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CHEMISTRY IN EXPLORATION OF A GEOTHERMAL FIELD

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ABSTRACT

Chemistry principles are some of the scientific techniques used in exploration for geothermal resources. The methods used include sampling of surface discharge from potential target areas and soil gas sampling followed by chemical analysis of the samples and finally data interpretation. The data obtained is used to assist in locating potential drill sites for geothermal generation, estimating the subsurface temperatures where the discharges are coming from and characterising the geothermal fluids using the chemistry to assess their usability for the intended purposes. This technique was used in exploration for geothermal resources in Menengai field, Kenyan Rift Valley. The results indicated availability of geothermal fluids at temperatures of up to 250 ºC. The reservoir was defined by both high CO_2 and Rn-222 measured in the soil gas and also high gas content in the fumarole discharges and the high volatile constituents in the fumarole steam condensates. Three deep exploration wells were proposed to be drilled in Menengai caldera using the chemistry of the surface discharges.

1. INTRODUCTION

The area under investigation has extremely few geothermal manifestations or expressions, which makes it quite difficult in terms of exploration using chemical methods. The few geothermal manifestations present include few low-pressured fumaroles mainly located inside the caldera. The chemical survey conducted involved fumarole sampling and soil gas survey with emphasis on carbon dioxide (CO_2) and radon (Rn-222) gas compositions in the soil air. The soil gas survey was conducted along traverse lines running E-W. The traverses were 1000 m apart while the sample points were taken at 500 m in areas of high geothermal manifestations and wider apart in areas of low geothermal manifestations. Sampling was done at a depth of 0.7 m below the surface.

2. PREVIOUS WORK

Previous geochemical investigations of this area were carried out by Geotermica Italiana Srl, (1987) and Ministry of Energy in 1985-1986 under the auspices of the United Nations Department for Technical Development (DTCD). The work covered the area from Menengai caldera to Lake Bogoria to the north. The work involved sampling water points and a few soil gas surveys targeting mainly carbon dioxide. The few soil gas samples were picked mainly along the major access roads in Olbanita and Ol'rongai areas. From the previous work few surface features of geothermal importance were covered and these consisted of hot springs and fumaroles of Lake Bogoria, the steam heated pools of Molo River and gas discharging boreholes. Other areas in the prospect area around Solai graben and

areas within the Ol'rongai and Olbanita volcanoes lacked water points. High flows of discharging fluids were recorded around Lake Bogoria springs and temperature estimates using solute geothermometry from the springs and boreholes ranged from 145-190°C for borehole and spring water. Gas geothermometry estimates provided higher temperature estimates, which ranged from 170–214°C.

Soil gas survey was carried out in areas adjacent to the Solai graben and the Olbanita and Ol'rongai areas. Carbon dioxide contents of the soil gas showed higher contents around the Olbanita and Ol'rongai areas than around the Solai graben. Since the work was carried out, more boreholes have been drilled in the prospect area. Some of these boreholes had temperatures measurements that were more than ambient. Soil gas data collected around and inside the caldera was scant. To obtain more information that would assist in siting exploration wells, further work was planned which included sampling boreholes and springs as well as soil gas surveys in the prospect.

3. METHODOLOGY

The procedures employed in the study can be divided into three categories:
(1) Fumarole steam discharge sampling,
(2) Borehole water sampling and analysis and
(3) Soil gas sampling to determine mainly the concentrations of carbon dioxide and radon radioactivity in the soil air. The sampling procedures are described separately below.

3.1 Fumarole steam sampling

The fumarole discharges in this area are mainly found inside the caldera and a few locations to the north-western part of the caldera (Figure 1). Nearly all the fumaroles are characterized by low discharge pressure and are highly contaminated with atmospheric air. The discharge was trapped using a stainless steel funnel whose contact points with the ground were sealed with mud to prevent any contact with air to avoid possible contamination of the sample. The trapped steam was delivered into a gas-sampling bulb through rubber tubing via a stainless steel cooling coil immersed in cold water to trap the steam condensate. A portion of the condensate collected was set aside for immediate analysis and measurements of pH, conductivity, total dissolved solids (TDS), hydrogen sulphide gas (H_2S) and CO_2. A measured quantity of zinc acetate was added to another portion of the condensate to preserve the sample for later laboratory analyses of the sulphates (SO_4^{-2}). Another (untreated) portion was reserved for analysis of chloride (Cl^-) and fluorides (F^-) in the laboratory. The immediate analysis of dissolved H_2S gas was done on the sampling site while measurements of conductivity, TDS, pH, CO_2 (as total carbonates) and Cl^- was done at the end of each sampling day at the base camp.

Electrical conductivity of the condensate was measured using a portable conductivity meter, Cole Palmer model 1481-40 at ambient temperatures while the pH was measured using a field pH meter. Cl^- and F^- were determined in the laboratory by using the Mohr titration and the selective electrode methods for both components respectively. Both CO_2 and H_2S gases were analysed by titration methods by using 0.1 M hydrochloric acid (HCl) and mercuric acetate respectively.

The fumarole gases were sampled by directing the steam into two evacuated gas sample flasks, one at a time, containing 50 ml of a 40% NaOH solution with cold water continuously pouring on top of the flask. The acidic gases mainly CO_2 and H_2S are absorbed into the solution giving room in the evacuated flask for the minor non-condensable gases usually found in thermal fluids to concentrate to measurable levels. One flask was used for analysis of hydrogen (H_2), methane (CH_4), nitrogen (N_2) and oxygen (O_2). This was done using a Varian Sigma 300 gas chromatograph at Olkaria geochemistry laboratory. From the second flask, CO_2 and H_2S were analysed by titrating with HCl and mercuric acetate, respectively.
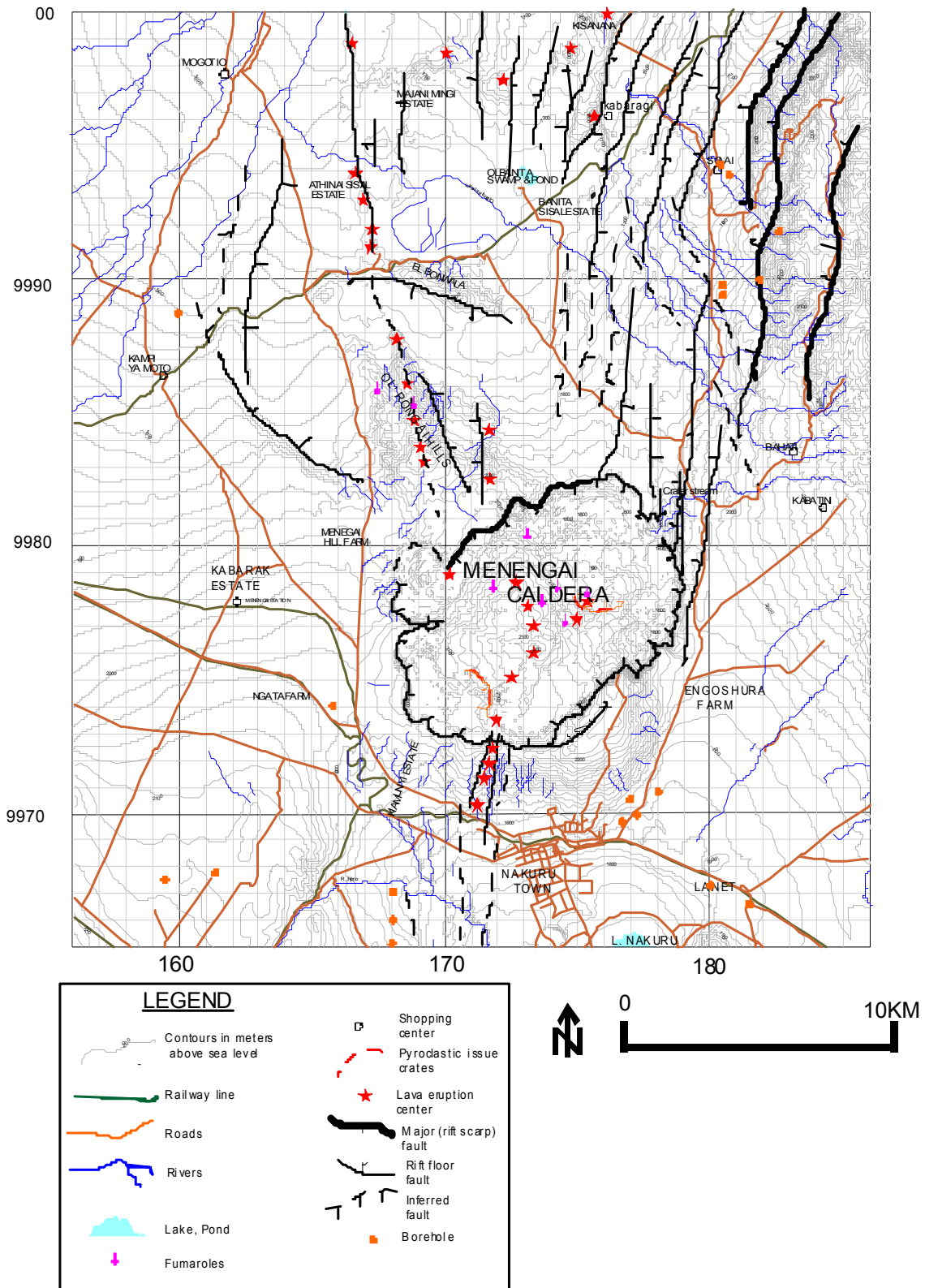
FIGURE 1: Fumarole and borehole locations in Menengai Prospect area

3.2 Soil gas survey

The survey was conducted along traverse lines running in an E-W direction. Sample points were located at an interval of 500 m except in some areas where the spacing was widened to 1000 m due to wider coverage required and low geothermal activity. The survey carried out involved measuring of CO_2, Rn in the soil gas as well as the ground temperatures measured at a depth of 0.7 m. All the measurements were done at the same point. The sample points for the soil gas survey are shown in Figure 2.

3.2.1 Carbon dioxide in the soil gas

The CO_2 gas was measured using an Orsat apparatus at a depth of 0.7 m below the surface. Gas samples were obtained by using a spike, which was equipped with a steel outer jacket to penetrate the ground to the desired depth. The spike was then removed and the outer jacket left inside the hole to allow for the sampling. A stopper and a hosepipe were fixed onto the mouth of the jacket and by using a hand operated vacuum pump, the soil air was driven into the analytical apparatus. The Orsat apparatus consist of absorption vessels, which measure about 100 ml and contain a 40% KOH solution for absorbing the acidic CO_2. The corresponding volume changes in the absorption vessel represent the corresponding amounts of the gases in volumes given as percent of the total gas.

3.2.2 Radon radioactivity measurement in soil gas

Radon radioactivity levels were measured in the soil gas and in fumarole steam by using a portable radon detector (emanometer). The soil gas was passed into the emanometer by using a hand-operated vacuum pump at a depth of 0.7 m below the ground using the same procedure as for CO_2 discussed above. The soil gas samples were collected at an interval of 500 m. Radon (Rn-222 and Rn-220) readings were recorded in counts per minute (cpm).

The soil gas sample containing the radon was forced into the decay chamber of the emanometer consisting of a cylindrical copper can. The walls of decay chamber are coated with zinc sulphide where the radon decays into other radioactive nuclides by emitting alpha particles. The alpha emissions are detected by a photomultiplier attached to the detector and the signals displayed by a rate meter. Three background counts were recorded at one-minute interval prior to introduction of sample into the emanometer. Upon introducing the sample, three more readings are taken at one-minute interval to give the total radon counts. Both the Rn-222 and Rn-220 (Tn) are detected by the emanometer but due to the difference in their half-lives, it is possible to differentiate between the two. Computations of the concentrations of both radioactive nuclides in the samples were done using computer software developed by GENZL for KPC.

3.3.3 Radon radioactivity measurements in fumarole steam

To sample the fumarole steam for the radon radioactivity and the percentage of CO_2 in the steam, the steam was condensed and the condensate trapped in a sampling flask. The dry gas was then driven into the radon emanometer by using a hand-operated vacuum pump just as is done for the soil gas sampling. The same method was employed for measuring the CO_2 in the steam using the Orsat apparatus.
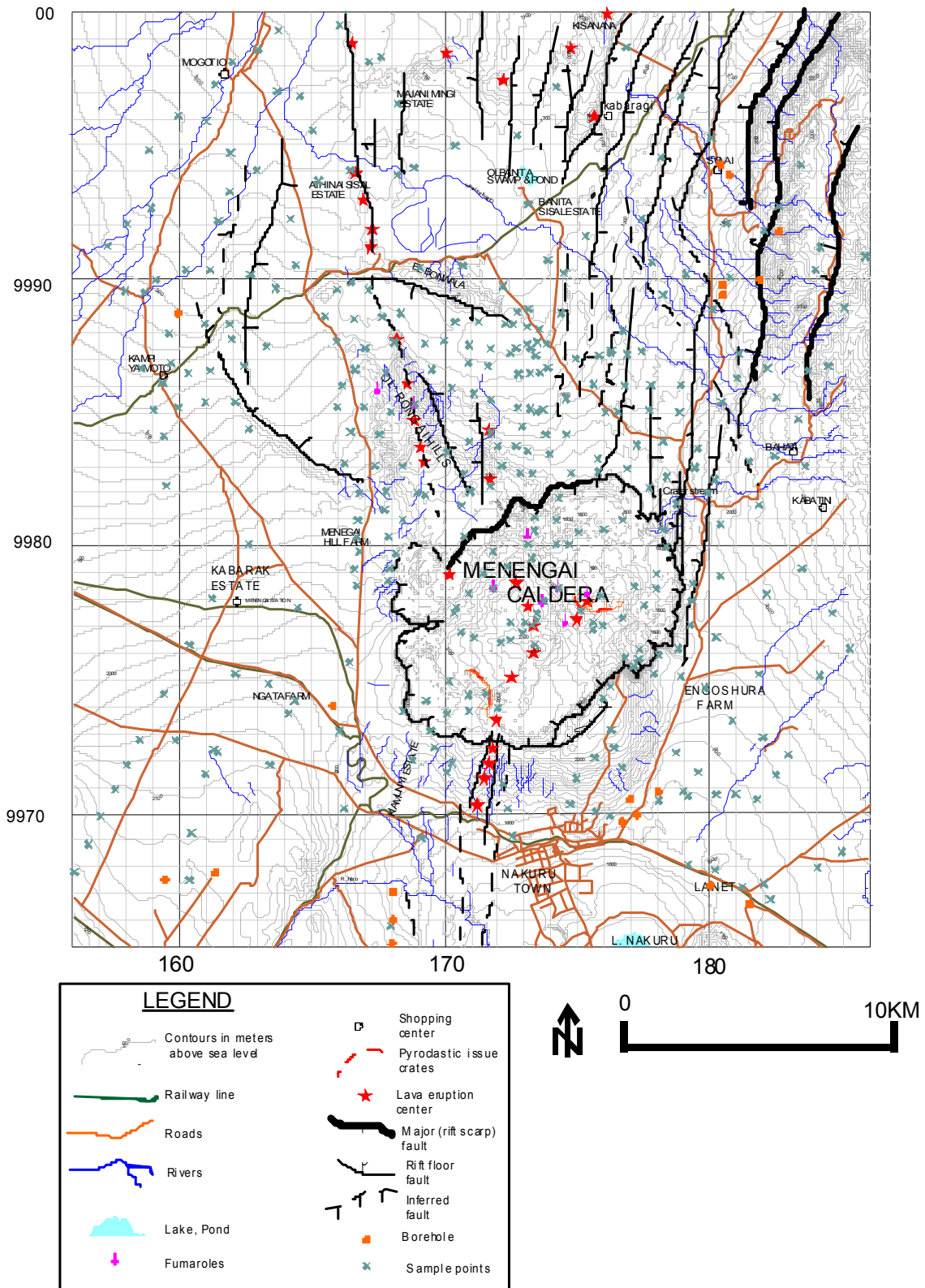
FIGURE 2: Soil gas survey sample points in Menengai Prospect

4. RESULTS

4.1 Fumarole gas analysis

The results of the chemical analysis of the fumarole gases collected are given in Tables 1, 2, 3 and 4. Only two samples gave complete gas analysis results and were the ones used for interpretation.

TABLE 1: Fumarole gas concentration in mmol/mol steam

Fumarole No.	Location	Sample Date	Temp °C	CO_2 mmol/mol	H_2S mmol/mol	H_2 mmol/mol	CH_4 mmol/mol	N_2 mmol/mol	O_2 mmol/mol
MF-1	E1724 N99759	29.1.04	60	0.509	0.1000	0.3	-	0.0354	0.013
MF-2	E1753 N9977	6.2.04	91.2	64.62	0.0076	0.0	0.006	0.0845	0.025

TABLE 2: Fumarole gas concentrations in mmol/Kg steam

Fumarole No.	CO_2 mmol/Kg	H_2S mmol/Kg	H_2 mmol/Kg	CH_4 mmol/Kg	N_2 mmol/Kg	O_2 mmol/Kg
MF-1	28.28	0.10	0.3	-	1.97	0.722
MF-2	3590.00	0.42	0.0	0.34	4.69	1.390

TABLE 3: Fumarole gas ratios

Fumarole No.	CO_2/H_2S	CO_2/H_2	H_2/H_2S	H_2/CO_2	CO_2/N_2
MF-1	282.8	94.25	3.0	0.011	14.4
MF-2	8547.6	-	-	-	764.8

TABLE 4: Fumarole gas geothermometry temperatures

Fumarole No.	TCO_2/H_2 °C	TH_2 °C	TH_2S °C	TCO_2 °C
MF-1	285.3	266.2	251.2	298.5
MF-2	-	-	265.5	371.6

4.2 Fumarole steam condensates

The chemical constituents analysed in the steam condensates are those which can be considered to be volatile enough to partition into the steam phase upon phase separation in a boiling system as is expected in an aquifer producing steam. Such elements include the soluble gaseous compounds such as CO_2, H_2S, F^-, and B, which are present in the geothermal steam. In addition, the concentration of other non-volatile elements like Cl^- and SO_4^{-2} was determined. The pH, TDS and the electrical conductivity were also measured in the steam condensate samples. The results are given in Table 5

4.3 Carbon dioxide and radon radioactivity in soil gas

The concentration of CO_2 in the soil gas in the surveyed area is given as a percentage of the total gas in the soil. It is possible that other acidic gases are likely to be absorbed together with CO_2 by KOH but their concentrations is out weighed by that of CO_2 assuming a magmatic source for the CO_2. CO_2 is considered to constitute over 90% of the geothermal gases. The results of the radon emanations were recorded in counts per minute (cpm) for both Rn-222 and Rn-220 and plotted in Figure 3.

TABLE 5: Fumarole steam condensate composition

| Fumarole No.	Temp °C	pH at 20°C	CO₂ ppm	H₂S ppm	Cl⁻ ppm	SO₄⁻² ppm	B ppm	F⁻ ppm	TDS ppm	Cond
MF-1	60	6.0	33	0.17	19.5	3.45	0.17	0.19	11	20
MF-2	94	6.0	38.5	0.176	24.14	5.1	0.07	0.96	20	50
MF-3	77	7.54	88	0.034	31.4	6.7	0.12	0.13	6	10
MF-4	81.2	5.8	143	0.17	15.62	7	0.14	< 0.1	4.0	10
MF-5	88.3	6.69	77	0.17	15.97	5.43	0.05	0.214	6	10
MF-6	84.6	6.7	33	0.74	16.33	6.74	0.2	< 0.1	5.6	10
MF-7	73.5	6.9	88	0.07	33	29	0.38	0.264	12	25
MF-8	90.1	6.9	220	0.034	34.1	8.6	0.14	1.64	8	15

Cond = conductivity given in μSM
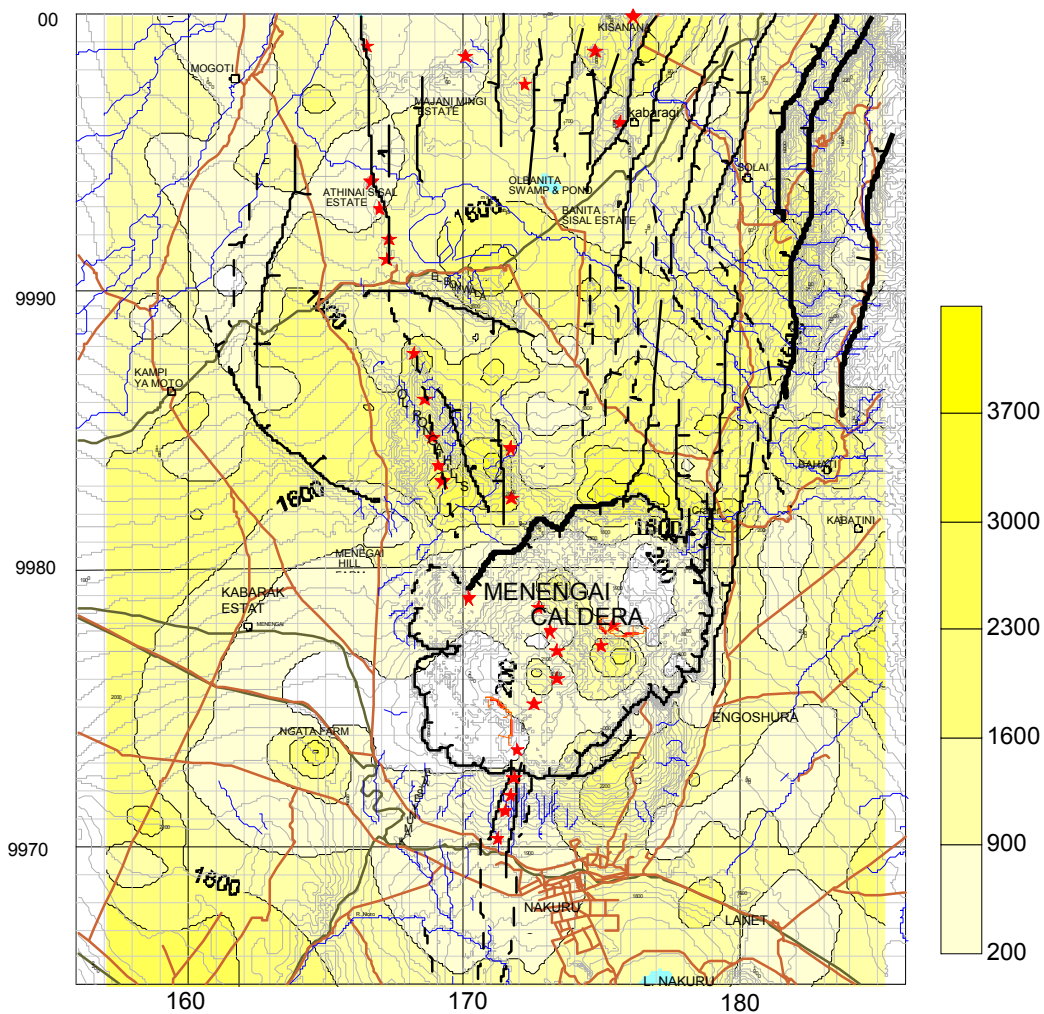
FIGURE 3: Radon radioactivity distribution in the Menengai prospect area

4.4 Carbon dioxide and radon radioactivity in fumarole steam

CO_2 and Rn-222 radioactivity were measured using the dry non-condensable fraction of the fumarole steam. The results are given in Table 6.

4.5 Borehole water

There are many water boreholes drilled in the area especially to the eastern part. All the boreholes were drilled for domestic water supply either for communities or for individual homesteads. Water samples were collected for chemical analysis and the results are given in Table 4.7. Majority of the boreholes in the western sector discharge water with elevated temperatures (above 30°C) while the ones in the south-eastern and southern parts discharge cold water.

TABLE 6: Rn-222 radioactivity and CO_2 concentration in fumarole steam

Fumarole No.	Location	Elevation (m)	CO_2 (%) vol.	Temp °C	Rn-222 (cpm)	Rn/CO2 ratio
MF-1	E 172400 N9975900	2160	15.1	60.0	1650	109.3
MF-2	E 175324 N 9977356	1992	25.6	94.0	12194	476.4
MF-3	E 171868 N 9977563	2081	16.7	77.1	2200	131.7
MF-4	E 169080 N 9984679	2016	48.2	81.2	3700	76.76
MF-5	E 167712 N 9985324	1896	43.8	86.1	2890	66.0
MF-6	E 173208 N 9979555	1908	32.6	84.6	16848	516.8
MF-7	E 173682 N 9977020	2106	18.3	73.5	1600	87.4
MF-8	E 174485 N 9976115	2098	24.6	90.1	1580	64.2

5. DISCUSSION

The area under consideration has very few fumaroles, most of which, occur within the Menengai caldera. However, a few weak fumaroles occur outside of the caldera in the north-western part of the prospect (Figure 1). The greater portion of the area shows little or no manifestations at all. This therefore, presents a problem in investigating geochemical indicators at this preliminary survey stage before thermal waters are obtained from deep wells.

It is against this background that the geochemical survey conducted in this area considered three sources of geochemical information to be able to understand the chemical and physical characteristics of the geothermal reservoir below Menengai caldera and surrounding areas. The available information is therefore derived from the chemistry of the fumarole gases (where applicable) and fumarole steam condensates; borehole water, and from soil air composition, particularly the concentration of radon radioactivity and carbon dioxide emission.

5.1 CO_2 distribution in the soil gas

High CO_2 values (>2.5%) are found at a narrow belt running in a NW-SE trend between grid lines Northings 9982000 to Northings 9910000 and Eastings 175000 to Eastings 184000 and also between Northings 9990000 and Eastings 158000 to Eastings 165000 (Figure 3). Other areas exhibit low values of <1%. The distribution of CO_2 in the soil gas is also controlled by the competence of the formation and other local sources of CO_2. Dealing with CO_2 anomalies especially in the Rift Valley should be treated with caution due to availability of localized sources of this gas as suggested by Darling et al. (1995).

TABLE 7: Borehole water analytical results

Date sampled	Location	Temp °C	pH at 20°C	CO_2	H_2S	SiO_2	SO_4	Cl	Na	Ca	K	Mg	F	Cond	TDS
12/3/04	E166346 N9973021	48.2	7.82	254.1	1.02	40.8	143	34	141	4.5	24	0.3	18	743	357
12/3/04	E168511 N9964610	39.2	7.7	147.1	0.13	30.7	14.2	18	44.3	0.8	20	0.4	4	440	215
12/3/04	E168670 N9965090	35.1	9.1	243.0	0.34	37.4	18.9	20	143	2.3	9	0.1	11	725	357
12/3/04	E1685890 N9963712	39.2	7.7	186.0	0.14	80.4	9.13	28	52	14	20	3	4	487	212
12/3/04	E168320 N9965694	37.5	8.7	116.4	0.41	16.8	14.3	17	48.5	7.2	17	1.8	5	415	192
19/3/04	E162001 N9966512	21.7	6.5	111.7	2.72	42.7	10.3	16	42.7	4.4	11	0.8	3	302	113
19/3/04	E160486 N9966214	21.7	6.7	206.0	2.0	36.4	7.3	16	30.1	5.3	11	0.8	3	455	190
5/2/04	E179955 N9966236	29.0	7.3	181.5	0.17	80.0	10.7	34	75.5	20	19	1.9	2	460	305
5/2/04	E180656 N9965524	27.0	8.2	176.0	0.3	55.0	29.4	34	17.4	16	9	1.6	3	30	16
3/2/04	E180163 N9989003	30.0	7.5	214.0	0.18	48.0	7.9	16	10.7	4.9	2	0.8	6	410	272
3/2/04	E181474 N9989679	40.0	8.2	193.0	0.1	75.5	9.1	35	46	2.3	4	0.4	8	480	359
3/2/04	E1822160 N9991512	20.0	6.8	55.0	0.18	116	4.2	17	45.8	10	18	1.8	1	150	105
3/2/04	E180350 N9993677	23.0	6.7	165.0	0.2	55.0	8.4	30	47.1	8.3	7	1.4	1	280	186
3/2/04	E180147 N9994015	26.0	8.1	24.5	0.18	48.0	21.9	62	100	16	4	0.5	7	810	532
3/2/04	E180147 N9994015	26.0	6.5	160.0	0.18	60.0	5.21	31	45.7	14	9	2.2	1	340	229
2/2/04	E176626 N9969390	35.3	8.5	270.0	0.27	30.2	14.0	33	64.4	5.8	6	0.3	7	640	422
2/2/04	E177434 N9969735	29.5	7.8	236.0	0.35	28.0	10.7	15	25.2	6	5	0.5	5	520	342
2/2/04	E180988 N9970889	29.0	7.1	176.0	0.88	30.0	6.0	19	59.3	12	13	1.1	2	360	234
2/2/04	E180988 N9970889	29.0	6.9	171.0	0.9	93.9	5.1	24	50.9	13	12	1.6	2		

5.2 Radon concentration in soil gas

From the results of the absolute values of Rn-222, the northern and north-western parts of the surveyed area show the highest concentrations (Figure 4). High radon values could be indicative of enhanced permeability where the Rn-222 passes to the surface rather fast before disintegrating into daughter products. However, the release of radon is dependent on other factors, which include the degree of rock fracture and the ability of the ground water to circulate through such rocks. Percolating ground water removes radon from fractured porous rocks by transport rather than diffusion mechanism. From the properties of radon described above, under high temperature conditions as would be expected in a geothermal reservoir, the radon will partition in the steam phase and be transported to higher elevations through permeable zones. There are however other alpha emitting isotopes but their half-lives are very short to give interference to Rn-222 like PO-214, which has a half-life of 0.000158 seconds.

Tanner (1975) calculated that the maximum mobility of Rn-222 in soil would be about 42 m. The alpha particle (α) which is emitted by Rn-222 is a Helium nuclei (^{4}He) which has a mobility of <50 mm in air and only a few microns in rocks. It means therefore that for an alpha particle to be detected by the radon emanometer, the Rn atom must be within about 50 mm of the detector. If the Rn-222 detected in the high concentration areas mentioned above is coming from a deep geothermal reservoir, then the areas to the north and north-western parts (Figure 4) would be areas of high permeability and therefore good prospects for further investigations. Other areas especially the south and south-eastern have relatively low absolute Rn-222 values averaging below 200 cpm and are considered of little interest. Most of the surveyed area has average Rn-222 values ranging from 2000-3700 cpm. The anomalous values may be taken to be those above the threshold reading (upper limit of the background value). Taking 1000 cpm to be the background value for Rn-222 in this area and the threshold to be twice the background, then Rn-222 values exceeding 2000 cpm are considered anomalous.

5.3 Radon-222/CO$_2$ ratio in the soil gas

The source of Rn-222 can be either magmatic where the uranium accumulates at the late stages of differentiation or from any other source containing radium the immediate precursor of Rn-222. When Ra-226 is present in the hydrothermal system, it indicates that the hot water percolates through the host rock thereby dissolving Rn-222, which is produced from alpha decay of the Ra-226. Upon heating up of the water the Rn-222 partitions into the steam phase and is transported to the surface through permeable zones. Due to its short half-life, Rn-222 has to travel for long distances within a relatively short period to be detected on the surface. Similarly, CO$_2$ have to travel through a relatively permeable zone to avoid dispersion and subsequent dilution for it to be detected in high concentrations. CO$_2$ may also originate from other sources like organic sources, which are likely to give false impressions of a geothermal source. The ratio of the two gases would be a good indicator of the magmatic source of the gases since the ratio is not expected to change if they are from the same source. High values of these ratios are found towards the north and north-western parts of the caldera wall (Figure 4). The values are highest between grid Northings 9982000-9985000 and grid Eastings 165000–180000. These areas apparently coincide with high CO$_2$ and high Rn-222 absolute values. The north-western parts of surveyed area (around Kampi Ya Moto), which shows extremely high absolute values of both Rn-222 and CO$_2$ has the lowest value of this ratio. This would imply presence of an external source of the CO$_2$ rather than from the geothermal activity. Other possible sources of CO$_2$ in this area could be from organic life since it is an inhabited area and considering the depth of sampling this could be a possibility. A mantle source of CO$_2$ as suggested by Darling et al. (1995) is another possibility due to intense faulting in the area. If a mantle source is inferred due to intense faulting, then the faults should be deep seated.
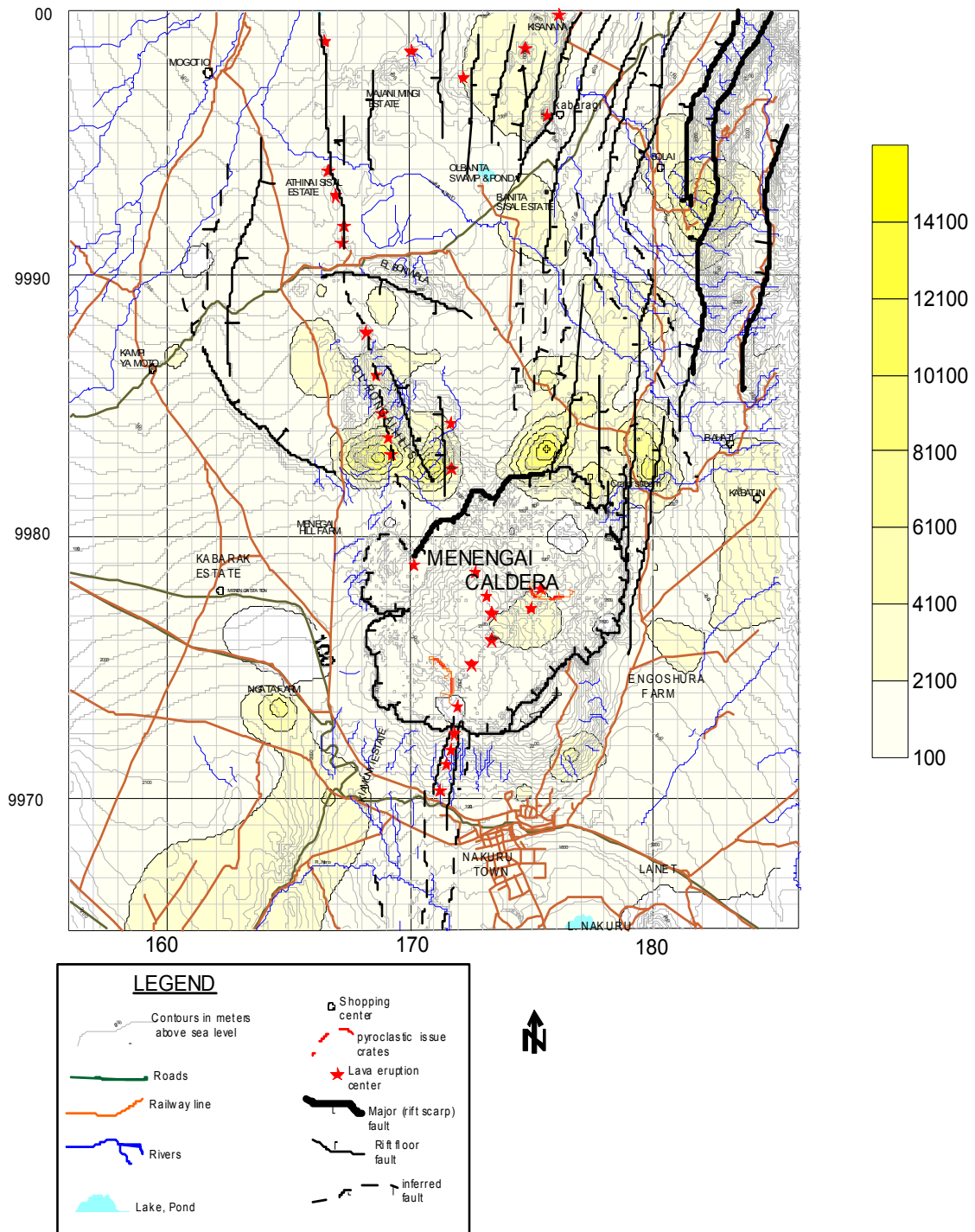
FIGURE 4: Radon/carbon dioxide ratio distribution in soil gas in the Menengai prospect

5.4 Radon-222/CO$_2$ in fumarole steam

The results of the fumarole steam Rn-222 and CO$_2$ are from the non-condensable fraction of the fumarole sample are given in Table 6. It is also possible for other gases present in the steam to be present in the non-condensable fraction of the steam (e.g. H$_2$S) but their concentrations are very low compared to those of CO$_2$. By assuming a geothermal origin of both Rn-222 and CO$_2$ in the fumarole steam, the ratio Rn-222/CO$_2$ would be a good indicator of fumaroles associated with potential

geothermal reservoirs and zones of good permeabilities, where both gases flow relatively fast. Among the sampled fumaroles, fumarole MF-6 located inside the caldera at the north-western parts, recorded the highest reading of 517 followed by fumarole MF-2 also located in the central part of the caldera, with recorded ratio of 476.4. Fumarole MF-8 also located inside the caldera but to the south of both fumaroles, MF-2 an MF-6 gave the lowest ratio value of 64.2. The fumaroles inside the caldera gave Rn-222 values ranging from 1,580-16,848 cpm.

The relatively high values recorded for fumaroles MF-2 and MF-6 indicate the two fumaroles are possibly tapping from a deep magmatic source. Though the gas chemistries of the steam did not have any H_2 for these fumaroles, only MF-2 recorded H_2S values of 0.42 mmol/kg steam. The low gas concentration of the steam from this fumarole could be due to dispersion and dilution of the gases as they migrate to the surface due to the cover of post-caldera volcanic products. These two fumaroles are located inside the outer caldera and coincide with the area, which recorded some of the highest values for Rn-222, CO_2 and Rn-222/CO_2. This could be a good indication of a potentially attractive site for further investigation.

5.5 Fumarole gas concentrations

The fumarole steam was analysed for the major gases associated with geothermal activity (CO_2, H_2S, H_2, CH_4 and N_2) and the results indicate low values for the reactive gases for most of the fumaroles sampled. Most of these fumaroles were issuing at extremely low pressures and it was quite difficult to obtain condensate samples from the fumaroles. From the analytical results obtained, such weak fumaroles have compositions indicating high air/steam ratios. Such high ratios are indicative of shallow surface waters being locally heated and the bulk composition of the gases is composed of atmospheric air.

The gas contents of fluids present in areas of high permeability and close to a hot geothermal fluid upflow are expected to be high especially with regards to the reactive gases like CO_2, H_2S and H_2. When the fluid travels for long distances there is a tendency for it to be depleted of these gases through possible reactions between the gases and the minerals forming the reservoir rocks. On the other hand, the concentration of N_2 in the fumarole steam could be an indicator of admixture with gas originating from the atmosphere. This could be taken to imply mixing of shallow ground waters with deep geothermal fluids. The N_2 gas is considered largely to be derived from air and then introduced into the geothermal system. There are possibilities of N_2 accumulating in the rocks from organic life. In terms of solubility of the common geothermal gases in water the following order prevails:

$$H_2S > CO_2 > N_2 > H_2 \hspace{3cm} \text{(Giggenbach, 1980)}$$

The gas concentrations in the discharged steam are controlled by temperature dependent fluid-mineral equilibrium in the reservoir or at least in the aquifer where the steam is being formed. The H_2 gas being the most reactive and least soluble in water is a good indicator of higher underground temperatures. The H_2 content of the deep geothermal water below the zone of flashing is possibly controlled by the temperature dependent equilibrium reaction with water, sulphates dissolved from the reservoir rocks and sulphides through a possible reaction shown in equation 1 below.

$$2H^+ + 4H_2 + SO_4 \longrightarrow H_2O + H_2S \hspace{3cm} (1)$$

High H_2 concentrations in the discharged steam would indicate proximity to a high temperature resource. There is only one sample (MF-1) with measurable quantities of H_2 with a value of 0.3 mmol/kg steam. This fumarole is located inside the caldera.

In the absence of H_2 and H_2S, CH_4 is considered to be the best indicator of reservoir characteristic assuming no biogenic source of the gas. Again only one fumarole (MF-1) had measurable concentration of CH_4 with a value of 0.34 mmol/kg steam.

Gas ratios from the fumarole steam have been calculated and presented in Table 3.3. From the gas solubility mentioned above, it is observed that in a boiling system the least water-soluble gases are released faster but the more soluble ones are released slowly. From this argument, close to the upflow of the hot geothermal fluids the ratio of a less soluble to that of a more soluble gas should be high and should decrease in the direction away from the upflow. There are only two gas samples whose data can be used in a comprehensive gas interpretation and are both located in the caldera. Fumarole MF-1 gave a CO_2/H_2S ratio value of 282.8 while fumarole MF-2 gave a value of 8547.6. This would imply that fumarole MF-2 is located closer to a hot geothermal source possibly an upflow and the fluids may be considered to be outflowing towards MF-1.

Presence of some hydrothermal minerals like epidote may reduce the concentration of H_2S gas where the H_2S would react with the mineral to precipitate prehnite at deep levels through a possible reaction shown in equation 2 below.

$$8 \text{ epidote} + H_2S + 14H^+ \longrightarrow 8 \text{ prehnite} + Fe^{+2} + SO_4^{-2} + 4H_2O \tag{2}$$
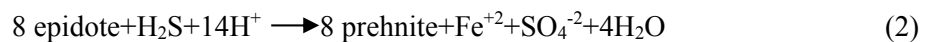
This would also affect the gas ratios involving H_2S since the concentration of H_2S in the fumarole steam is not representative of the reservoir H_2S. Darling et al. (1995) suggested a mantle source of CO_2 under the Rift Valley, which would be expected to enter the geothermal system anywhere within the rift. If this would be the case, then the concentration of CO_2 would not be expected to decline away from the source of the geothermal fluids while other gases would.

5.6 Geothermometry

Prediction of sub-surface temperatures in this area is compounded by the lack of any source of geothermal water issuing to the surface. There are many drilled water boreholes at shallow depth, which are relatively cold. A few boreholes situated to the north and north-western parts have temperatures above 30°C. These cannot be convincingly used for subsurface temperature calculations due to lack of sufficient water-rock interactions and thus have not attained equilibrium. This leaves us with only the gas based temperature indicators to rely on. Several gas-based geothermometers have been developed with the most commonly used being the CO_2, H_2 and H_2S. These are considered the best to use since the reactions controlling their concentrations seem to approach equilibrium over a large temperature range.

The temperature inferences made here are based on only two fumarole gas samples and therefore the conclusions arrived at are tentative.

The geothermometry functions used in this report are from Arnorsson and Gunnlaugsson (1985) based on the concentration of CO_2, H_2S and H_2. The following equations were used to calculate the temperatures:

$$TH_2S°C = 246.7 + 44.81*mH_2S \tag{3}$$

where TH_2S is the temperature using H_2S gas and mH_2S is the concentration of H_2S in mmol/Kg steam

$$TCO_2/H_2°C = 341.7 – 28.57*\log(CO_2/H_2 \tag{4}$$
where: TCO_2/H_2 is the temperature using the ratio CO_2/H_2 where the concentrations are in Mmol/Kg of steam.

$$TH_2 = 277.2 + 20.99\text{Log}(H_2) \tag{5}$$

$$TCO_2 = -44.1 + 269.25\text{Log } mCO_2 – 76.88(\text{Log}mCO_2)^2 + 9.52(\text{Log}mCO_2)^3 \tag{6}$$

Only two samples from MF-1 and MF-2 were conclusively used in geothermometry. All the other fumaroles had no complete chemical data with most of them having no H_2 and H_2S gas content in their

steam discharge. This was largely as a result of the very high air to steam ratio in these discharges. The temperatures calculated for MF-1 ranged from 251.2-298.5°C calculated for T_{H2S} and T_{CO2} respectively while fumarole MF-2 had values ranging from 265.5–371.6°C calculated for T_{H2S} and T_{CO2} respectively (Table 4). Fumarole MF-1 gave a TH_2 temperature of 266.2°C. The temperatures calculated using CO_2 geothermometer gave relatively high values for both fumaroles. The relatively high value given by this geothermometer may be due to probable injection of CO_2 probably from recent volcanic activity in the caldera. CO_2 may also originate in the reservoir from equilibration with a mineral buffer.

From the temperature estimation using the gas geothermometers, it is clear that the reservoir temperatures beneath Menengai caldera are over 250°C taking into consideration that both H_2 and H_2S gases are representative.

5.7 Fumarole steam condensate chemistry

Fumarole condensate samples were analysed for pH, TDS, CO_2, H_2S, Cl^-, F^-, B, SO_4^{-2} and the electrical conductivity (Table 5). All the condensates gave pH values ranging between 5.8 and 7.5 measured at 20°C. Low pH values imply the fluids contain high concentrations of acid gases, which form the acidic condensed water. Most of the acidic emanations are mainly magmatic with large amounts of volatile components such as H_2O, HCl, SO_2, H_2S, CO_2 and H_2. However, chemical properties of magmatic emanations collected on the surface are expected to be different from those under the ground on account of severe distillation on the surface caused by depression of pressures and temperatures.

Volatile chemical constituents dissolved in the deep water would be transported to the surface with steam from greater depth through vaporization. High volatility elements like F^-, B, NH_3, arsenic (As) and mercury (Hg) would therefore be expected to dominate in the steam composition in addition to the geothermal related gaseous elements (CO_2, H_2S and H_2). High concentration of volatiles in a steam condensate would be proportional to temperatures of the steam source.

All the condensate samples gave F^- values ranging from 0.1-1.64 ppm (Table 5) while the B values ranged from 0.05-0.38 ppm for fumaroles MF-5 and MF-7 respectively. The relatively high F^- content in the steam condensate may indicate deep crustal water circulation while at the same time the relatively high B values in the condensate may indicate high formation temperatures. Boron is considered a mobile component since it does not take part in rock forming reactions and its concentration in the geothermal fluids is controlled by the leaching rate from the reservoir rocks. At high temperatures (>250°C) boron is expected to partition into the steam phase (Arnorsson, pers. comm.) and if boiling is occurring in the reservoir, then the temperatures should be more than 250°C. The difference in boron concentration of different fumarole steam condensates would only be due to the compositions of the source rocks.

The Cl^- content of the condensate samples from fumaroles MF-4 and MF-8 ranged from 15.6–34.1 ppm respectively. Very high Cl^- values in a steam condensate would represent a water dominated system while extremely low values would be expected to originate from a vapour dominated system since chlorides are not known to partition into steam phase at any temperatures.
The total dissolved solids measured for the condensates range from 4-20 ppm measured for fumarole MF-4 and MF-2 respectively. High TDS values may result from:

  i.   Deep circulation of the geothermal fluids enhancing water-rock interaction,
 ii.   Long residence time in the reservoir allowing for water to dissolve more solutes and
iii.   High ambient temperatures, which is common in the Kenyan rift.

From the measured TDS values, fumarole MF-2 gave the highest reading suggesting possibly deep circulating fluids or long residence time of the waters in the reservoir.

The electrical conductance of the condensates was measured and the values range from 10–50 mΩcm^{-1} for fumarole MF-3, MF-4, MF-5, MF-6 and MF-2 respectively. The highest conductivity readings coincide with the highest TDS readings. These values are slightly lower than those measured in the Greater Olkaria geothermal field. In Olkaria field fumarole steam condensates have TDS ranging from 30–264 ppm but with an average of 60–100 ppm. The lowest value of 10 ppm recorded for fumaroles MF-3, MF-4, MF-5 and MF-6 suggest a dilute fluid around this area which could result from modification of the deep original geothermal fluids through possible mixing reactions (could result from dilution processes). High values are recorded at fumarole MF-2 and this could probably suggest deep geothermal fluids discharge around this area.

H_2S and CO_2 are some of the primary gases associated with volcanic gaseous emissions and are therefore usually found in geothermal reservoir fluids. The concentration of H_2S is mainly affected by oxidation reactions while CO_2 is largely affected by biogenic inputs. When an upflowing deep geothermal fluid mixes with shallow ground waters or steam condensates, oxidation of H_2S occurs and this lowers the content of this gas in the analysed portion (condensate or gas). The dissolved H_2S gas content of the condensates range from 0.034–0.74 ppm measured in fumarole MF-3 and MF-6 respectively. These values are again lower than those from the Olkaria Domes field where the measured H_2S levels range from 0.1–1.46 ppm. The very low concentrations of this gas suggest a large influence of shallow circulation ground water and or condensates. The CO_2 measured in the steam condensates ranged from 33–220 ppm for fumarole MF-1 and MF-8 respectively. These values are generally higher than the values recorded in Olkaria, which has values ranging from 50-60 ppm. Such high values of CO_2 could imply good permeability where the dissolved gas reaches the surface relatively fast avoiding any reactions, which may affect its concentration. The level of CO_2 in the condensate may be enhanced in a field where calcite ($CaCO_3$) is found, at relatively shallow levels where the steam dissolves the CO_2 as it ascends to the surface. The concentration of CO_2 is mainly controlled by the reactions shown in equations 3.7 and 3.8 below.

$$Ca^{+2} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O \tag{7}$$

and

$$HCO_3^- + H^+ = CO_2(aq) + H_2O \tag{8}$$
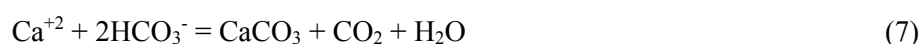
5.8 Borehole water chemistry

Most of the water sampled from boreholes to the south and eastern parts of the area discharge cold-water with little dissolved solids. Some of the water from some boreholes is suitable for domestic use. However, some boreholes to the western part discharge warm water with some recording up to 40°C. Temperatures of about 80°C have been calculated for some borehole water samples using the silica geothermometer assuming a boiling spring model as is described in the speciation programme WATCH by Arnorson et al. (1990) and Bjarnason (1994). However, due to the shallow depth where the water is discharging, the data needs a lot of caution when making subsurface inferences.

5.9 Proposed exploration well sites

To be able to pinpoint areas of high potential in terms of geothermal resource development, several factors have been considered bearing in mind the geochemical exploration methods employed. Rn-222 radioactivity have been used in this survey to infer possible zones of high permeabilities and also areas of geothermal potential by assuming that the Rn-222 gas was being carried in the geothermal steam. Similarly, the CO_2 survey in the soil gas was conducted with the same assumption. This was in addition to the study of the few available fumarole samples in this prospect.

It would be inaccurate to use the concentration of a single component to make a decision to commit a field for exploratory drilling. Areas with coinciding anomalies of Rn-222, CO_2 and Rn-222/CO_2 ratios, supported by fumarole steam chemistry data are here considered sites for exploration drilling.

6. CONCLUSIONS

1. There exists a geothermal resource in this area possibly underneath the Menengai caldera and immediately to the north and northeast with reservoir temperatures >250°C as deduced from gas geothermometry.

2. The high values of carbon dioxide measured in the north and north-western parts of the caldera floor suggest that the area has high geothermal potential.

3. From chemical data obtained during this study, the area in the south and south-eastern portions of the caldera floor is not attractive.

7. RECOMMENDATIONS

It is recommended that three deep exploratory wells be drilled in Menengai as indicated in the proposed drill sites (Figure 5).

(a) MW-1: The proposed drill site coordinates 173000 E and 9978000 N is proposed as a priority site for an exploration well for the following reasons:

(i) The area gave anomalously high Rn-222 counts for both the soil gas and in the fumarole steam, which would infer good permeability and possibly a high temperature geothermal reservoir.
(ii) The high Rn-222 anomaly coincides with high CO_2 values in this area.
(iii) The Rn-222/CO_2 ratio is also high implying that the CO_2 emanating from this zone could be of magmatic origin .
(iv) Gas chemistry indicates the caldera floor to be the hottest with temperatures of over 250°C.

(b) Well MW-2: A second drill site has been proposed at approximate coordinates 168000 E and 9984000 N (Figure 5). The site is located outside the caldera floor to the north-western part near Ol'rongai hills. The site would be useful in testing the occurrence of a geothermal system as indicated by the high radon and CO_2 values.

(c) Well MW-3: A third drill site has been proposed at approximately 175500 E and 9983000 N (Figure 6). This area is in the north immediately adjacent to the caldera wall. The site exhibits high values of both radon and CO_2.
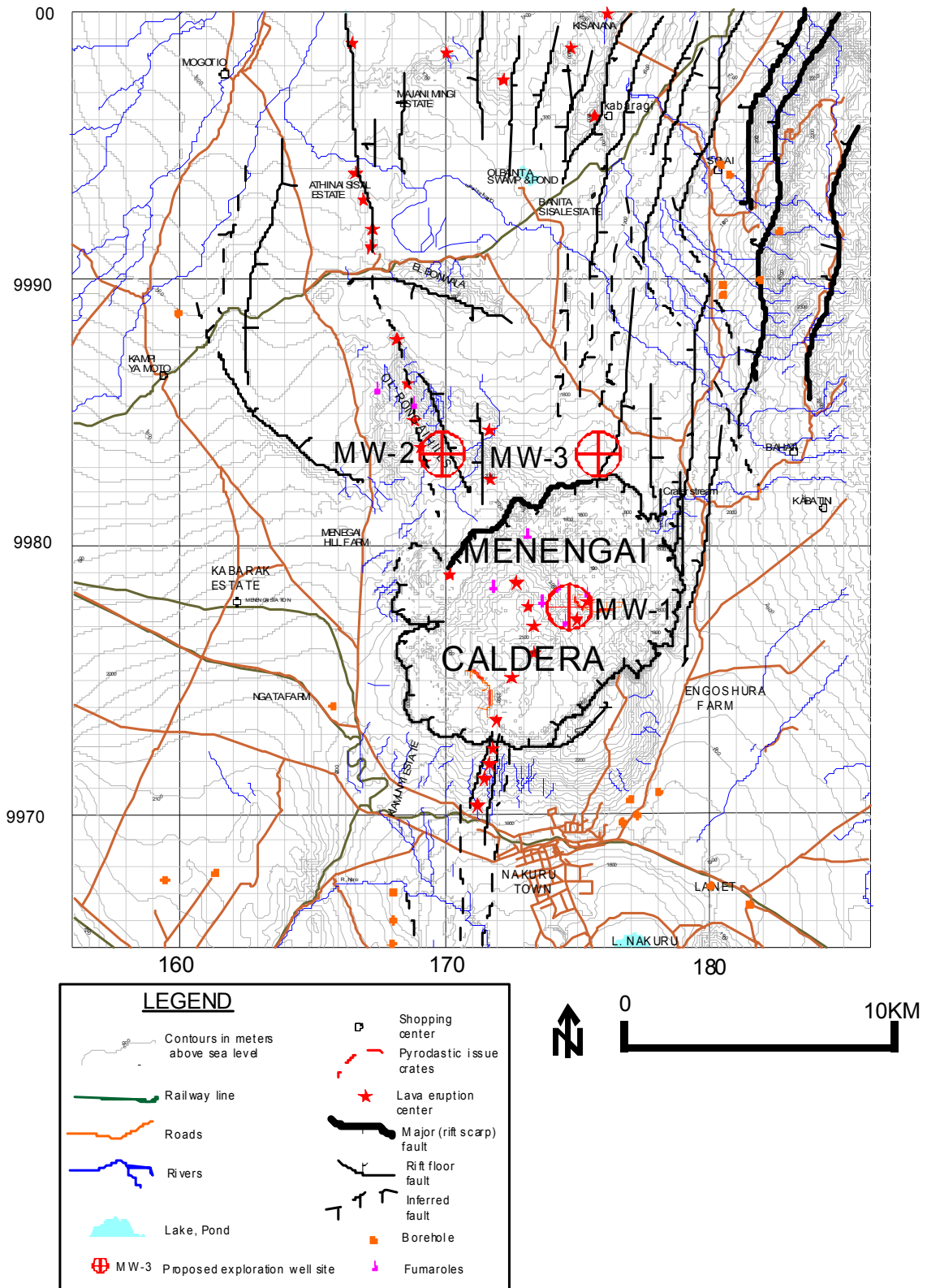
FIGURE 5: Map of Menengai prospect area showing the locations of the proposed drill sites based on geochemical studies

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