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INTRODUCTION TO GEOCHEMICAL MAPPING

Jeremiah Kipng'ok and Isaack Kanda
Geothermal Development Company,
P.O. Box 17700-20100,
Nakuru
KENYA
jkipngok@gdc.co.ke, ikanda@gdc.co.ke

ABSTRACT

Geochemistry plays a relatively crucial role in the exploration for geothermal resources and subsequent utilization. Its major contribution in geothermal resource assessment includes; estimation of subsurface temperatures, determination of the origin of the waters and flow patterns within the reservoir. The major tools used in geochemical mapping are water and gas. Geothermal waters have been classified with respect to their anion and cation constituents into alkali-chloride water, acid sulphate water, acid sulphate-chloride water and bicarbonate water. This paper discusses sampling and analyses of fumaroles and hot springs, soil gas survey, geochemical data interpretation.

1. INTRODUCTION

Geothermal systems can be defined and classified on the basis of their geological, hydrological and heat transfer characteristics. Active geothermal systems consist of hot fluid and hot rock within the upper part of the Earth's crust. The fluid is, for the most part or solely, meteoric water or seawater by origin, or a mixture thereof. Since the thermal energy of the earth crust is stored in large rock masses, a working fluid (water) is needed to carry and transfer this heat to the surface.

Generally, geothermal systems develop by deep density-driven convection of ground water. Yet, in some systems of relatively low temperature the convection may be driven by hydraulic head only. The water convection transports heat from the deeper to the shallower parts of geothermal systems. The heat source may be a magma intrusion (in volcanic geothermal systems) or the hot rock at the roots of the convection cycle (in non-volcanic geothermal systems).

Geothermal water can be broadly defined as ground water which has a temperature appreciably higher than that of the local average annual air temperature. Generally the geothermal water of an area contains large concentrations of dissolved minerals, such as sodium, calcium, sulphate, chloride, or silica higher than that of the local non geothermal ground water. The water warms as it descends, possibly along fault zones that overlie the magma chamber, until it absorbs enough heat to become lighter than overlying water. The warm water then rises to the surface. The mechanism for the circulation of the water is the same, regardless of whether the water becomes heated by the geothermal gradient or by the buried, cooling magma.
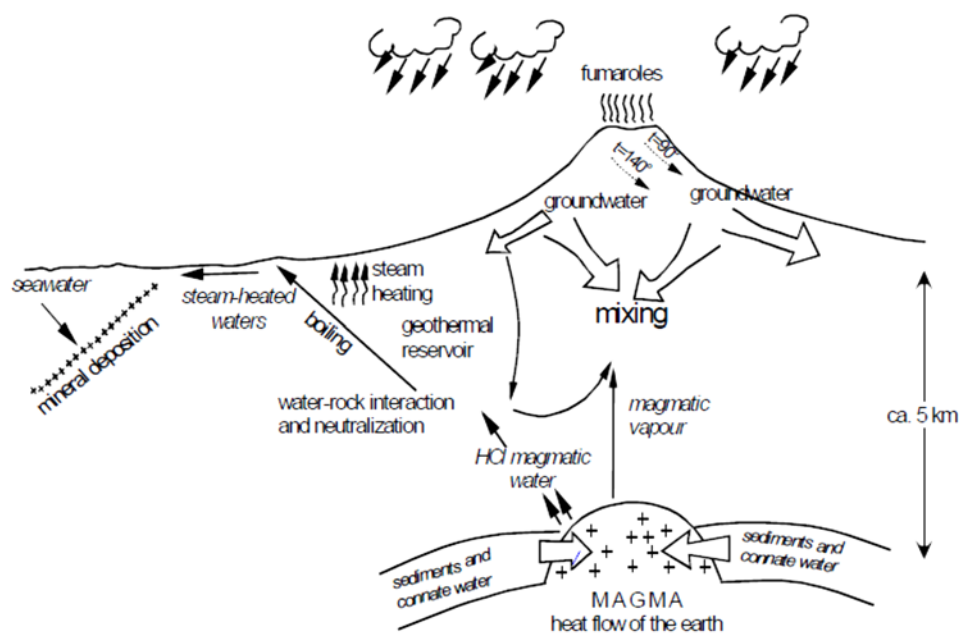
FIGURE 1: Diagram displaying geothermal fluid origin and flow pattern

2. WHY GEOCHEMICAL EXPLORATION?

Geothermal fluids rising to the surface include both hot water and steam with dissolved solutes and gases. They may be discharged from hot springs, fumaroles, soil and wells. The source of the dissolved constituents in the geothermal fluids is the rock with which the deep ground water has reacted and constituents present in the parent water. In the case of volcanic geothermal systems, the magma heat source may also supply chemical constituents to geothermal fluids through its degassing. The chemical composition and isotope ratios of geothermal fluids provide important information about the geological, chemical and hydrological characteristics of geothermal systems. An understanding of these characteristics is essential for the exploration and development of geothermal resources and the environmental impact of their utilization (Truesdell, 1976; Fournier, 1977; Arnórsson et al., 2000).

Information gathering on the surface thermal manifestations, such as springs, shallow wells or natural artesian etc. and their physical and chemical characteristics is of primary importance in geothermal energy exploration. The major goals of geochemical exploration are to obtain the subsurface composition of the fluids in a geothermal system and use this to obtain information on temperature, origin, and flow direction, which help in locating the subsurface reservoir. Equilibrium speciation is obtained using speciation programs and simulation of processes such as boiling and cooling to get more information to predict potential deposition and corrosion. Environmental effects can be predicted and the general information is used as a contribution to the model of the geothermal system. This is one of the lowest cost exploratory techniques and is a useful starting point in any hydrothermal exploration program.

3. CLASSIFICATION OF GEOTHERMAL WATERS

It has proved difficult to obtain a genetic classification of subsurface waters (Ármannsson and Fridriksson, 2009), since water tends to flow away from its point of origin and undergo water-rock interaction during its travels making it increasingly difficult to decipher its origins.

According to White (1986), subsurface waters can be classified as follows based on their origin: meteoric water, which circulates or has recently been circulating in the atmosphere, co-existing with near-surface, uncemented sediments, can circulate in subsurface rocks and dissolve constituents; ocean water, which is partly evaporated products of meteoric water; evolved connate water, which forms in young marine sediments; metamorphic water, which is contained in or driven from rocks undergoing metamorphic dehydration reactions; magmatic water is derived from oceanic and evolved connate waters subducted along with oceanic crust into the mantle, and; juvenile water, which is classified as water that has never circulated in the atmosphere.

Ellis and Mahon (1977) classified geothermal water into four categories based on major ions: (i) Alkali-chloride water which has a pH 4-11, least common in young rocks. These are mostly sodium and potassium chloride waters although in brines Ca concentration is often significant; (ii) Acid sulphate waters which arise from the oxidation $H_2S \rightarrow SO_4$ near the surface and most of its constituents are dissolved from surface rock. Thus such water is generally not useful for prediction of subsurface properties; (iii) Acid sulphate-chloride water which may be a mixture of alkali chloride water and acid sulphate water, or it can arise from the oxidation $H_2S \rightarrow SO_4$ in alkali-chloride water or dissolution of S from rock followed by oxidation. Sulphate-chloride waters need not be very acid and may then reflect' subsurface equilibria and be used for prediction of subsurface properties; (iv) Bicarbonate water which may derive from CO_2 rich steam condensing or mixing with water, it is quite common in old geothermal waters or on the peripheries of geothermal areas in outflows. They are commonly at equilibrium and may be used to predict subsurface properties. A good way of distinguishing between the differences between the different types of geothermal water is the use of the chloride-sulphate-bicarbonate ternary diagram described by Giggenbach (1991).

As discussed by Ármannsson and Fridriksson (2009), it is possible to deduce the properties of subsurface water from the chemical composition of water collected at the earth's surface. The dissolved constituents of geothermal water to some degree originate in the original meteoric or oceanic water. However, water-rock interactions and sometimes additions of magmatic gases will further modify geothermal solutions. The dissolved components are divided into rock forming constituents, e.g. Si, Al, Na, K, Ca, Mg, Fe, Mn and incompatible constituents, e.g. Cl, B, Br. Products of geothermal alteration are controlled by temperature, pressure, chemical composition of water (e.g. CO_2, H_2S), original composition of rock, reaction time, rate of water and steam flow, permeability and type of permeability and these products in turn control the chemical composition of the fluid.

Some of the effects are that the silica concentration depends on the solubility of quartz/chalcedony, temperature dependent Al-silicate ion-exchange equilibria control Na/K, Na/Rb ratios, pH is controlled by salinity and Al-silicate equilibria involving hydrogen and alkali ions, Ca^{+2} and HCO_3^- concentrations depend on pH and CO_2 concentration because of equilibrium between the fluid and calcite, F^- and SO_4^{-2} concentrations are related to that of Ca^{+2}, limited by solubility of fluorite and anhydrite and temperature and salinity dependent silicate equilibria control a very low Mg^{+2} concentration. The results of alteration studies show that the chemical composition of geothermal fluids originates in controlled reactions dependent on temperature, pressure and rock composition.

4. SAMPLING AND ANALYSIS OF GEOTHERMAL FLUIDS

4.1 Sampling of hot springs

Obtaining information on the distribution of the geothermal manifestations in the area as well as on the temperatures and flow rates of the springs and fumaroles is very useful step during sampling of geothermal fluids from a particular field. The variability of surface activity between and within geothermal fields is highly intense. Although it may not be practical to sample all springs in a particular field, specific representative sites need to be selected for sampling. The criteria used to select hot springs for sampling include temperature, flow rate, geographic distribution, whether the

water issues from soil or directly from the bedrock and any hydro-geological observations that might indicate mixing of the geothermal water with surficial water (Arnórsson, 2006).

In essence, the most favourable sites are springs with the highest temperature, the highest flow rate, the smallest aperture and minimum contact with any soil. In addition to springs, sampling and analysis of ground and surface waters is important for evaluation of possible mixing of the geothermal water with such shallow water in upflow zones.

The layout of sampling apparatus is presented in Figure 2. If the water temperature is below 30–40°C, a cooling coil is not necessary as thermal contraction of water is not significant when cooled from this temperature to room temperature. If the water in the well is under pressure, the peristaltic pump is not needed to push the sample through the filtering apparatus. Contact of the water to be sampled with the atmosphere should be minimal, certainly for those components which may undergo changes in their concentration upon exposure to air. This can be done by immersing tubing into the hot springs well below the surface, if the surface area of the hot spring is sufficiently large and deep and withdrawing water through the tubing with a peristaltic pump and pushing it through the cooling coil and the filtering apparatus. If the aperture is small and on a slope, it is convenient to place a funnel just below the aperture and let the water flow by gravity into the tubing to the peristaltic pump.
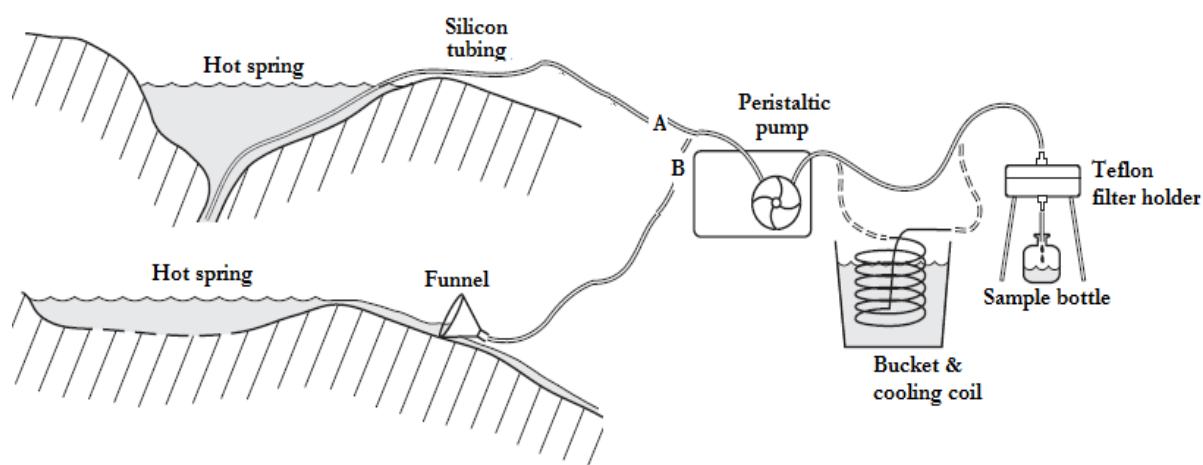

FIGURE 2: The layout of the apparatus for sampling a hot spring waters
(modified from Arnórsson, 2006)

4.2 Sampling of fumaroles

Selecting fumaroles for sampling is not as simple as that of hot springs. It is generally best to sample small outlets, which discharge steam at considerable velocity. The gas phase discharged from such thermal manifestations tends to be low in H_2S compared with that of adjacent fumaroles because of its oxidation by oxygen dissolved in the surface water through which the steam passes (Arnórsson, 1987). Sampling fumarole steam provides information on individual gas concentrations in the steam and is for this reason also preferred to the sampling of gases bubbling through steam-heated or hot-spring water. The latter only provide information on the relative amounts of the gases in the gas phase and not their absolute concentrations in the steam. In addition, it is useful to measure the temperature when collecting samples from fumaroles so as to eliminate any uncertainty about the nature of the discharge.

The types of fumarole steam samples to be collected depend on which chemical and isotopic constituents are to be analysed. Chemical analyses for applied studies of geothermal systems routinely include CO_2, H_2S, NH_3, H_2, CH_4, O_2, N_2 and Ar. Analysis may also include the noble gases, CO, Rn and the heavier hydrocarbons. Isotopes routinely determined in steam include δ^2H and $\delta^{18}O$ and

occasionally δ^3He and δ^{20}Ne. Sometimes isotope ratios are also determined in individual gas components. They include δ^2H in CH_4 and H_2, and δ^{13}C in CO_2 and CH_4.

Three types of gas samples can be collected from fumaroles and hot springs (Figure 3 and 4). One is a sample of the total discharge of a fumarole, the second type is the gas fraction in the fumarole discharge and the third type consists of gas bubbles emerging from hot springs. No analysis or sample treatment is required on site for these steam and gas samples. Before collecting a sample, it is necessary to allow steam to pass through the tubing and the sample ports of the gas sampling bulb, and through the wash bottle when used, to displace any air in the system.
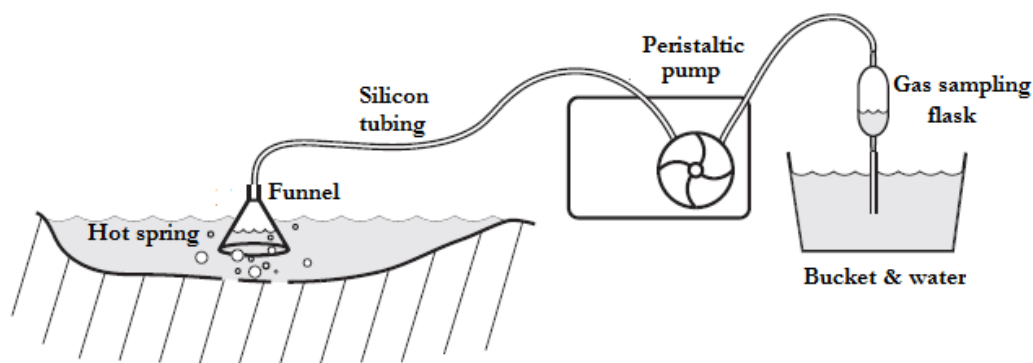

FIGURE 3: The layout of the apparatus for sampling gases bubbling from hot spring waters
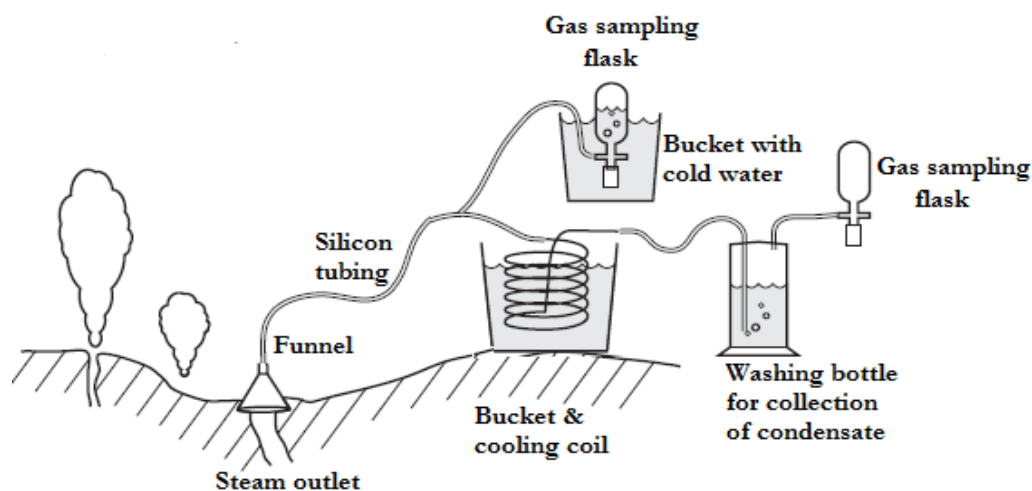(modified from Arnórsson, 2006)

FIGURE 4: The layout of the apparatus for sampling fumarole steam
(modified from Arnórsson, 2006)

The sampling methods depicted in the diagram assume that the sampling bulb to have been evacuated in the laboratory before going into the field. For sampling of gas from hot springs, the gas sampling bulb, which must have a stopcock at both ends, should not be evacuated. After immersing the funnel upside-down into the spring water over the rising gas bubbles, the peristaltic pump is used to suck up water to displace any air in the whole system, including the sampling bulb. Gas is then allowed to accumulate under the funnel, and is subsequently pumped into the sampling bulb.

Some studies focus on analysing dissolved gases in water, such as the noble gases, including Rn. Because of its short half-life (3.8 days), Rn must be analysed soon after collection. Sampling methods for such studies are those used to sample hot springs and hot-water wells. Samples for He analysis

must be collected into vessels which are not permeable to this gas, such as copper tubing or special Al-silicate glass.

As discussed by Arnórsson (2006), the gas phase in geothermal steam is most often largely CO_2 and H_2S (> 90% by volume). In order to obtain better analytical results for the less abundant major gases (H_2, CH_4, N_2, O_2, Ar), the most common practice is to collect samples into evacuated bulbs containing a solution of either NaOH or KOH. The CO_2 and H_2S present in the steam dissolve quantitatively in the alkaline solution, thus concentrating the remaining gases in the head space above the solution and allowing their more precise determination by gas chromatography.

When sampling fumarole steam the main concern is usually to avoid air contamination of the sample. Generally, the presence of oxygen in geothermal steam is taken as evidence for atmospheric contamination during sampling. However, oxygen in fumarole steam may have originated from degassing of near-surface steam-heated water and could truly be present in the steam.

In the discharges of dry and wet-steam wells, on the other hand, the presence of oxygen in gas samples can safely be considered to be a measure of atmospheric contamination during sampling. Atmospheric contamination reduces the value of data on N_2, Ar and other atmospheric gases. It also tends to yield low values for H_2S, which is easily oxidized by atmospheric oxygen in alkaline solution. The best samples are generally obtained from fumaroles discharging from ground highly altered by acid surface leaching. The funnel should be placed upside down over the steam vent and covered with compacted clay using a shovel.

5. DETERMINATION OF SOIL GAS CONCENTRATIONS/FLUXES

Several studies have shown that globally significant amounts of CO_2 are released to the atmosphere by quiescent degassing of volcanoes and soil diffuse degassing from volcanic geothermal systems. It has been demonstrated that soil diffuse degassing on flanks of volcanoes is sensitive to changes in magmatic activity, thus providing a potential, relatively safe method for volcano monitoring. Soil diffuse CO_2 degassing has also been shown to be a good indicator of the energetic state of geothermal systems. This is because CO_2 gas reaches the surface more easily than steam that can condense in the subsurface where groundwater flow can transport the resulting thermal energy laterally out of the systems (Chiodini et al., 1996). The study of diffuse degassing is one of the recent methodologies that have contributed in the monitoring of gases in soils and fumaroles. In Kenya, it has been part of the geochemical activities for monitoring fumaroles and for further exploration of geothermal areas. Gas studies confirm possible permeable zones, geologic structures and faults and the chemical and thermal evolution of hydrothermal areas.

5.1 Soil gas concentration (CO_2, Rn and Hg)

CO_2 gas concentration can be effectively measured using an Orsat apparatus. Radon radioactivity levels can be determined by a portable radon detector (emanometer) and mercury by mercury analyzer. The Orsat apparatus consist of absorption vessels, which measure about 100 mls 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 as a percentage.

The soil gas is passed into the emanometer where Rn-222 and Rn-220 readings are recorded in counts per minute (cpm). Three background counts are recorded at three-minute interval prior to introduction of the sample into the emanometer. Upon introducing the sample, three more readings are taken at the same intervals to give the total radon counts. The CO_2 and Rn-222 obtained in the survey is corrected and used to construct concentrations contour maps. A ratio of CO_2/Rn-222 is used to eliminate other sources of CO_2 other than magmatic.

5.2 Soil gas flux (CO₂)

The CO_2 flux can be measured directly using a survey chamber CO_2 flux meter equipped with a non-dispersive infrared gas analyzer. The flux measurement is based on the rate of CO_2 increase in the chamber. The Survey chamber allows rapid measurements to be made at many sites and it is has carefully designed pressure vents to prevent pressure gradients and wind incursion from outside the chamber. The chamber closes automatically, minimizing mechanical disturbances during the measurement.

6. DATA INTERPRETATION

Application of chemical techniques has become an integral part of any geothermal exploration programme. Waters and gases discharged at the surface generally carry imprints of their deeper histories with them. The constituents encountered in these fluids has been subdivided into non-reactive or tracers (Cl, B, Li, Rb, Cs, N_2, He and Ar) and reactive or geoindicators (Na, K, Mg, Ca, H_2, H_2S, CH_4, CO_2 and SiO_2) (Giggenbach, 1991). The most important processes affecting geothermal fluid compositions include the overall irreversible dissolution of primary rock minerals and precipitation of secondary minerals. The dissolution process leads to increased concentrations of the aqueous components, including conservative Cl, Br and B. Other components, brought into solution by primary rock mineral dissolution, are removed again by precipitation of secondary or hydrothermal minerals.

As a result, the relative proportions of components in geothermal waters differ very much from those in common rock types. Components that largely reprecipitate include Al, Mg and Fe, whereas Li, Rb and Cs reprecipitate to a small extent. Chlorine and boron, together with many others, exist as fugitive components – chlorine as HCl, boron as borates, sulphur as SO_2, carbon as CO_2, and a lesser extent, as CO, fluorine as HF, and hydrogen as H_2O and H_2. The fugitive compounds tend to leave the magma by the process of degassing depending on the rate of ascent of magma, initial concentration, external pressure, its viscosity and rate of solidification.

In spite of being affected to some degree by secondary chemical processes, the above five constituents Li, Rb, Cs, B and Cl provide very useful markers for the identification of, and tracers to the origins of geothermal fluids, however, constituents Na, Mg, Ca and SiO_2, are chemically more reactive and form the basis for a number of valuable geoindicators.

6.1 Relative Cl, SO₄ and HCO₃ contents

Using the relative Cl, SO_4 and HCO_3 contents, waters can be characterized as steam-heated, mature, peripheral or volcanic waters (Figure 5). Volcanic and steam-heated waters formed by the absorption of high temperature, HCl-containing volcanic, or lower temperature, H_2S-containing
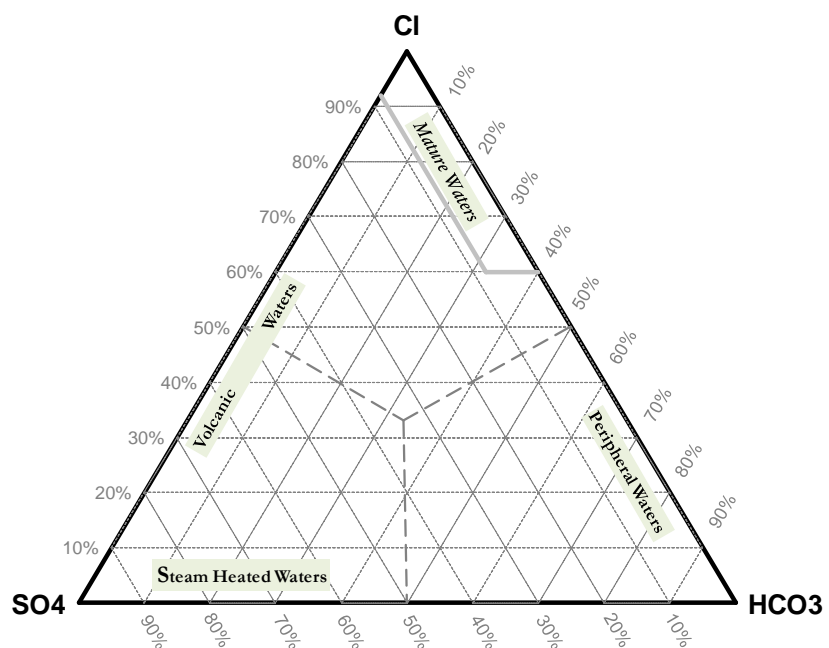

FIGURE 5: Relative Cl-SO₄-HCO₃ contents

"geothermal" vapours, into groundwater. Most geochemical techniques are not suitable for application to these generally quite acid waters.

The group best suited comprises the neutral, low sulphate, high chloride "geothermal" waters along the Cl-HCO$_3$ axis, close to the Cl corner. The relationship of these constituents allows the weeding out of unsuitable waters, but may already provide initial indication of mixing relationships or geographic groupings. High SO$_4$ steam-heated waters are usually encountered over the more elevated parts of a field. The degree of separation between data points for high chloride and bicarbonate waters gives already an idea of the relative degrees of interaction of the CO$_2$ charged fluids at lower temperatures, and of the HCO$_3$ contents increasing with time and distance travelled underground.

6.2 Relative Li, Rb and Cs contents

The relationship of Li, Rb and Cs stresses differences among waters, largely brought by comparatively shallow processes (Figure 6). An indication of the existence of a common origin, or of common, deep processes shaping the composition of surface water discharges, is provided by use of less reactive, "conservative" components, added at depth, but not affected by shallow processes, such as the rare alkalies Li, Rb and Cs. In the application of this triangular plot (Figure
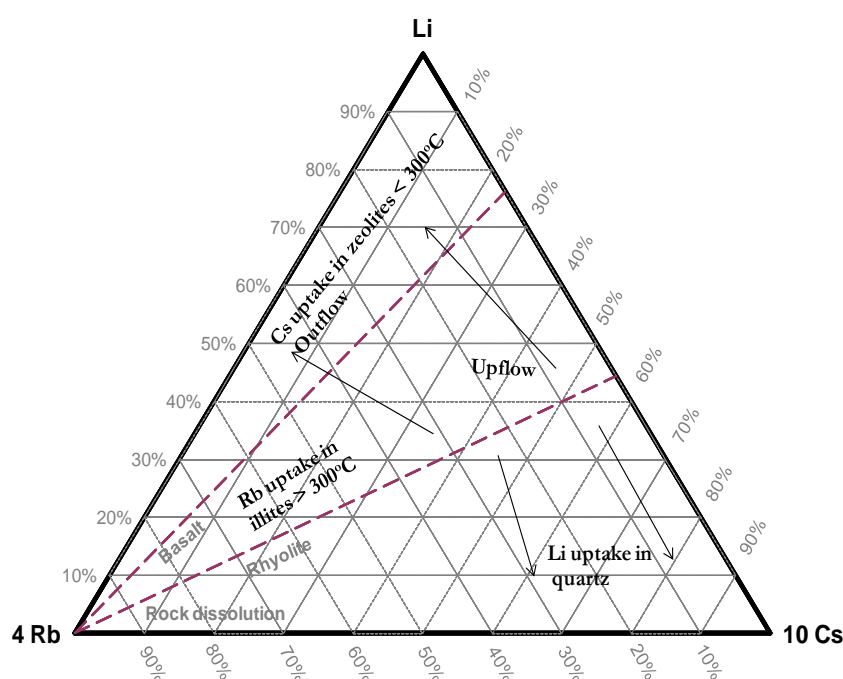

FIGURE 6: Relative Li-Rb-Cs contents

6), advantage is taken of its insensitivity to dilution by little mineralized ground water or steam loss due to boiling of the rising fluids. As a result, data points for deep and shallow waters, having undergone any amount of dilution or steam-loss, plot on the same position. However, Rb closely parallels K in that it is readily taken up at quite high temperatures (> 300ºC) in most K-containing alteration products, such as illite. Cs is incorporated into secondary zeolites, especially at temperatures < 250ºC. Li is to minor degree incorporated into secondary quartz and chlorite.

6.3 Relative Cl, Li and B contents

The alkali metal probably least affected by secondary process is Li, and therefore can be used as a "tracer" for the initial deep rock dissolution process and as reference to evaluate the possible origin of the other two important "conservative" constituents of thermal waters, Cl and B (Figure 7). Once Li is added into waters in hydrothermal systems it remains largely in solution since there is no obvious major sink for this element in hydrothermal systems. The B content of thermal fluids is likely to reflect to some degree the maturity of a geothermal system. Because of their volatility, constituents such as B, As, Sb and Hg are likely to be expelled during the early heating up stages, and therefore, fluids from "older" hydrothermal systems can be expected to be depleted in these elements.

6.4 The Relative Na-K-Mg contents

The Na-K-Mg-geothermo-meters is a 'self-policing' technique that gives an automatic indication as to the suitability of given water for the application of ionic solute geoindicators (Giggenbach, 1988). It characterizes waters to immature, partial equilibrated and fully equilibrated (Figure 8). Immature waters are not suitable for K-Na- and K-Mg-geothermometers and care should be taken while interpreting such temperatures.
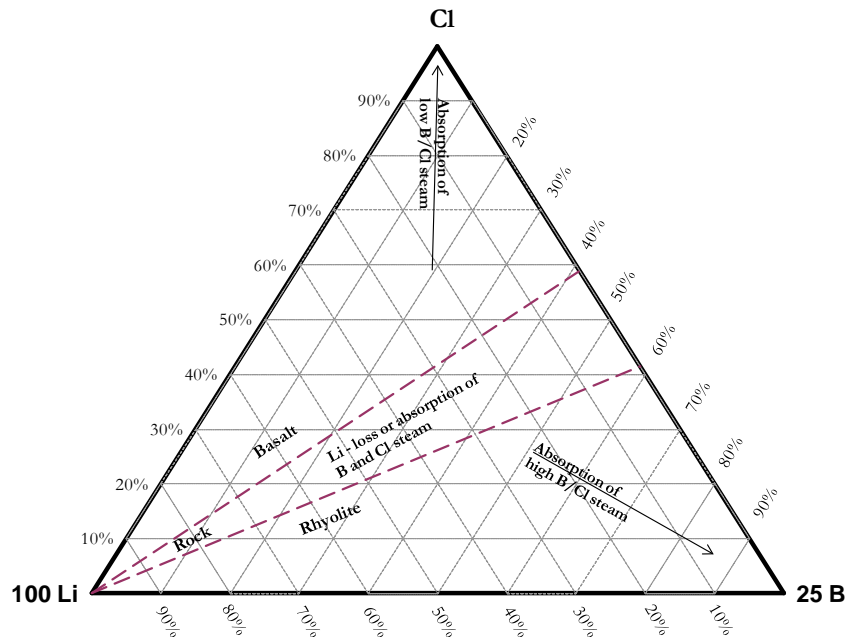
FIGURE 7: Relative Cl-Li-B contents

7. GEOTHERMO-METRY

Applications of geothermometry constitute one of the major tools for the exploration and development of geothermal resources.
Geothermometry is simply the estimation of the reservoir (subsurface) temperatures using the chemical and isotopic composition of surface discharges from wells and/or natural springs/fumaroles. When employing geothermometry, a basic

FIGURE 8: Relative Na-K-Mg contents

assumption is usually made that temperature dependent chemical and isotopic equilibria prevail in the source aquifer. Since the fluids may travel long from the source aquifer to the surface for collection, an approximation is made that chemical and isotopic reactions do not significantly modify the composition of the fluid during its ascent.
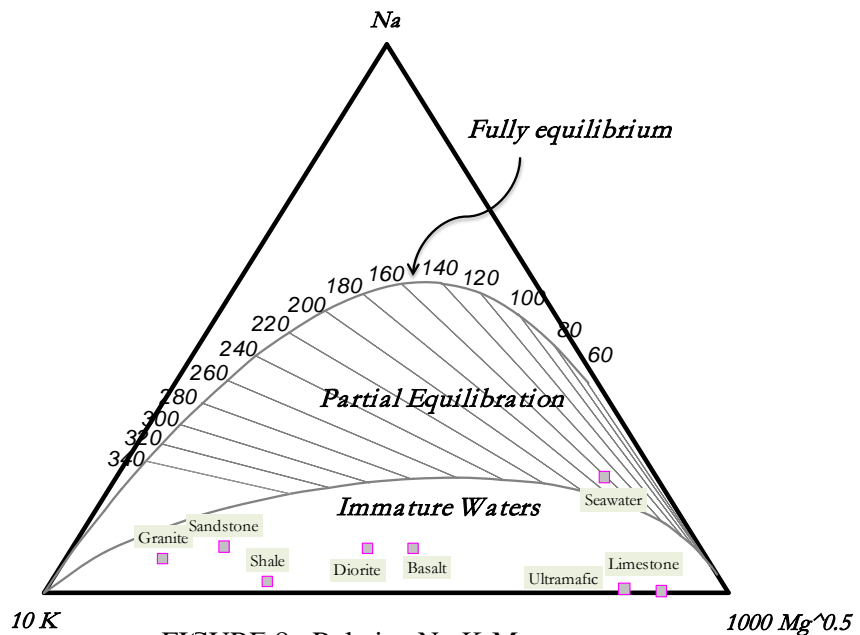
Geothermometers are classified into two groups: Chemical Geothermometers and Isotopic Geothermometers. The former utilizes the chemical composition (essentially the silica and major cation contents of water discharges, and the gas concentrations or relative abundances of gaseous components in steam discharges), whereas the latter is based on isotope exchange reactions between various phases (water, gas, mineral) in geothermal systems.

Chemical geothermometers are developed on the basis of temperature-dependent chemical equilibrium between water and minerals under deep reservoir conditions. The use of chemical geothermometers basically relies upon chemical species (solutes, gases, isotopes) reaching a state of reaction equilibrium in the reservoir, then leaving the reservoir and appearing at wells/springs/fumaroles before significant re-equilibration can occur.

8. SOIL GAS SURVEY

Early geochemical studies on diffuse soil degassing have been carried out in a number of geothermal areas. CO_2 soil gas investigations have been conducted in volcanic areas to examine unexpected rise in CO_2 flux (Farrar et al., 1995; McGee and Gerlach 1998; Gerlach et al., 1998), estimate total volcanic flux from volcanic vents and diffuse flank emissions (Allard et al., 1991; Chiodini et al., 1996), and to classify tectonic structures related to volcanic degassing (Giammanco et al., 1997; Bergfeld et al., 1998).

The term volcanic gas defines a gas exsolved from a magmatic source of an active volcano whereas hydrothermal gas defines a gas exsolved from the envelope of hot water that surrounds the magmatic environment. Volcanic gases have composition different from the hydrothermal gases; the first is richest in SO_2 and the second in H_2S. CO_2 occurs in both magmatic and hydrothermal gases and is the most abundant gas after water vapor. The deep-seated faults in the crust tap magmatic CO_2, which is transmitted to the surface where it is naturally lost through the soil. Carbon dioxide (CO_2) of magmatic origin is normally channelled through deep-seated tectonic structures close to the surface of the earth and then seeps out of the ground through the soil. CO_2 may also originate from other sources like organic matter, or localized like in the rift valley, which are likely to give false impressions of a geothermal source.

Thoron gas (Rn220) is a short lived isotope of radon produced by the thorium (Th-232) decay series with a half-life of 55 seconds (Lopez et al., 2004). Due to its short half-life, thoron's transportation is limited to a few centimetres either by diffusive or convective flows, as compared to Rn222 (t ½ = 3.8 days) (Hutter, 1993). As a result, the high concentrations of thoron are more likely to be due to convective movement of gases rather than diffusive processes and therefore it is difficult to achieve an exact quantitative measurement of its concentration. If we measure the disintegration of thoron, it shows a decrease during the first three minutes after collection of the sample, as opposed to the radon that presents a half-life of almost 4 days (Magana et al., 2002). High thoron values could be suggestive of enhanced permeability, as it may as well depend on other factors such as the degree of rock fracture and the ability of groundwater to circulate and remove thoron.

8.1 Soil gas survey of Silali geothermal prospect (case example)

Silali geothermal prospect is located in the axis of the northern Kenya rift. The northern segment of the Kenya Rift is a unique petrographic province composed of six Quaternary to Recent volcanic complexes namely Korosi, Paka, Silali, Emuruangogolak, Namarunu, and Barrier from south to north (Figure 9). Silali is the largest caldera volcano in the axis of the northern Kenya rift. It is characterized by a large caldera volcano, situated on the floor of the northern Kenya rift. Previous studies of the volcano and the surrounding area indicated occurrence of a hydrothermal system, signifying probable occurrence of a high temperature geothermal resource.

Detailed geo-scientific exploration was carried out in 2010 to determine its geothermal potential. Soil gas measurements of CO_2 and radon was part of the survey carried out. The soil gas survey anomalies are depicted in Figures 10 and 11 below.
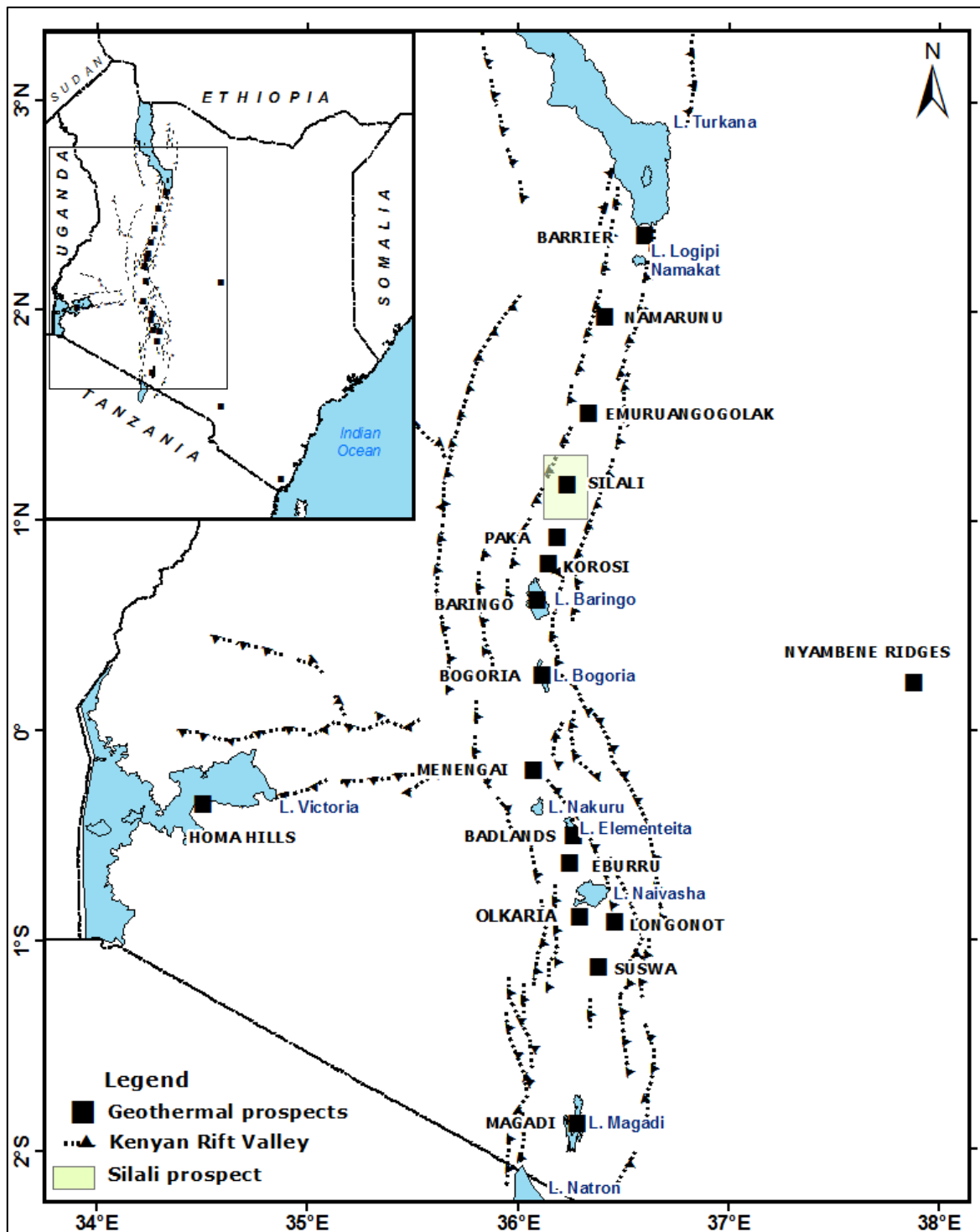
FIGURE 9: Map of the Kenya rift showing the location of Silali geothermal prospect (GDC internal database, 2011)

The CO_2 and Rn-222 anomalies observed on the maps are indicative of gas leakages through fluid transporting structures. This is because a big percentage of the gases are transported convectively. The elevated values of CO_2 and radon are useful in delineating areas with enhanced subsurface permeability which are good targets for siting exploration wells. The results should be correlated well with geological and geophysical findings.
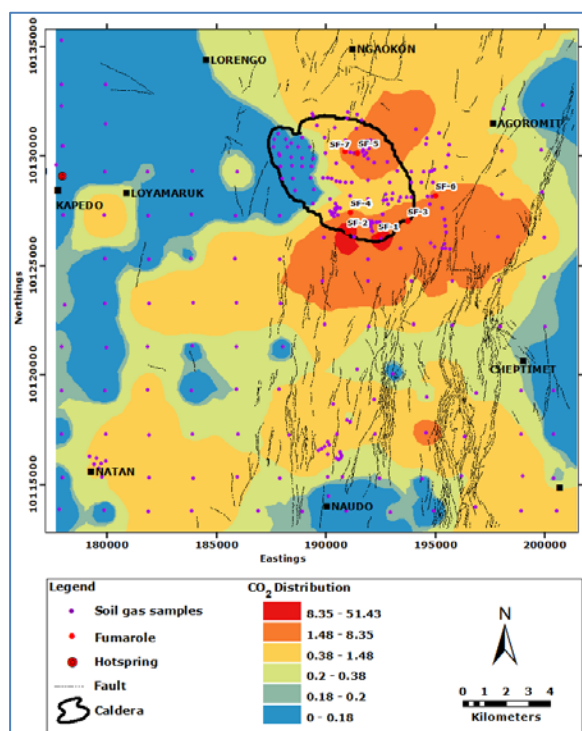
FIGURE 10: CO_2 distribution in the
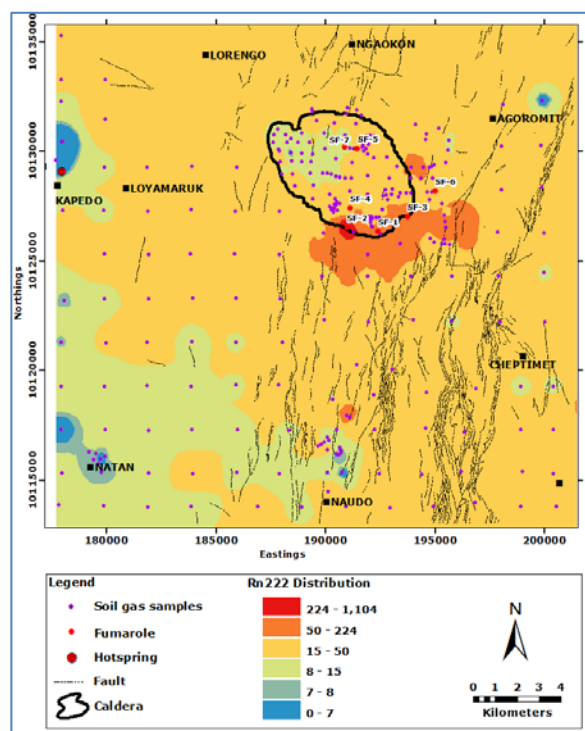Silali prospect

FIGURE 11: Rn-222 distribution

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