



GEOTHERMAL TRAINING PROGRAMME



LaGeo S.A. de C.V.

APPLICATION OF GEOCHEMICAL METHODS IN GEOTHERMAL EXPLORATION

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ABSTRACT

The main objective of geochemical exploration of geothermal resources is to assess the subsurface temperatures in the reservoir, the origin of the fluid, and flow directions within the reservoir. Natural subsurface waters have been classified into meteoric water, ocean water, evolved connate water, magmatic water and juvenile water. Geothermal solutions are most commonly meteoric and oceanic water although solutions in andesitic geothermal systems, near subduction areas often contain significant proportions of evolved connate and magmatic waters. Geothermal waters have been classified with respect to their anion and cation contents into alkali-chloride water, acid sulphate water, acid sulphate-chloride water and bicarbonate water. Acid waters are generally unsuitable for elucidation of subsurface properties. Conservative constituents are used for tracing origin and flow of geothermal fluids, stable isotopes (especially ^2H and ^{18}O) along with B and Cl being most important. Radioactive isotopes and chlorofluorocarbons (CFCs) have been used for dating. Rock forming constituents (e.g. SiO_2 , Na, K, Ca, Mg, CO_2 , H_2) are used to predict subsurface temperatures and potential production problems such as deposition and corrosion. Triangular diagrams and $\log(\text{Q}/\text{K})$ diagrams are introduced as powerful tools in the interpretation of geothermal geochemistry.

1. INTRODUCTION

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 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.

2. CLASSIFICATION

Subsurface waters: It has proved difficult to obtain a genetic classification of subsurface waters. The waters that have been studied in detail are mostly those that are of economic interest as potable water.

Water also tends to flow away from its point of origin and also undergo water-rock interaction during its travels making it increasingly difficult to decipher its origins. White (1986) attempted a classification which is summarized below:

- Meteoric water circulates in the atmosphere, co-existing with near-surface, uncemented sediments, can circulate in subsurface rocks and dissolve constituents, e.g. evaporites.
- Ocean water is partly evaporated products of meteoric water
- Evolved connate water forms in young marine sediments. Variable salinity is observed and may be due to filtration, evaporation or dissolution of evaporites.
- Metamorphic water is contained in or driven from rocks undergoing metamorphic dehydration reactions. Being over pressured at depth, it may escape in response to lithostatic load.
- Magmatic water is derived from oceanic and evolved connate waters subducted along with oceanic crust into the mantle. At deep crustal level it is mostly due to rocks undergoing metamorphism.
- Juvenile water is classified as water that has never circulated in the atmosphere. If it exists it must be extremely rare. Juvenile ^3He and CO_2 of mantle origin exist and thus suggest that juvenile H_2O may exist too but it has not yet been identified conclusively.

Geothermal waters: Ellis and Mahon (1978) classified geothermal water into four categories based on major ions:

- Alkali-chloride water: pH 4-11, least common in young rocks, e.g. Iceland. These are mostly sodium and potassium chloride waters although in brines Ca concentration is often significant.
- Acid sulphate water: These waters arise from the oxidation $\text{H}_2\text{S} \rightarrow \text{SO}_4$ 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.
- Acid sulphate-chloride water: such water may be a mixture of alkali chloride water and acid sulphate water, or it can arise from the oxidation $\text{H}_2\text{S} \rightarrow \text{SO}_4$ 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.
- Bicarbonate water: Bicarbonate water 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). An example from Uganda is shown in Figure 1, where the geothermal water from one area, Kibiro, is typical alkali-chloride water, the water from another, Buranga is relatively alkaline chloride-sulphate-bicarbonate water, but the geothermal water from the third one, Katwe, is sulphate water. The cold groundwater in the areas is scattered.

The dissolved constituents of geothermal water do 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. Therefore it is possible to deduce the properties of subsurface water from the chemical composition of water which has been collected at the earth's surface.

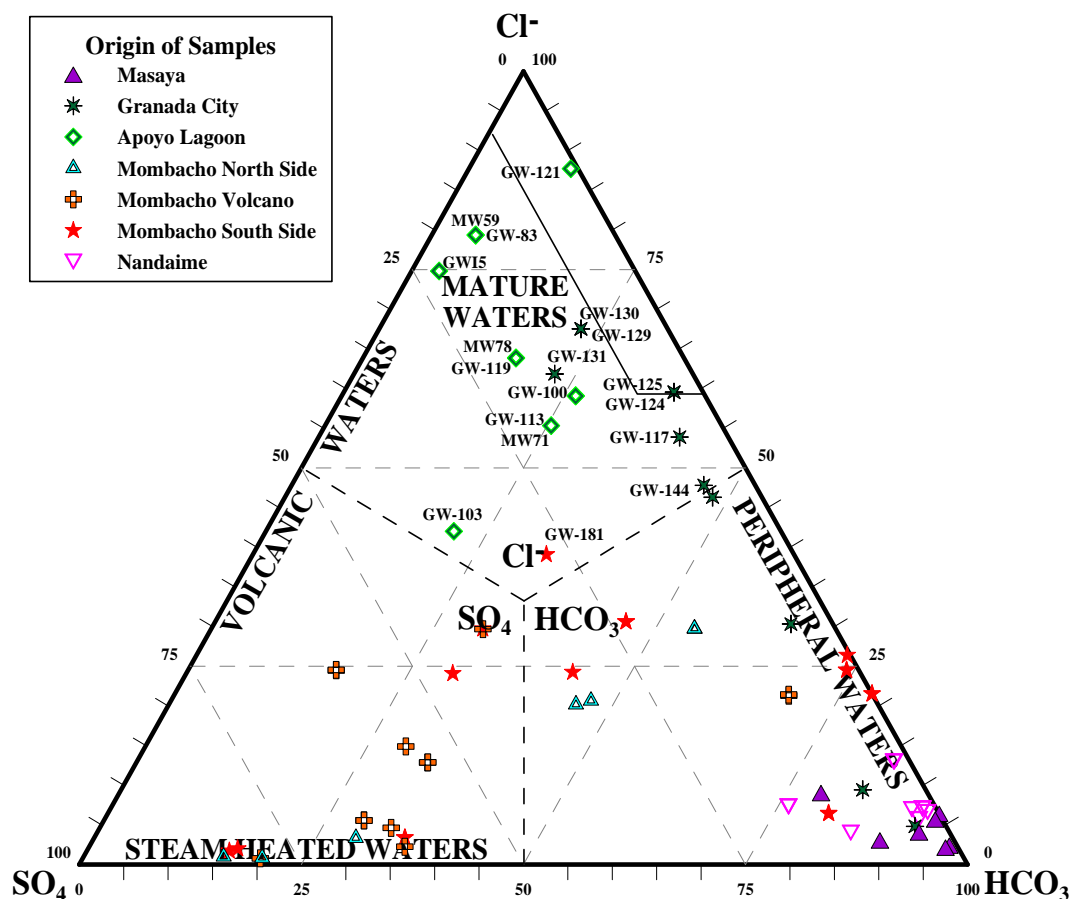


FIGURE 1: A ternary $\text{Cl-SO}_4\text{-HCO}_3$ diagram showing the characteristics of waters from the Masaya-Granada-Nandaime region in Nicaragua (after Ruiz Cordero, 2008).

3. TRACING THE ORIGIN AND FLOW IN GEOTHERMAL SYSTEMS

Stable isotopes and conservative constituents, such as Cl, B, and Br, are the most powerful tracers of the origin of geothermal systems. The relationships of major ions, e.g. seen in ternary diagrams such Cl^- - SO_4^{-2} - HCO_3^- give an insight into the origin of the constituents of the water.

3.1 The use of stable isotopes

In sea water δD and $\delta^{18}\text{O}$ are close to 0‰ (SMOW). Evaporation subsequently causes the formation of clouds into which light isotopes preferably find their way. The clouds are eventually precipitated and the relative concentration of light and heavy isotopes depends on several factors, i.e. latitude as lower isotope ratios are found at high than low latitudes, altitude and distance from sea shore where relatively lower isotope ratios are found in precipitation at higher than lower altitudes and greater than

shorter distances from the shore. Temporal effects may cause variations in isotopic composition at the same place. Single showers may travel different distances and their composition depends on the origin of the cloud and the temperature of condensation. Seasonal changes are observed with lower isotope ratios in winter than summer. This effect is more pronounced at high than low latitudes. Long-term climatic changes produce a similar effect with low isotope ratios in precipitation from cold climates but higher ones from times of warmer climate. A quantitative effect is sometimes observed as an inverse relationship between isotope ratios and quantity of precipitation. This effect is more pronounced at low than high latitudes (Truesdell and Hulston 1980).

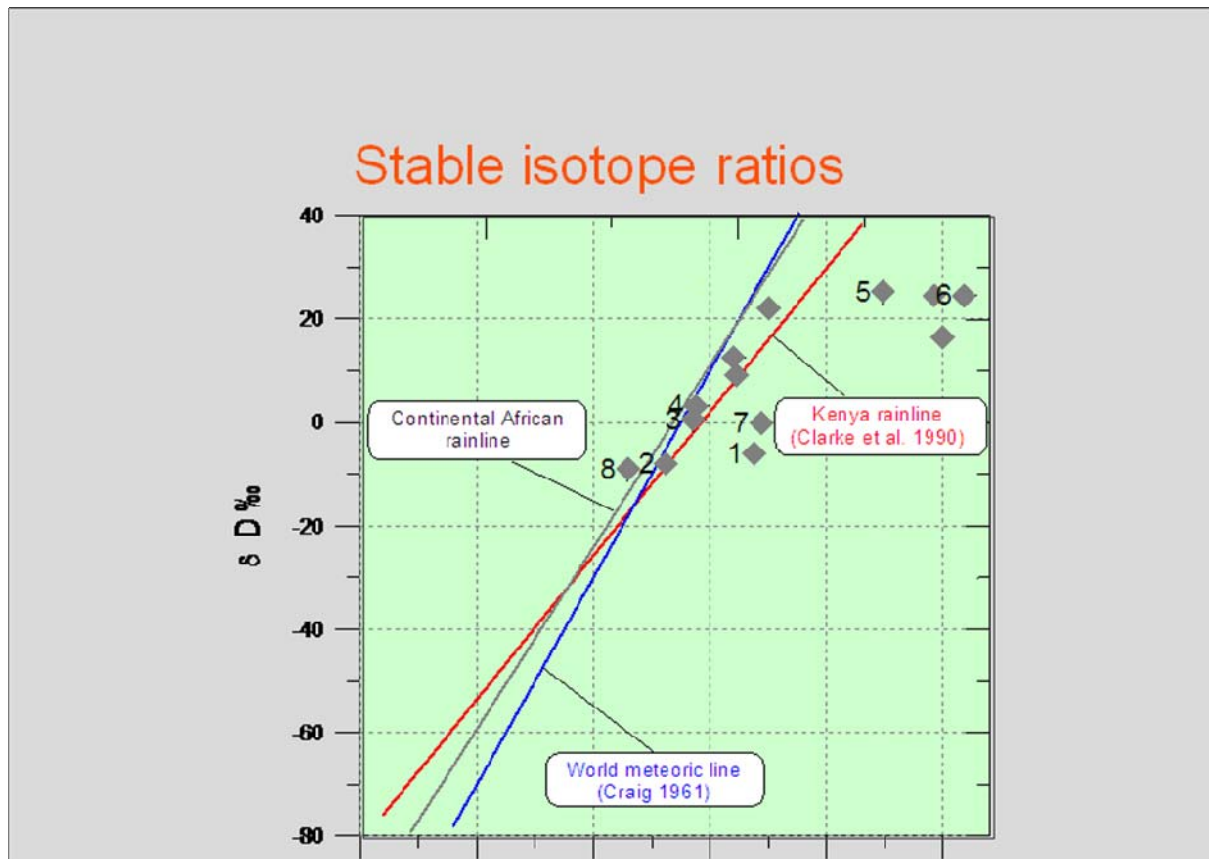


FIGURE 2: World meteoric line, Continental African rainline, Kenya rainline. Samples from Ugandan areas plotted and show variation. The oxygen isotope shift is probably due to poor permeability

The reason for the usefulness of stable isotope ratios for tracing water origin is that after precipitation there is little change in them although the water may travel long distances. Local annual means for precipitation have been established and (Craig 1961) showed that a meteoric line describing the relationship between δD and $\delta^{18}O$ applies all over the world although deviations are known and local lines have been described. However isotopic ratios of geothermal water values suggest its origin but mixing, water-rock interaction, condensation and age may have to be accounted for.

3.2 The use of conservative constituents

The boron concentration of sea water and thus precipitation is low but that of rocks and of volcanic steam is relatively much higher and boron is extremely soluble. The chloride concentration of sea water and thus evaporation is high but in rocks and some magmatic steam relatively low. Thus the B/Cl ratio can be used to trace mixing of sea water or magmatic steam with precipitation.

3.3 Dating

One way of studying the origin of geothermal water is by dating. For this two types of methods have been used, i.e. determination of radioactive materials and chlorinated fluorocarbons. Of radioactive substances ^3H with a half life of 12.43 years has been extremely useful for relatively young waters. It is measured in tritium units (1 TU = 1.185 Bq/L). The natural cosmogenic level in precipitation is a few TU but rose to ≈ 2000 TU from the nineteen fifties to 1963/1964 but is down to ≈ 10 TU at present. For older waters dating with ^{14}C with a half life of 5730 years has been used. It is present in atmospheric CO_2 , the living biosphere and hydrosphere after production by cosmic radiation but underground production negligible and therefore it cannot be used for carbon from a magmatic source. The ^{14}C content is often presented as % modern carbon (pMC), grown in in 1950. Fallout ^{14}C (in CO_2) has been used to date water with mean residence time less than 150 years. Organic compounds of chlorine and fluorine are man-made and first appeared in 1928. They are unreactive and non-toxic. CFC-11, CFC-12 and CFC-113 are the most common of these. The release of CFC-11 and CFC-12 to the atmosphere rose in the 1930s. Deviations in the release were first noted following 1974, when possible ozone depletion by chlorine-containing species was first announced, but much more significant ones after the signing of the Montreal Protocol in 1987. Release of CFC-113 increased significantly through the early- and mid-1980s until the Montreal Protocol was signed, after which production significantly diminished.

TABLE 1: Atmospheric lifetime of chlorinated fluorocarbons

CFC	Lifetime (years)
CFC-11	45 \pm 7
CFC-12	87 \pm 17
CFC-13	100 \pm 32

3.4 Geothermal gases

The origins of geothermal gases are diverse and can be magmatic, in rock dissolution, organic, atmospheric and radiogenic. Studies of isotopes, inert gases, and thermodynamic calculations help elucidate the origin in each case. The $\delta^{13}\text{C}$ signatures for CO_2 of different origins are -10 to -1‰ in magmatic gases, -2 to +2‰ in gas derived from marine limestone, <-20‰ for CO_2 of organic origin and -5 to -8 ‰ in atmospheric CO_2 . Sulphur isotope ratio ($\delta^{34}\text{S}$) for H_2S leached from rock is <0‰, of magmatic origin ≈ 0 ‰ and of marine origin >0‰. Hydrogen isotope ratio (δD) in H_2 leached from rock or sediments -300 - 450‰ and from magmatic sources: <-450‰. In biogenic hydrocarbons $\delta^{13}\text{C}_{\text{CH}_4}$ is <-55‰ in thermogenic (wet) gas, $\delta^{13}\text{C}_{\text{CH}_4}$ is higher in thermogenic (dry) gas of terrestrial origin, $\delta^{13}\text{C}_{\text{CH}_4}$ but lower in such gas of marine origin. It is rather high in magmatic gas and is expected at -20 to -10‰ in hydrocarbons of inorganic origin. Nitrogen is often to a large degree of atmospheric origin with $\delta^{15}\text{N} \approx 0$ ‰ mixing with sedimentary sources can result in $\delta^{15}\text{N} > 0$ but mantle derived nitrogen can result in $\delta^{15}\text{N} < 0$.

4. GEOTHERMOMETRY

4.1 Assumptions

Chemical geothermometry, in the context of geothermal studies, refers to the use of chemistry to evaluate the temperature in geothermal reservoirs. The composition of geothermal solutions is commonly, to a large extent, controlled by local and partial chemical equilibria between the fluid and

the host rock. These chemical equilibria are in many cases temperature-sensitive, i.e. the composition of the fluid is a function of the temperature in the system. Chemical geothermometry makes use of this by inferring subsurface temperatures from observed fluid compositions.

One of the fundamental assumptions in the use of chemical geothermometers is that a partial chemical equilibrium is attained in the geothermal reservoir. Dissolved chemical components in geothermal solutions are referred to as either *conservative components* or *rock-forming components*. The conservative components, such as Cl^- , are generally not controlled by water-rock equilibria but their concentration is determined by their initial concentration in the source fluid (or fluids) or dissolution from the rock. The concentrations (or more correctly the activities) of the reactive components are, on the other hand, controlled by equilibria between the fluid and secondary minerals in the rock that are in contact with it. Most of the major and minor elements dissolved in geothermal solutions are considered reactive components. However, under some circumstances the assumption of partial equilibrium does not hold for some of the dissolved components. Dissolved silica, for example, is almost universally controlled by equilibrium with quartz in most geothermal systems with the exception of young basalt hosted geothermal systems at temperatures below $\sim 180^\circ\text{C}$ in which the silica is controlled by the solubility of chalcedony, a metastable silica polymorph (Árnórsson, 1975; Stefánsson and Arnórsson, 2000, Gíslason et al. 1997). Similarly, dissolved CO_2 is generally considered a reactive component, but in some volcanic geothermal systems the rate of CO_2 influx from magma may, at least periodically, exceed the capacity of the secondary mineral assemblages to incorporate the CO_2 . During such periods of high magmatic gas influx, the concentration of CO_2 is controlled by the flux of gas from magma; not by chemical equilibria between the fluid and the rocks. Under such conditions CO_2 can not be considered a reactive component and the application of CO_2 -geothermometers will give erroneous results. Considering that dissolved silica and CO_2 are involved in the most common chemical geothermometers it should be clear from these examples that caution must be exercised in the application of chemical geothermometers.

Another fundamental assumption is that the composition of the different geothermal fluids has not been affected by secondary processes, other than boiling, on the way to the surface. While this assumption holds true in some cases it is by no means a law of nature. Steam may be affected by condensation on the way to the surface, a process that increases the concentration of all the gases in the steam. Similarly, geothermal solutions that boil and/or cool on the way to the surface may react to re-equilibrate with the rock under the changing temperature conditions. There is, fortunately, a fair number of chemical geothermometers that are affected in different ways by such secondary changes. Consequently, it is very important to use as many geothermometers as possible for any given fluid sample, be it of steam or liquid, as the discrepancy between the results of the different geothermometers may be indicative of the secondary processes affecting the fluid (D'Amore and Arnórsson, 2000).

4.2 Chemical geothermometers

A brief discussion is given below on some of the most commonly used chemical geothermometers. This publication does not attempt to present an exhaustive literature review of this topic but rather present some examples that will be used in practical exercises during the short-course. Isotope geothermometers will, for instance, not be discussed in this publication. For thorough literature reviews of chemical geothermometry the readers are referred to Zhao-Ping and Ármannsson (1996), D'Amore and Arnórsson (2000b), and Zheng-Xilai et al. (2002). The readers are also referred to Arnórsson (2000) for discussion of mixing models.

4.2.1 Univariant geothermometers

Chemical geothermometers can be univariant, i.e. based on the concentration of one reactive constituent (gas or aqueous species) or based on ratios of reactive components. The most widely used univariant geothermometer is probably the silica geothermometer and univariant gas geothermometers

(using the concentrations of CO₂, H₂, and H₂S) are also common. Several calibrations are available for these geothermometers. The most widely used silica geothermometers are based on equilibrium between quartz and the geothermal solution but geothermometers for other silica polymorphs (most importantly for chalcedony) have also been published. The quartz geothermometer of Fournier and Potter (1982) for boiling springs is given in Table 2 below.

TABLE 2: Selected geothermometers

Name	Equation
Quartz ^a	$T(^{\circ}\text{C}) = -53.5 + 0.11236S - 0.5559 \cdot 10^{-4}S^2 + 0.1772 \cdot 10^{-7}S^3 + 88.39 \cdot \log S$
Na/K ^b	$T(^{\circ}\text{C}) = \frac{1217}{1.438 + \log(\text{Na}/\text{K})} - 273.15$
CO ₂ ^c	$T(^{\circ}\text{C}) = \frac{\log(\text{CO}_2) + 3.28 + 1.5 \log(a_{\text{pre}}) - \log(a_{\text{czo}})}{0.0097}$
H ₂ S ^c	$T(^{\circ}\text{C}) = \frac{\log(\text{H}_2\text{S}) + 6.853 + \frac{2}{3} \log(a_{\text{epi}}) - \frac{2}{3} \log(a_{\text{pre}})}{0.01343}$
H ₂ ^c	$T(^{\circ}\text{C}) = \frac{\log(\text{H}_2) + 4.686 + \frac{2}{3} \log(a_{\text{epi}}) - \frac{2}{3} \log(a_{\text{pre}})}{0.007962}$

a: Fournier and Potter (1982); S = concentration of SiO₂ in mg/kg; applies to solutions boiled to 100°C; shown as reported by D'Amore and Arnórsson (2000).

b: Fournier (1979); Na and K refer to concentrations in mg/kg; shown as reported by D'Amore and Arnórsson (2000).

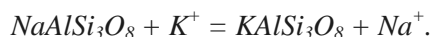
c: Arnórsson et al. (2007); CO₂, H₂S, and H₂ refer to concentrations in steam in mmole/kg steam; a_{epi} and a_{czo} refer to the activities of the end-members of the epidote solid solution (Ca₂FeAl₂Si₃O₁₀(OH) and Ca₂Al₃Si₃O₁₀(OH)) and a_{pre} refers to the activity of prehnite.

The univariant gas geothermometers are more complicated as several possible assemblages of secondary minerals can be identified at potential buffers of the gas concentrations. Arnórsson et al. (2007), for instance propose two possible mineral assemblages for controlling CO₂ concentrations in geothermal fluids and four different assemblages as buffers for the concentration of H₂ and H₂S in geothermal solutions. Predictions of reservoir temperature based on the different mineral assemblages do, fortunately, agree fairly well with each other so the choice of reaction does not greatly affect the predicted temperature. Three of the gas geothermometers reported by Arnórsson et al. (2007) for CO₂, H₂S, and H₂, based on the assumption of equilibrium with quartz, epidote, prehnite, and calcite in the case of CO₂ and pyrite and pyrrhotite in the case of H₂S and H₂ are listed in Table 2.

Simplicity is a benefit of the univariant geothermometers but they are also susceptible to secondary processes such as dilution and condensation. Errors due to condensation on univariant gas geothermometers can be prevented by using ratios of the reactive gases to conservative gas species such as Ar or N₂. In such cases the concentration of the conservative gas species is taken to be equal to that of air-saturated water.

4.2.2 Geothermometers based on ratios

The most commonly used geothermometer that utilizes cation ratios is the Na/K geothermometer. Several calibrations have been published, both empirical and theoretical. The Na/K geothermometer of Fournier (1979) is shown in Table 2. It is commonly assumed that the Na/K ratio in geothermal solutions is constrained by simultaneous equilibria between the geothermal solution and Na- and K-feldspar, described by the reaction:



However, it has also been postulated that the Na/K ratio may in some geothermal systems just as well be controlled by ion-exchange equilibrium between Na- and K-clay minerals. Cation ratio geothermometers have been calibrated and published for other cation pairs such as K/Mg, Na/Ca, K/Ca, Na/Li and Li/Mg (see D’Amore and Arnórsson, 2000b, for discussion). A characteristic feature of the Na/K thermometer is that it seems to equilibrate slowly, which can be both an advantage and a disadvantage. For example, a discrepancy between the temperatures predicted by the Na/K geothermometer and other, more rapidly equilibrated thermometers, such as the quartz thermometer, the discrepancy can be indicative of the cooling or heating history of the geothermal fluid.

The Na/K/Ca geothermometer proposed by Fournier and Truesdell (1973) uses both the Na/K and the Na/Ca^{0.5} ratios to predict reservoir temperature. It has been used successfully on many occasions and it has been found to give reliable results at low temperatures, at which the Na/K geothermometers have a tendency to give erroneously high results (D’Amore and Arnórsson, 2000b). Giggenbach (1988) proposed a graphical method involving the simultaneous use of a Na/K and K/Mg^{0.5} ratio geothermometers. The advantage of this method is that it gives both an estimate of the reservoir temperature and indicates the “maturity” of the geothermal solution by combining the results of the fast equilibrating K/Mg^{0.5} geothermometer and the slow Na/K geothermometer. An example of a Na-K-Mg ternary diagram is shown on Figure 3.

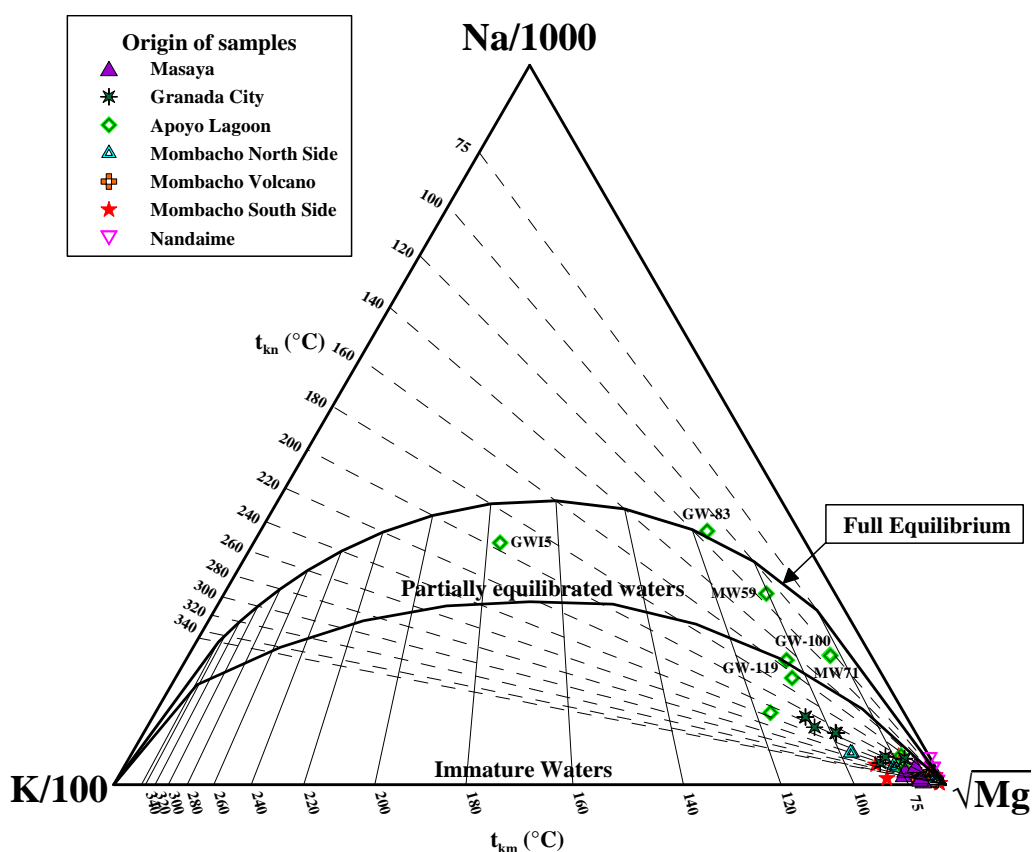


FIGURE 3: Na-K-Mg ternary diagram showing the temperature and “maturity” water samples in the Masaya-Granada-Nandaime region in Nicaragua (after Ruiz Cordero, 2008).

4.2.3 Multiple mineral equilibria approach

Reed and Spycher (1984) proposed this method for evaluating reservoir temperatures. It is based on computation of the saturation state of typical secondary minerals in geothermal systems over a range

of temperatures. The results are presented on a graph showing the saturation state (presented as $\log(Q/K)$) for the different minerals as a function of temperature. If the fluid has been in equilibrium with a certain assemblage of secondary minerals the $\log(Q/K)$ curves for these minerals will intersect at zero (indicating equilibrium). The temperature at which the curves intersect zero is then the reservoir temperature. This method has the advantage of discriminating between equilibrated and non-equilibrated solutions. However, this method is sensitive to the choices of secondary minerals considered, the quality of thermodynamic data for the minerals, and to the quality of analysis of elements such as Mg, Al, and Fe that occur in the geothermal solutions in very low concentrations. An example of a multiple mineral equilibria analysis is shown on Figure 4.

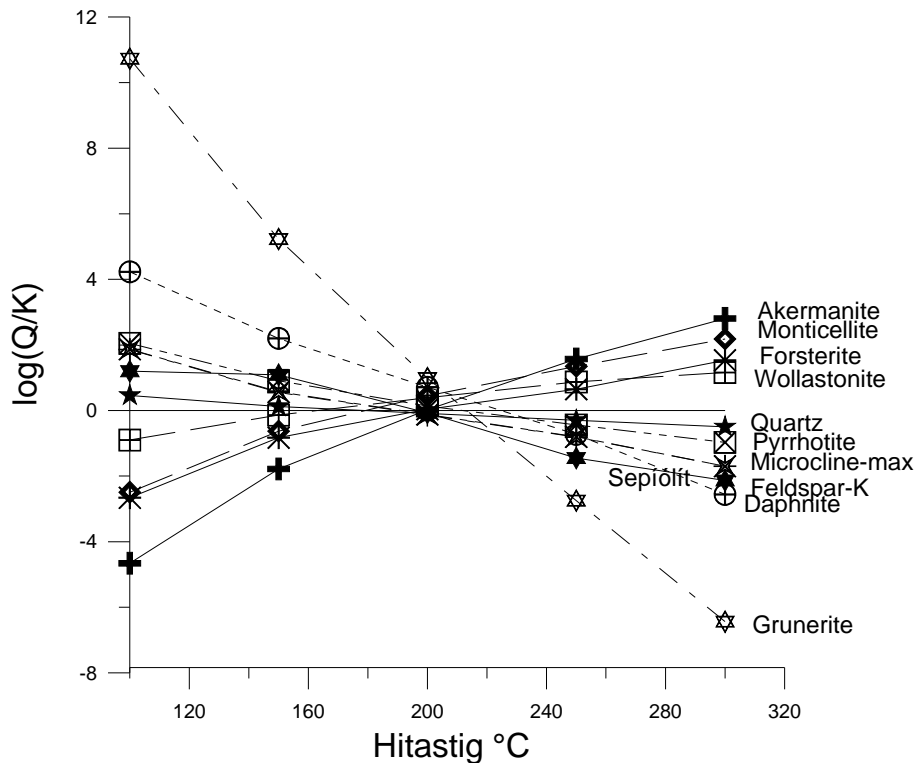


FIGURE 4: Multiple mineral equilibria analysis of sample ThG-2 shown in Figure 3. This analysis indicates that the reservoir temperature is around 200 °C, in good agreement with the Na-K-Mg analysis shown in Figure 3.

5. PRODUCTION PROBLEMS

The common production problems due to the chemistry of geothermal fluids are deposition and corrosion. Pollution is usually dealt with as an environmental problem.

5.1 Deposition

The most common deposits in geothermal utilization are due to silica, iron oxides, iron silicates, sulphides, calcium carbonate and magnesium silicates. Deposits due to aluminium silicates, anhydrite, barite, apatite, borates and sulphur are also known. Studies of deposits are twofold, i.e. a theoretical thermodynamic study to find out whether deposition can take place and experimental, kinetic studies to find out whether the deposition is fast enough to cause problems.

It was noted above that quartz is almost universally at equilibrium with geothermal solutions in high-temperature geothermal systems. Boiling (and consequent cooling) of such fluids leads to super

saturation with respect to quartz. However, the relatively slow kinetics of quartz precipitation prevents the precipitation of this phase in production wells. Silica scaling does not become a problem until progressive boiling and cooling has brought the fluid to supersaturation with respect to amorphous silica. Amorphous silica scales are usually not formed inside wells but may form in surface equipment and reinjection wells. The saturation temperature and pressure of amorphous silica control the deposition. This can be calculated but rate experiments may be performed to find out whether it is possible to operate at a lower temperature. Figure 5 illustrates the results of modeling of boiling of geothermal solutions from the Reykjanes system in Iceland. Large symbols indicate the silica concentrations in the reservoir. These liquids are near equilibrium with quartz. Smaller symbols illustrate the evolution of the silica concentration in the liquid phase as it boils. The liquid from the two wells becomes super saturated with respect to amorphous silica at different temperatures; RN-10 at 210 °C and RN-19 at 175 °C.

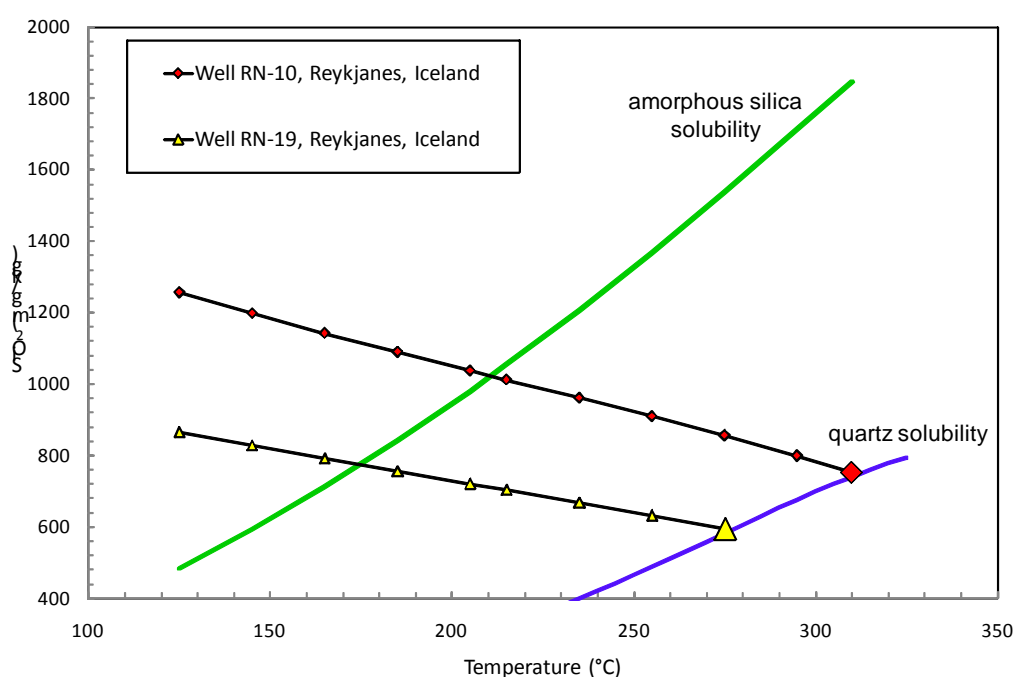


FIGURE 5: Silica concentration in two wells from the Reykjanes geothermal system in Iceland at reservoir conditions (large symbols) and during boiling (small symbols). The liquids from RN-10 and RN-19 will become super saturated with respect to amorphous silica at 210 and 175 °C, respectively.

Flashing causes CO₂ stripping and a pH increase, which may lead to calcite deposition according to

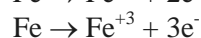


Calcite solubility is retrograde, i.e. it decreases with increasing temperature. The extent of supersaturation can be calculated and the reaction is very fast so rate experiments need not be carried out. Magnesium silicates are formed upon heating of silica containing ground water or mixing of cold ground water and geothermal water. They have been shown to consist mainly of poorly developed antigorite (Gunnarsson et al., 2005). Their solubility decreases (deposition increases) with increased temperature and pH. The rate of deposition has been found to increase linearly with supersaturation but exponentially with temperature.

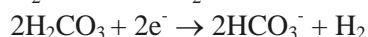
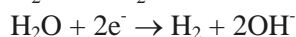
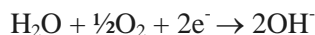
5.2 Corrosion

The term corrosion is used about the chemical destruction of materials. Steel is the most important material used in geothermal installations and its corrosion is due to the following half reactions

Anodic half reactions



Cathodic half reactions



The most common corrosive species in geothermal fluids are O_2 at low temperatures; H^+ (pH) but low pH favours the first two cathodic half-reactions; Cl^{-} which gives $\text{Fe}^{+2} + \text{Cl}^{-} \Leftrightarrow \text{FeCl}^{+}$ thus favouring the first anodic half-reaction; CO_2 which controls pH and favours the last cathodic half-reaction. H_2S attacks Cu, Ni, Zn and Pb. H_2S , CO_3^{-2} and SiO_2 may form protective films on steel.

6. CONCLUSIONS

Subsurface waters are divided into six categories but have mostly at one time or another circulated in the atmosphere. In areas of spreading the origin of geothermal waters is almost exclusively meteoric or oceanic but in subduction areas components of evolved connate and magmatic water are found. Geothermal waters have been divided into four groups according to their major ion composition, i.e. alkali chloride, acid sulphate, acid sulphate-chloride and bicarbonate waters.

Conservative constituents are used to trace origin and flow but rock-forming constituents are used to determine subsurface temperature and other conditions.

REFERENCES

- Aiuppa A., Bellamo S., Brusca L., D'Alessandro W., and Federico C., 2003: Natural and anthropogenic factors affecting groundwater quality of an active volcano (Mt. Etna, Italy). *Applied Geochemistry*, v. 18, 863-882.
- Arnórsson S., 1975: Application of the silica geothermometer in low-temperature hydrothermal areas in Iceland. *American Journal of Science*, v. 275, 763-784.
- Arnórsson S., 2000: Mixing processes in upflow zones and mixing models. In: Arnórsson S., (ed.), *Isotopic and chemical techniques in geothermal exploration, development and use*. International Atomic Agency, Vienna.
- Arnórsson S., Stefánsson A., and Bjarnason J.Ö., 2007: Fluid-Fluid Interactions in Geothermal Systems. *Reviews in Mineralogy and Geochemistry*, v. 65, 259-312.
- Bjarnason, J.Ö. 1994: *The speciation program WATCH, version 2.1*. Orkustofnun, Reykjavík, 7 pp.
- Craig, H. 1961: Isotopic variations in meteoric water. *Science* 153, 10702-10703.
- D'Amore F. and Arnórsson S., 2000aL: Geothermal manifestations and hydrothermal alteration. In: Arnórsson S., (ed.), *Isotopic and chemical techniques in geothermal exploration, development and use*. International Atomic Agency, Vienna.
- D'Amore F. and Arnórsson S., 2000b: Geothermometry. In: Arnórsson S., (ed.), *Isotopic and chemical techniques in geothermal exploration, development and use*. International Atomic Agency, Vienna.

- Ellis, A.J. and Mahon, W.A.J. 1977: *Chemistry and geothermal systems*. Academic Press, New York, 392 pp.
- Fournier, R.O., 1979: A revised Na/K geothermometer. *Geothermal Resource Council Transactions*, v. 3, 221-224.
- Fournier, R.O. and Potter, R.W.II., 1982: A revised and expanded silica (quartz) geothermometer. *Geothermal Resource Council Bulletin*, v. 11, 3-9.
- Fournier, R.O. and Truesdell, A.H., 1973: An empirical Na-K-Ca geothermometer for natural waters. *Geochimica et Cosmochimica Acta*, v. 37, 1255-1275.
- Giggenbach, W.F., 1988: Geothermal solute equilibria. *Geochimica et Cosmochimica Acta*, v. 52, 2749-2765.
- Giggenbach, W.F. 1991: Chemical techniques in geothermal exploration. In D'Amore, F. (coordinator), *Applications of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 119-142.
- Gíslason, S.R., Heaney, P.J., Oelkers, E.H., and Schott, J., 1997: Kinetic and thermodynamic properties of moganite, a novel silica polymorph. *Geochimica et Cosmochimica Acta*, 61, 1193-1204.
- Gunnarsson, I., Arnórsson, S. and Jakobsson, S. 2005: Precipitation of poorly crystalline antigorite under hydrothermal conditions. *Geochim. Cosmochim. Acta* 69, 2813-2828.
- Reed M. and Spycher N., 1984: Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution. *Geochimica et Cosmochimica Acta*, v. 48, 1479-1492.
- Reed, M.H. and Spycher, N.F., 1989: *SOLVEQ: A computer program for computing aqueous-mineral-gas equilibria. A manual*. Department of geological Sciences, University of Oregon, Eugene, Oregon, 37 pp.
- Ruiz Cordero, J.F., 2008: Geochemical interpretation of the Masaya-Granada-Nandime chemical data, Nicaragua. Report 26 in: *Geothermal training in Iceland 2008*. UNU-GTP, Reykjavík, Iceland, 477-518.
- Stefánsson A. and Arnórsson S., 2000: Feldspar saturation state in natural waters. *Geochim. Cosmochim. Acta*, 64, 2567-2584.
- Tole, M.P., Ármannsson, H., Pang, Z. and Arnórsson, S. 1993: Fluid/mineral equilibrium calculations for geothermal fluids and chemical geothermometry. *Geothermics* 22, 17-37.
- Truesdell, A.H. and Hulston, J.R. 1980: Isotopic evidence on environments of geothermal systems. In Fritz, P. and Fontes, J.C. *Handbook of Environmental Isotope Chemistry, Vol. 1. The Terrestrial Environment*, Elsevier, 179-226.
- White, D. 1986: Subsurface waters of different origins. In: Ólafsson, J. and Ólafsson, M. (editors) *Fifth International Symposium on Water-Rock Interaction. Extended abstracts*. International Association of Geochemistry and Cosmochemistry, Orkustofnun, Reykjavík, 629-632.
- Zhao-Ping and Ármannsson H., 1996: Gas geothermometry in selected Icelandic geothermal fields with comparative examples from Kenya. *Geothermics*, v. 25, 307-347.
- Zheng-Xilai, Ármannsson H., Li-Youngle, and Qiu-Hanxue, 2002: Chemical equilibria of thermal waters for the application of geothermometers from Guanzhong basin, China. *Journal of Volcanology and Geothermal Research*, v. 113, 119-127.