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CHEMICAL GEOTHERMOMETERS FOR GEOTHERMAL EXPLORATION

Cyrus W. Karingithi

Kenya Electricity Generating Company PLC (KenGen)

P.O. Box 785, Naivasha

KENYA

ckaringithi@kengen.co.ke

ABSTRACT

Chemical and isotope geothermometers constitute an important geochemical tool for the exploration and development of geothermal resources. They are also important during exploitation in monitoring the response of geothermal reservoirs to production load. During the exploration phase, geothermometry is used to estimate subsurface temperatures, i.e., temperatures expected to be encountered by drilling, using the chemical and isotopic composition of the hot spring and fumarole discharges.

During the later phases in geothermal development and monitoring, geothermometry has been successfully applied to interpret the composition of well discharges with respect to locating the levels of producing horizons in the wells. Geothermometry is also useful in elucidating chemical reactions occurring in the zone of depressurization around wells that result from boiling and or cooling by recharging cold water.

1. INTRODUCTION

Geothermal fluids have diverse chemistries, which largely reflect their geological setting. Many of these chemical differences largely depend on the source of recharge waters and the contribution of gases from magmatic or metamorphic sources. The constituents may be solutes gases or isotopes. Most geothermometers are based on specific chemical equilibrium reactions. Geothermometers can be applied to both natural spring discharges and well fluids. They provide valuable insight as to the nature of the system and “the choice and interpretation of the geothermometer data are the art of the exploration geochemist”.

Geothermometers take advantage of specific mineral –solute reactions, which are slow to re-equilibrate at cooler temperatures, especially under conditions where the fluid is effectively separated from the minerals which controlled the equilibria. The result is that hot equilibrium temperature is “frozen in” to the fluid as reflected by solute concentration or solute ratios.

Care must be taken in applying geothermometers, otherwise the results and interpretations may give rise to serious errors. Therefore, the limitations of any geothermometer must be considered. The initial requirement is that samples are correctly taken, and the analyses are accurate. It is good practice to compare temperatures indicated by different geothermometers.

Note that some geothermometers are empirical (e.g. Na-K-Ca, D'Amore and Panichi (1980) gas geothermometer), whereas others are based on thermodynamic properties (e.g. Na-K, K-Mg). As the factors controlling empirical geothermometers are not completely known, theoretical geothermometers may in some cases be more reliable.

Geothermometers have been classified into three groups:

- 1) Water or solute geothermometers;
- 2) Steam or gas geothermometers; and
- 3) Isotope geothermometers.

2. CHEMICAL GEOTHERMOMETERS

Water and steam geothermometers are collectively termed chemical geothermometers. During the ascent of geothermal waters from a deep reservoir to the surface, they may cool by conductive heat loss as they travel through cooler rocks or by boiling because of decreasing hydrostatic head.

Figure 1 shows a conceptual model of the Rift geothermal system. The geothermometers are expected to give accurate prediction of the reservoir temperatures within the production zone before drilling using the data acquired from geothermal manifestations. Cooling by conduction does not by itself cause any changes in the chemical and isotopic composition of the water. Yet, cooling may change its degree of saturation with respect to both primary and secondary minerals. As a result, conductive cooling can bring about some modification in the chemical composition of the ascending water by mineral dissolution or precipitation. Boiling invariably causes changes in the composition of rising geothermal waters. These include degassing and an increase in the solute content of the water due to steam loss. The boiling mechanism affects the gas content of the steam that forms. The principle application of chemical and isotopic geothermometers during geothermal exploration involves estimation of reservoir temperatures below the zone of cooling. When applying these geothermometers it is invariably assumed that no changes in water composition occur in conjunction with conductive cooling; boiling is taken to be adiabatic.

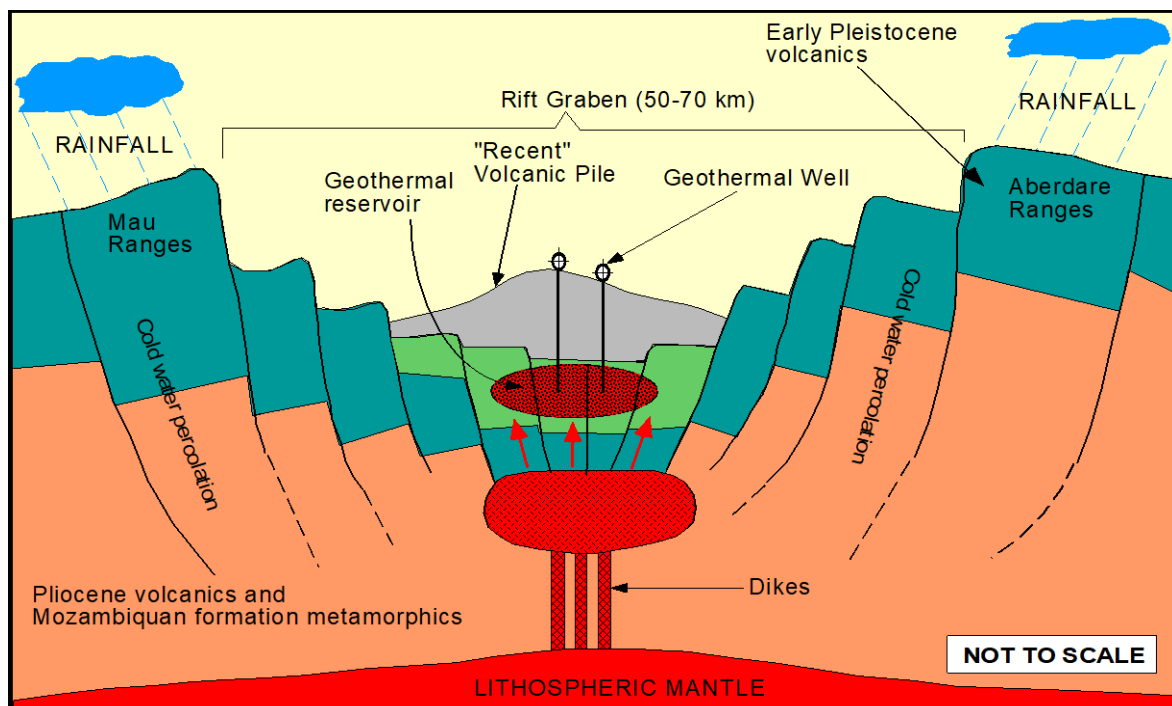


FIGURE 1: The conceptual model of the Rift geothermal system

The amount of conductive heat loss of ascending geothermal waters is proportional to the distance travelled and inversely proportional to the flowrate. For vertical pipe flow, Truesdell et al., (1977) have calculated that temperatures are reduced by half for waters flowing at 0.4 l/s from a 1 km deep reservoir. Conductive cooling can be expected to be important for isolated springs with flow of less than 1 l/s. In the case of closely spaced springs, trying to envisage the amount of conductive cooling in the upflow, the aggregate flow should be considered.

When geothermometers are applied to estimate subsurface or aquifer temperatures, a basic assumption is that temperature dependent chemical or isotopic equilibria prevail in the source aquifer. Further, as stated above, the approximation is made that chemical and isotopic reactions do not significantly modify the composition of the fluid as it ascends from the source aquifer to the point of sampling, whether it is a thermal spring, fumarole, or wellhead.

Equilibrium between mineral-solution or solute-solute is assumed for geothermometry to be applied. Equilibrium between quartz and solution as well as between alkali feldspar and solution is invariably attained in geothermal reservoirs when temperatures exceed about 150-180°C. Accordingly, the application of the quartz and the Na/K geothermometers to high temperature geothermal reservoirs can be regarded as thoroughly established.

Experience shows that results for different chemical and isotope geothermometers sometimes compare well for a particular discharge although sometimes, large differences are seen. Good conformity between individual geothermometers is usually taken to indicate that the assumption of equilibrium is valid and that faith can be put into the results. Discrepancy in results, on the other hand, is indicative of dis-equilibrium. A discrepancy may, however, be utilized to quantify various processes in geothermal systems such as boiling and mixing with cooler water in the upflow zones. Therefore, differences in the results of individual geothermometers need not be a negative outcome for their interpretation.

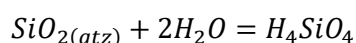
3. WATER GEOTHERMOMETERS

The most important water geothermometers are silica (quartz and chalcedony), Na/K ratio and Na-K-Ca geothermometers. Others are based on cation ratio and any uncharged aqueous species as long as equilibrium prevails (Arnorsson and Svavarsson, 1985). A temperature equation for a geothermometer is a temperature equation for a specific equilibrium constant referring to a specific mineral-solution reaction.

3.1 Silica geothermometers

Silica geothermometer is based on experimentally determined variations in the solubility of different silica species in water, as a function of temperature and pressure.

The basic reaction for silica dissolution is:



In most geothermal systems, deep fluids at temperatures > 180°C are in equilibrium with quartz; it is stable up to 870°C and has the lowest solubility compared to other silica polymorphs. Quartz is common as a primary and secondary (hydrothermal) rock-forming mineral. Silica polymorphs with a less ordered crystal structure (i.e. chalcedony, opal CT, cristobalite) have higher solubilities than quartz and form at cooler temperatures of < 180°C.

$$t^{\circ}\text{C} = \frac{1309}{5.19 - \log S} - 273.15 \quad (\text{Fournier, 1977})$$

where $t^{\circ}\text{C}$ = Geothermal temperature in $^{\circ}\text{C}$; and
 S = Silica concentration as SiO_2 in mg/kg (quartz; no steam loss).

The quartz geothermometer is best for reservoir conditions $> 150^{\circ}\text{C}$. Below this temperature chalcedony rather than quartz probably controls the dissolved silica content. Six main silica geothermometers exist.

1. Adiabatic (Maximum steam loss) – this equation compensates for loss of steam from boiling solutions and the resultant increase in concentration of silica, plus the cooling of the solution by adiabatic expansion due to decrease in the hydrostatic – hydrodynamic pressure head. The silica quartz adiabatic geothermometer is best used for well discharges and vigorously boiling springs, Figure 2, and pools with high discharge rates (≥ 2 kg/s), especially those with silica sinter deposits.

$$t^{\circ}\text{C} = \frac{1522}{5.75 - \log(\text{SiO}_2)} - 273.15 \quad (\text{Fournier, 1977})$$



FIGURE 2: Hot geysers at Lake Bogoria geothermal prospect in the Kenya Rift

2. Conductive (no steam loss) – this equation represents experimentally determined solubilities and applies to those waters that cool solely by conduction during ascent. The silica quartz conductive cooling geothermometer is best used for springs at sub-boiling temperatures (giving a maximum estimate of the reservoir temperatures based on quartz solubility), or for well data that have been calculated to reservoir conditions.

$$t^{\circ}\text{C} = \frac{1309}{5.19 - \log(\text{SiO}_2)} - 273.15 \quad (\text{Fournier, 1977})$$

3. If the quartz geothermometer, other geothermometers, indicate temperature of $120\text{-}180^{\circ}\text{C}$ it is possible that chalcedony may control silica solubility. Under these circumstances, test the chalcedony geothermometer.

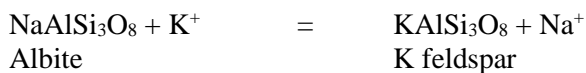
$$t^{\circ}C = \frac{1112}{4.91 - \log(SiO_2)} - 273.15 \quad (\text{Arnórsson et al., 1983})$$

4. If the chalcedony geothermometer gives temperatures of 100-120°C, it may represent the true deep temperature. However, if the calculated temperature is below 100°C, the amorphous silica may control the solubility. At lower temperatures in systems with silicic host rocks, the abundance of volcanic glass may enable saturation of a fluid with respect to amorphous silica.

$$t^{\circ}C = \frac{731}{4.52 - \log(SiO_2)} - 273.15 \quad (\text{Fournier, 1977})$$

3.2 Na-K geothermometer

The response of the Sodium/Potassium (Na/K) ratio, decreasing with increasing fluid temperature, is based on temperature dependant cation exchange reaction between albite and K feldspar (adularia):



$$t^{\circ}C = \frac{1217}{1.438 + \log(\text{Na}/\text{K})} - 273.15 \quad (\text{Fournier, 1979})$$

$$t^{\circ}C = \frac{1112}{4.91 - \log(SiO_2)} - 273.15 \quad (\text{Giggenbach et al., 1988})$$

Waters from high temperature reservoirs (180°C) of chloride waters are suitable for this geothermometer. For lower temperature reservoirs where fluids have long residence times, the Na-K geothermometer may in some cases be applicable.

The advantage of this geothermometer include that it is less affected by dilution or steam loss given that it is based on a ratio. This is if the diluting waters are low in Na, K, and Ca. Note that seawater is not a diluent but an end member fluid of distinct composition. The geothermometer is applicable to 350°C, as the re-equilibration is slower than that of the silica-quartz geothermometer. Therefore, the Na-K geothermometer may give indications regarding the deeper part of the system in comparison to the silica – quartz geothermometer, depending on the system’s hydrology. A slow rising fluid can, however, re-equilibrate at shallower levels and cooler temperatures.

3.3 Limitations on the Na-K geothermometer

The Na-K geothermometer gives poor results below 100°C. It is also unsuitable if the waters contain high concentration of calcium (Ca) as is the case for springs depositing travertine. The following general rules apply;

- 1) Use for waters indicating reservoir temperatures >100;
- 2) Use if the waters contain low Ca; i.e. the value of $(\log(\text{Ca}^{1/2}/\text{Na}) + 2.06)$ is negative; and
- 3) Use for near neutral pH chloride waters.

3.4 Na-K-Ca geothermometer

The Na-K-Ca geothermometer was developed by Fournier and Truesdell (1973), for application to waters with high concentrations of calcium. This is an empirical geothermometer and theoretical constraints include equilibrium between Na-K feldspars plus conversion of calcium aluminosilicate minerals (e.g. Plagioclase) to calcite. The main advantage of the Na-K-Ca geothermometer in

comparison with the quartz geothermometer, and especially the Na/K geothermometer, is that it does not give high and misleading results for cold and slightly thermal, non-equilibrated waters.

The assumptions included in development of the empirical equation are:

- 1) Excess silica is present; and
- 2) Aluminium is conserved in solid phases.

The following considerations apply in application of this geothermometer:

- 1) Calculate $\{\log(\text{Ca}^{1/2}/\text{Na}) + 2.06\}$; if its value is positive, the use $\beta = 4/3$ in the formula in determining the temperature. If that calculated temperature is $<100^\circ\text{C}$, then this temperature is appropriate.
- 2) If the $\beta=4/3$ calculated temperature is $>100^\circ\text{C}$, or $\{\log(\text{Ca}^{1/2}/\text{Na}) + 2.06\}$ is negative, then use $\beta=1/3$ to calculate the temperature.

$$t^\circ\text{C} = \frac{1647}{\log(\text{Na}/\text{K}) + \beta \log(\sqrt{\text{Ca}}/\text{Na}) + 2.24} - 273.15$$

$$\begin{aligned} \text{where } \beta &= 4/3 \text{ for } (\sqrt{\text{Ca}}/\text{Na}) > 1 \text{ and } t < 100^\circ\text{C}; \text{ and} \\ \beta &= 1/3 \text{ for } (\sqrt{\text{Ca}}/\text{Na}) < 1 \text{ or if } t_{4/3} > 100^\circ\text{C}. \end{aligned}$$

3.5 Limitations of the Na-K-Ca geothermometer

The mineralogical background of the geothermometer must not be forgotten. It is not correct to apply the Na/K or the Na-K-Ca geothermometer to acid waters, which would not be in equilibrium with feldspars, nor are they applicable to water systems in rocks with unusually high or low concentrations of a particular alkali unless direct correlations with measured temperatures are available.

Changes in concentration resulting from boiling and dilution will affect the Na-K-Ca temperature. The main effect is loss of carbon dioxide due to boiling, causing calcite to precipitate. The loss of dissolved Ca results in the Na-K-Ca temperatures, which are too high. The amount of error is proportional to the amount of carbon dioxide in the fluid.

The effect of dilution is minimal if the geothermal fluid is much more saline than the diluting fluid. For dilution $>50\%$, Na-K-Ca temperatures are too low as the $(\text{Ca}^{1/2}/\text{Na})$ relationship is strongly affected.

In some dilute high temperature waters containing high dissolved carbon dioxide and in waters with low Ca concentrations, the term β may become strongly negative. Under these conditions the Na-K geothermometer may be more useful.

3.6 Mg correction for the Na-K-Ca geothermometer (Fournier and Potter, 1979)

Most fluids $>180^\circ\text{C}$, contain <0.2 mg/kg Mg. In more saline fluids Mg is low relative to other cations. This strong temperature dependence of Mg concentration is mainly due to the formation of chlorite. At higher temperatures, other minerals such as biotite or actinolite may also remove Mg from solution. At cooler temperatures, Mg may be incorporated into clays or carbonates. The Mg correction is applied to those geothermal waters (unaffected by mixing) that contain high dissolved Mg, because they are saline, or because the reservoir temperature is $<180^\circ\text{C}$. The presence of high Mg gives anomalously high temperature results.

The following correction was derived empirically:

- 1) If $T_{Na-K-Ca}$ is $<70^{\circ}C$ do not apply correction.
- 2) Calculate R, using equivalents (Molality/Charge) where

$$R = \frac{Mg}{Mg + Ca + K} (100).$$

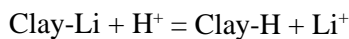
- 3) If $R > 50$ assume the water is from relatively cool equilibrium conditions with temperatures about equal to the measured water temperature irrespective of the high $T_{Na-K-Ca}$.
- 4) If $T_{Na-K-Ca} > 70^{\circ}C$ and $R < 50$, use R to determine ΔT_{Mg} (Fournier 1979) and subtract ΔT_{Mg} from the $T_{Na-K-Ca}$ to get the correct geothermometer temperature.

The Mg-correction is usually applied to cooler temperature systems; it is best applied to sub-boiling springs with high discharge rates.

3.7 Na-Li geothermometer

Sodium – Lithium (Na-Li) geothermometer, which is empirical and based on the Na/Li ratio. Two equations exist, one for fluids containing < 11000 mg/kg Cl and the other for fluids containing > 11000 mg/kg Cl. Both require molar values.

The theory behind this geothermometer is based on the temperature dependent reaction:



In reality, the controlling equilibria are probably based on cation exchange reactions with clays and zeolites rather than formation of discrete mineral phases. The ratio is thought to be constant as the fluid ascends from the reservoir to the surface. However, some Li may be lost from solution to alteration minerals during cooling.

$$t^{\circ}C = \frac{1195}{0.130 + \log(mNa/mLi)} - 273.15 \quad (\text{Fouillac et al., 1981})$$

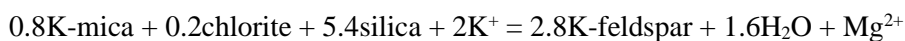
(Valid for Cl concentrations of > 0.3 mol/kg)

$$t^{\circ}C = \frac{1000}{0.389 + \log(mNa/mLi)} - 273.15 \quad (\text{Fouillac et al., 1981})$$

(Valid for Cl concentrations of < 0.3 mol/kg)

3.8 K-Mg geothermometer

This geothermometer is applied to situations where dissolved Na and Ca have not equilibrated between fluid and rock. This geothermometer re-equilibrates quickly at cooler temperatures related to the reaction:



$$t^{\circ}C = \frac{4410}{14.0 + \log(K^2/Mg)} - 273.15 \quad (\text{Giggenbach et al., 1988})$$

4. GAS GEOTHERMOMETERS

Surface manifestations in most geothermal fields consist mainly of fumaroles, springs and hot grounds (Arnorsson, 2000). Where the shallow ground water table is deep in the subsurface, springs are not

available, for example, Figure 3, in Kenya Rift. When this is the case, water geothermometers cannot be used to predict the subsurface temperatures. This motivated the early scientists to develop gas geothermometers, e.g. D'Amore and Panichi (1980). There are 3 types of gas geothermometers based on:

- 1) Gas- gas equilibria;
- 2) Gas-mineral equilibria; and
- 3) Mineral – gas equilibria involving the residual gases such as, CH₄, H₂, H₂S.



FIGURE 3: Fumaroles in the Kenya Rift

Temperature dependent gas-gas and or mineral gas equilibria are believed to control the concentrations of gases like CO₂, H₂S, H₂, N₂, NH₃ and CH₄ in geothermal reservoir fluids. Arnorsson and Gunnlaugsson (1985) proposed temperature functions for six geothermometers applicable to fumarolic steam. Three (3) were based on the concentrations of CO₂, H₂S, and H₂ respectively. Two (2) were based on the gas ratios (CO₂/H₂) and H₂/H₂S). The gas concentration is in mmol/kg of steam.

$$t^{\circ}\text{C} = 44.1 + 269.25Q - 76.88Q^2 + 9.52Q^3$$

$$Q = \log (\text{mmol} / \text{kg}) \text{CO}_2$$

$$t^{\circ}\text{C} = 246.7 + 44.8Q$$

$$Q = \log (\text{mmol} / \text{kg}) \text{for H}_2\text{S}$$

$$t^{\circ}\text{C} = 277.2 + 20.99Q$$

$$Q = \log (\text{mmol} / \text{kg}) \text{for H}_2$$

$$t^{\circ}\text{C} = 341.7 + 28.57Q$$

$$Q = \log (\text{mmol} / \text{kg}) \text{for CO}_2/\text{H}_2$$

$$t^{\circ}\text{C} = 304.1 + 39.48Q$$

$$Q = \log (\text{H}_2\text{S} / \text{H}_2)$$

$$t^{\circ}\text{C} = \frac{4625}{10.4 + \log(\text{CH}_4/\text{CO}_2)} - 273.15 \quad (\text{Giggenbach, 1991})$$

5. ISOTOPE GEOTHERMOMETERS

Isotope exchange reactions, which achieve equilibrium in the natural system, are temperature dependent. Isotopes of elements are fractionated in the chemical processes operating in natural water-rock systems (Ellis & Mahon, 1977). The fractionation is largest for lighter elements found in geothermal systems, such as, Helium, hydrogen, carbon, oxygen, and sulphur. Isotope exchange reactions may be between gases and steam phase, a mineral and gas phase, water and a solute or a solute and a solute. Although there are many isotope exchange processes, few have been used because of simplicity of sample collection and preparation, ease of isotopic measurement, a suitable rate of achieving isotopic equilibrium, and knowledge of the equilibrium constants.

5.1 Oxygen isotopes

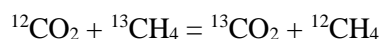
Chemical elements with the same atomic number (protons) and different atomic mass are defined as Isotopes. Isotopes have identical chemical behaviour but different physical properties. Hydrogen has three isotopes, ^1H , ^2H and ^3H , respectively and oxygen also has three isotopes, ^{16}O , ^{17}O and ^{18}O . Isotope geothermometers involving oxygen or hydrogen exchange reactions with water assumes equilibrium. An isotopic fractionation occurs when steam separates from hot water. The isotopic compositions of both the steam and water in a well sample may be determined from the total discharge, whose steam and water fraction is known. Isotopic fractionation factors are generally symbolized by α . The general expression for fractionation between two compounds, A and B, is as follows:

$$1000 \ln \alpha_{AB} = \delta_A - \delta_B$$

where δ_A and δ_B designate the respective isotopic ratios in compounds A and B (Arnorsson, 2000). Four isotopic geothermometers based on exchange reactions have been developed and extensively used.

5.2 Carbon dioxide and methane isotope geothermometer

Reaction:



Temperature equation:

$$1000 \ln \alpha = 15.25 \times 10^3 / T + 2.432 \times 10^6 / T^2 - 9.56$$

(Valid in the range 100-400°C)

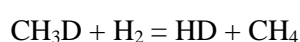
and

$$t^{\circ}\text{C} = \frac{15790}{1000 \ln \alpha + 9.0} - 273.15$$

(Valid in the range 150-500°C)

5.3 Methane – Hydrogen gas isotope geothermometer

Reaction:



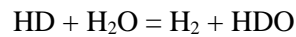
Temperature equation:

$$1000 \ln \alpha = 288.9 \times 10^3 / T + 31.86 \times 10^6 / T^2 - 238.28$$

(Valid in the range 100-400°C)

5.4 Water-hydrogen gas isotopic geothermometer

Reaction:



Temperature equation:

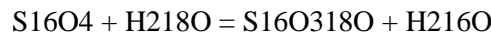
$$1000 \ln \alpha = 396.8 \times 10^3 / T + 11.76 \times 10^6 / T^2 - 217.3$$

(Valid in the range 100-400°C for equilibrium between H₂ and steam)

5.5 Sulphate-water oxygen isotope geothermometer

The isotope exchange reaction rate is temperature dependent and is inversely proportional to the aquifer pH. The limitation with this geothermometer is that mixing with sulphate bearing shallow ground waters and oxidation of H₂S may modify the isotopic composition of the dissolved sulphate, such that it no longer reflects the deep geothermal sulphate. Evaporation and mixing with shallow ground water will also affect the water isotopic composition.

Reaction:

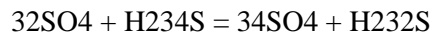


$$1000 \ln \alpha = 3.25 \times 10^6 / T^2 - 5.6$$

(Valid in the range 100-350°C)

5.6 Sulphate – hydrogen sulphide geothermometer

Reaction:

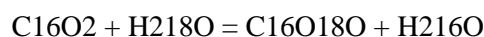


$$1000 \ln \alpha = 6.04 \times 10^6 / T^2 - 2.6$$

(Valid for $t > 150^\circ\text{C}$)

5.7 Carbon dioxide – water isotopic geothermometer

Reaction:



Temperature equation:

$$1000 \ln \alpha = 7.849 \times 10^3 / T + 2.941 \times 10^6 / T^2 - 887.28$$

(Valid in the range 100-400°C for equilibrium between CO₂ and steam)

and

$$1000 \ln \alpha = -18.29 \times 10^3 / T + 7.626 \times 10^6 / T^2 - 19.6$$

(Valid in the range 100-400°C for equilibrium between CO₂ and water)

6. CONCLUSIONS

Chemical and isotope geothermometers constitute an important geochemical tool for the exploration and management of geothermal reservoirs. They are also important during exploitation in monitoring the response of geothermal reservoirs to production load, Figure 4. During the exploration phase, geothermometry is used to estimate subsurface temperatures, i.e., temperatures expected to be encountered by drilling, using the chemical and isotopic composition of the hot spring and fumarole discharges.

The geothermometers are based on chemical reactions, which are temperature dependent and at equilibrium. During the later phases in geothermal development and monitoring, geothermometry has been successfully applied to interpret the composition of well discharges with respect to locating the levels of producing horizons in the wells. Geothermometry is also useful in elucidating chemical reactions occurring in the zone of depressurization around wells that result from boiling and or cooling by recharging cold water.

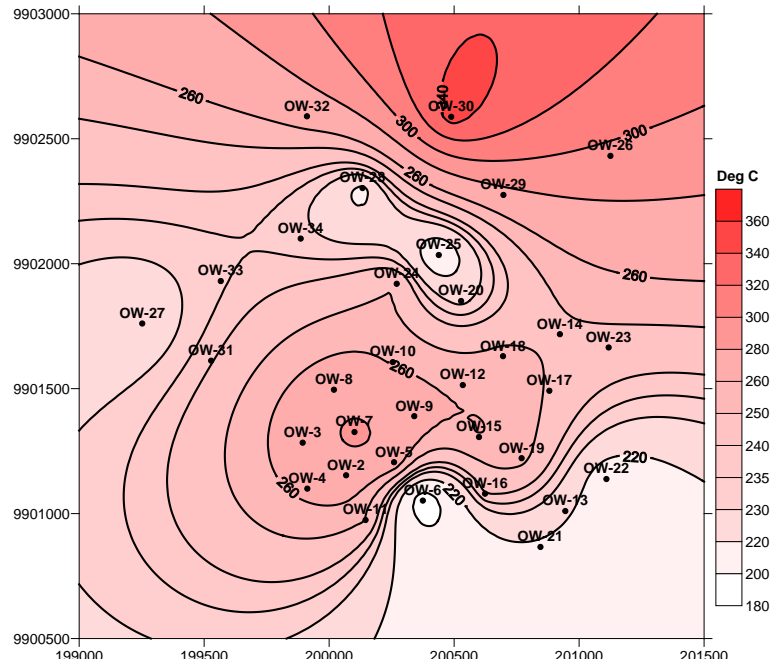


FIGURE 4: Using geothermometers as a monitoring tool in Olkaria, Kenya.

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