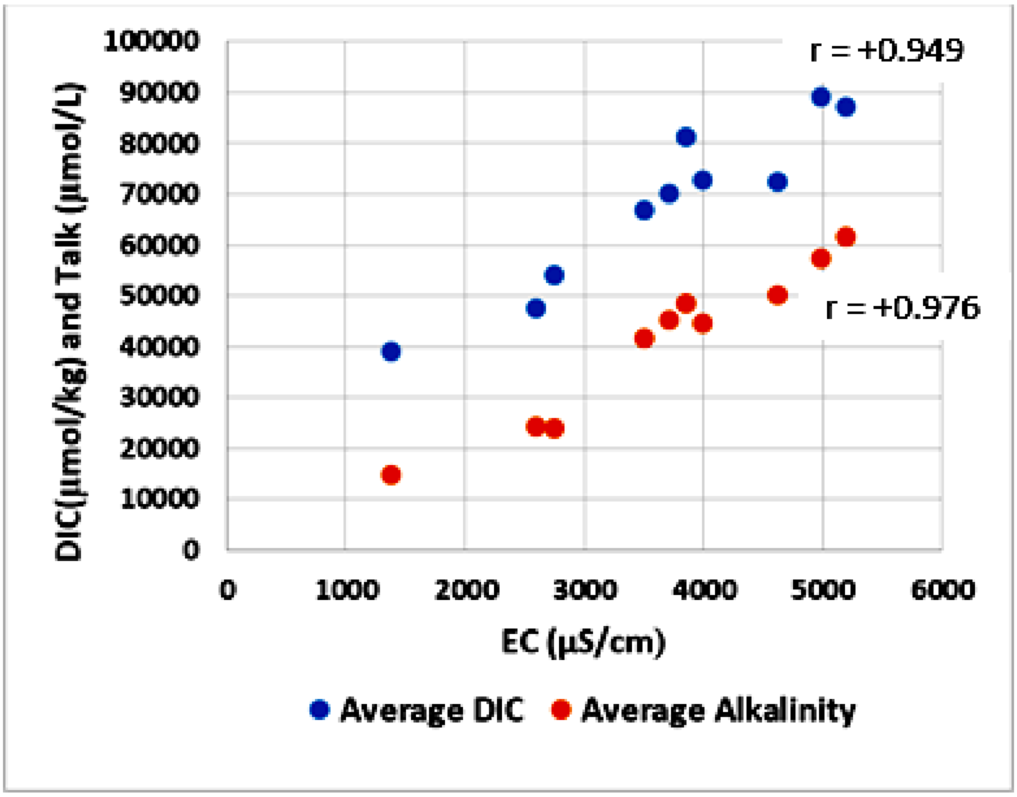

Figure 5. Correlation of EC with DIC and Talk.

Fig. 6 shows a piper diagram for the classification of water-types based on the major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^- and SO_4^{2-}). Whereby Na^+ and HCO_3^- are the predominant ions constituting more than 50% of the major ions. The main water-type is therefore Na-HCO_3 (Bicarbonate-alkaline waters). The waters can also be classified into Na-Ca-HO_3 and Na-Mg-HCO_3 to some extent at Gikumene and Mulathankari springs. The dominance of Na^+ largely counterbalanced by HCO_3^- rather than Cl^- and SO_4^{2-} is evidence for magmatic source of CO_2 as opposed to carbonate dissolution. Abundance of Na^+ in the cations also suggest that silicates are the dominant source of weathering products [41, 42].

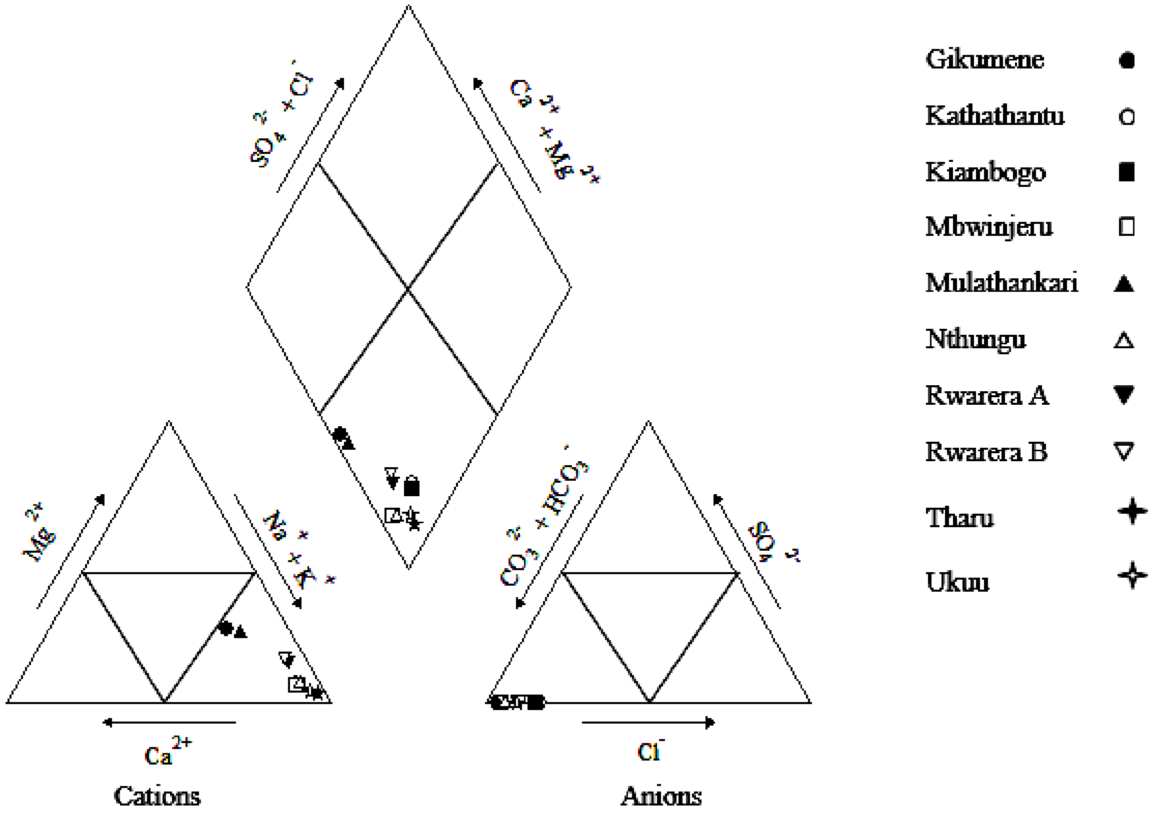

Figure 6. Piper plot for the classification of spring waters.

Conclusion

The established $\delta^{13}C_{DIC}$ values of the springs ranged from −3.394 to +0.283 ‰, VPDB and are higher than the mantle range (-6 ± 2.5 ‰). This isotope signature indicates that the CO_2 is from a deep-seated source or is mantle derived but could be partially mixed with CO_2 from deep carbonate minerals. Geologically, this suggests a passive magmatic CO_2 degassing through volcanic faults and fractures on the flanks of Mt. Kenya which could be enhanced by some carbonate rock formation in the region. However, the dominance of Na^+ (5,261-55,348 µmol/L) in the water suggest a minor contribution of carbonates to the dissolved solids in the spring waters. Due to the large dissolution of CO_2 in the groundwater, the springs are characterised by slightly acidic pH, elevated DIC, total alkalinity, EC and ionic species.

The research findings contribute data which helps to understand the degassing behaviour of solid Earth in a volcano setting and closes some information gaps on the spatial distribution of the isotopic signature. The reported data show that probably different CO_2 sources need to be accounted for. Isotope systematics for more degassing sub-aerial volcanoes ought to be established for further comparison with the reported data.

The CO_2 flux is a major environmental concern because of the greenhouse effect associated with it. Therefore, the volcanic CO_2 degassing taking place around the Mt. Kenya region requires to be fully established and be included in the estimates of global CO_2 budget. On the other hand, there could be potential for commercial exploitation of CO_2 gas and mineral waters in the region. Hence, feasibility studies on the commercial viability of the CO_2 deposits are recommended. It is important to undertake thorough water quality analysis of the springs to ensure that it is free from contamination and safe for human consumption.

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References

[1] Bissig, P., Goldscheider, N., Mayoraz, J, Surbeck, H. and Vuataz, F. D. (2006) Carbogaseous spring waters, coldwater geysers and dry CO_2 exhalations in the tectonic window of the Lower Engadine Valley, Switzerland. *Eclogae geol. Helv*. **99** (2): 143–155.

[2] Hutchison, W., Mather, T. A., Pyle, D., M, Biggs, J. and Yirgu, G. (2015) Structural controls on fluid pathways in an active rift system: A case study of the Aluto volcanic complex. *Geosph.* **11** (3): 542-562.

[3] Hunt, J. A., Zafu, A., Mather, T. A., Pyle, D. M. and Barry, P. H. (2017) Spartially variable CO_2 degassing in the Main Ethiopian Rift: Implications for magma storage, volatile transport and rift related emissions. *Geochem. Geophys. Geosyst.* **18** (10): 3714-3737.

[4] Laughrey, C. D. and Baldassare, F. J. (2003) ome applications of isotope geochemistry for determining sources of stray carbon dioxide gas. *J. Environ. Geosci.* **10** (3): 107-122.

[5] Chiodini, G., Caliro, S., Cardellini, C., Avino, R., Granieri, D. and Schmidt, A. (2008) Carbon isotopic composition of soil CO_2 efflux, a powerful method to discriminate different sources feeding soil CO_2 degassing in volcanic-hydrothermal areas. Earth Planet. Sci. Lett. **274** (3-4): 372–379.

[6] Crossey, L. J., Karlstrom, K. E., Springer, A. E., Newell, D., Hilton, D. R. and Fischer T. (2009) Degassing of mantle-derived CO_2 and He from springs in the southern Colorado Plateau region-Neotectonic connections and implications for groundwater system. *GSA Bull.* **121** (7): 1034-1053.

[7] Srivastava, A. and Vekouteren, R. M. (2018) Metrology for stable isotope reference materials: 13C/12C and 18O/16O isotope ratio value assignment of pure carbon dioxide gas samples on Vienna Pee Dee Belemnite-CO_2 scale using dual-inlet mass spectrometry. *Anal. Bioanal. Chem*. **410** (17): 4153-4163.

[8] Barry, P. H., Hilton, D. R., Fischer, T. P., de Moor, J. M., Mangasini, F. and Ramirez, C. (2013) Helium and carbon isotope systematics of cold 'mazuku' CO_2 vents and hydrothermal gases and fluids from Rungwe Volcanic Province, south Tanzania. *Chem. Geol.* **339**: 141-156.

[9] Harris, C., Stock, W. D. and Lanham, J. (1997) Stable isotope constraints on the origin of CO_2 gas exhalations at Bongwan, Natal. *S. Afr. J. of Geol.* **100** (3): 261–266.

[10] Giggenbach W.F. (1990) Water and gas chemistry of Lake Nyos and its bearing on the eruptive process. *J. Volcanol. Geotherm. Res.* **42** (4): 337-362.

[11] Shestakova, A., Guseva, N., Kopylova, Y., Khvaschevskaya, A., David A. Polya, D. A. and Tokarev, I. (2018) Geothermometry and Isotope Geochemistry of CO_2-Rich Thermal Waters in Choygan, East Tuva, Russia. *Water* **10** (6): 729-59.

[12] Marques, J. M., Carreira. P. M. M., Aires-Barros, L. and Graça, R. C. (2000) Nature and role of CO_2 in some hot and cold HCO_3/Na/CO_2-rich Portuguese mineral waters: A review and reinterpretation. *Environ. Geol.* **40** (1-2)**:** 53-63.

[13] Siebe, C., Goff, F., Armienta, M. A., Counce, D., Poreda, R. and Chipera, S. (2007) Geology and Hydrogeo-chemistry of the Jungapeo CO_2-rich thermal springs, State of Michoacán, Mexico. *J. Volcan. Geotherm. Res.* **163** (1-4): 1-33.

[14] Pulfrey, W. and Wash, J. (1969) The Geology and mineral resources of Kenya 2nd ed. Bulletin No. 9: 20. https://s3-eu-west-1.amazonaws.com › samsamwater1 › maps › The+geolo...Accessed 23 August 2019.

[15] Mungai, G. N., Njenga, L. W., Mathu, E. M. and Kamau, G. N. (2014) Study of minerals in the water and source rocks of Rurii spring in Meru County, Kenya. *Int. J. Biochemiphys.* **22**: 11-19.

[16] Mason, P. (2007) Geology of the Meru - Isiolo Area Report No.31: 3-5. https://s3-eu-west-1.amazonaws.com/.../geology/Geology+of+the+Meru+Isiolo.pdf Accessed 23 August 2019.

[17] Chiodini, G., Cioni, R., Guidib, M., Raco, B. and Marini, L. (1998) Soil CO_2 flux measurements in volcanic and geothermal areas. *Appl. Geochem.* **13** (5): 543-552.

[18] Shinohara, H. (2008) Excess degassing from volcanoes and its role on eruptive and intrusive activity. *Rev. Geophys.* **46** (4): 1-31.

[19] Lee, H., Muirhead, J. D., Fischer, T. P., Ebinger, C. J., Kattenhorn, S. A., Sharpand, Z. D. and Kianji, G. (2016) Massive and prolonged deep carbon emissions associated with continental rifting. *Nature Geoscience* **9** (2): 145–149.

[20] Brune, S., Williams, S. E. and Müller, R. D. (2017) Potential links between continental rifting, CO_2 degassing and climate change through time. *Nat. Geosci.* **10** (12): 941–946.

[21] Maas, B. J. and Wicks, C. M. (2017) CO_2 Outgassing from Spring Waters. *Aquat. Geochem*. **23** (1): 53-60.

[22] Aiuppa, A., Fischer, T. P., Plank, T. and Bani, P. (2019) CO_2 flux emissions from the Earth's most actively degassing volcanoes, 2005-2015. *Sci. Rep.* **9** (1): 5442.

[23] Kucharič, L., Bodiš, D., Panák, D., Liščák, P. and Božíková, J. (2015) A contribution of CO_2 released from mineral springs into overall volume of annual CO_2 emissions in the Slovak Republic. *Environ. Earth Sci.* **73** (1): 231-238.

[24] Swanner, G. M. (1988) Saratoga – '' Queen of spas'' North County Books. INC. Utica, New Yolk: 8-14pp.

[25] Zink, S. (1993) New Yolk office of parks, recreation and Historic preservation, Saratoga – capital District region, Saratoga Springs. Person Communication, New Yolk: 11-14pp.

[26] Kenya National Bureau of Statistics. (2018) KNBS Statistical Abstract 2018. pp156. https://www.knbs.or.ke [Accessed 28 October 2019].

[27] Wahl, E. D., Fidric, B., Rella, C., Koulikov, S., Kharlamov, B., Tan, S., Kachanov, A., Richman, B., Crosson, E. R., Paldus, B., Kalaskar, S. and Bowling, D. R. (2006) Applications of cavity ring-down spectroscopy to high precision isotope ratio measurement of $^{13}C/^{12}C$ in carbon dioxide. *Isotopes Environ. Health Stud.* **42** (1): 21-35.

[28] Becker, M., Andersen, N., Fiedler, B., Fietzek, P., Körtzinger, A., Steinhoff, T. and Friedrichs, G. (2012) Using cavity ringdown spectroscopy for continuous monitoring of $\delta^{13}C(CO_2)$ and $ƒCO_2$ in the surface ocean. *Limnol. Oceanogr. Methods* **10** (10):752-766.

[29] Dickinson, D., Bode, S. and Boeck, X. P. (2017) Measuring ^{13}C enriched CO_2 in air with a cavity ring-down spectroscopy gas analyzer: Evaluation and calibration. *Rapid Comm. in Mass Spectrom.* **31** (22): 1892-1902.

[30] Gros, N. and Gorenc, B. (1997) Performance of ion chromatography in the determination of anions and cations in various natural waters with elevated mineralization. *J. Chromatogr. A.* **770** (1-2):119–124.

[31] Michalski, R. (2006) Ion chromatography as a reference method for determination of inorganic ions in water and wastewater. *Crit. Rev. Anal. Chem.* **36** (2):107–127.

[32] US EPA. (2001) Method 200.7 Revision 5.0. Trace elements in water, solids, and biosolids by inductively coupled plasma-atomic emission spectrometry. U.S. Environmental Protection Agency. Washington, D.C. 20460.
https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1002CW0.TXT Accessed 23 August 2019.

[33] Cauduro, J. and Ryan, A. (2017) Ultra-fast ICP-OES determination of trace elements in water, as per US EPA 200.7. Agilent Technologies Melbourne, Australia: 5991-4821EN. https://www.agilent.com/cs/library/applications/5991-4821EN.pdf Accessed 21 August 2019.

[34] Thomas, D. L., Bird, D. K., Arnorsson, S. and Maher, K. (2016) Geochemistry of CO_2-rich waters in Iceland. *Chem. Geol.* **444**: 158-179.

[35] Andrews, J. E., Brimblecombe, P., Jickells, T. D., Liss, P. S. and Reid, B. (2004) *An* Introduction to Environmental Chemistry, Second edition. Blackwell Publishing, Oxford UK: 83-86, 151-153pp.

[36] Mason, E., Edmonds, M. and Turchyn, A. V. (2017) Remobilization of crustal carbon may dominate volcanic arc emissions. *Sci.* **357** (6348): 290-294.

[37] Stefansson, A., Sveinbjornsdottir, A. E., Heinemeier, J., Arnorsson, S., Kjartansdottir, R. and Kristmannsdottir, H. (2016) Mantle CO_2 degassing through the Iceland crust: Evidence from carbon isotopes in groundwater. *Geochem. et Cosmochim. Acta* **191**: 300-319.

[38] Crundwell, F. K. (2014) The mechanism of dissolution of minerals in acidic and alkaline solutions: Part II Application of a new theory to silicates, aluminosilicates. *Hydrometall.* **149**: 265–275.

[39] WHO. (2011) Guidelines for drinking-water quality 4th Ed. Geneva, World Health Oganization, Geneva. ISBN 978 92 4 154815 1.
apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf Accessed 23 August 2019.

[40] Kanduti, D., Sterbenk, P. and Artnik, B. (2016) Fluoride: A review of use and effects on health. *Mater Sociomed*. **28** (2): 133–137.

[41] Kumar, P. J. S. (2013) Interpretation of groundwater chemistry using piper and Chadha's diagrams: a comparative study from perambalur taluk. *Elixir Geosci.* **54**: 12208-12211.

[42] Marques, J. M., Monteiro, S. F. A., Graca, R. C., Castro, R. Aires-Barros, L. and Mendes Victor, L. A. (2001) A geochemical and geophysical approach to derive a conceptual circulation model of CO_2-rich minerals waters: A case study of Vilarelho da Raia, northern Portugal. *Hydrogeol. J.* **9** (6): 584–596.