



## APPLICATION OF GEOCHEMICAL METHODS IN GEOTHERMAL EXPLORATION

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### ABSTRACT

Subsurface waters have been classified into meteoric water, ocean water, evolved connate water, magmatic water and juvenile water. Geothermal water is mostly meteoric and oceanic water although andesitic waters 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  $^2\text{H}$  and  $^{18}\text{O}$ ) along with B and Cl being most important. Radioactive isotopes and chlorofluorocarbons (CFCs) have been used for dating. Rock forming constituents (e.g.  $\text{SiO}_2$ , Na, K, Ca, Mg,  $\text{CO}_2$ ,  $\text{H}_2$ ) are used to predict subsurface temperatures and potential production problems such as deposition and corrosion. Triangular diagrams and  $\log(Q/K)$  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 reproduced here.

- 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. It is initially 10-50% oceanic or pore water mixed with combined water. Upon increased burial depth more interaction takes place at modest temperatures, and compaction leads to lower pressure environments. 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  $^3\text{He}$  and  $\text{CO}_2$  of mantle origin exist and thus suggest that juvenile  $\text{H}_2\text{O}$  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  $\text{CO}_2$  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 a typical alkali-chloride water, the water from another, Buranga is a relatively alkaline chloride-sulphate-bicarbonate water, but the geothermal water from the third one, Katwe, is a sulphate water. The cold groundwater in the areas is scattered.

The dissolved constituents of geothermal water may originate in the original meteoric or oceanic water, but more likely they are the result of water-rock interaction and possibly modification by magmatic gas. They 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.  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ), 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,  $\text{Ca}^{+2}$

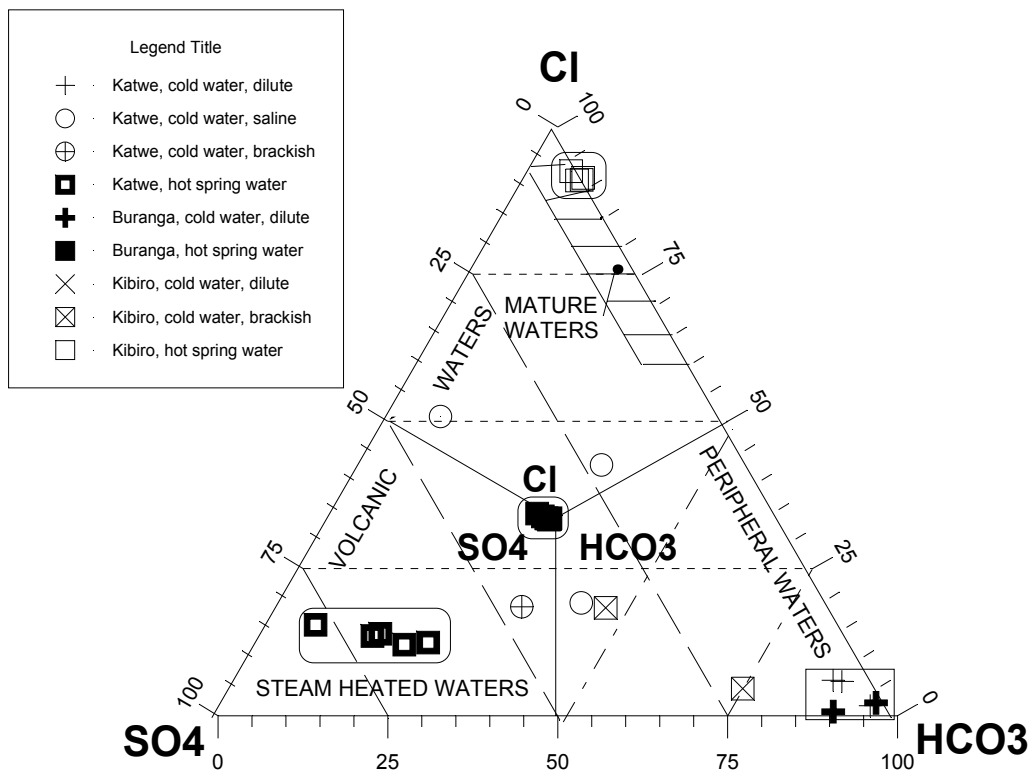


FIGURE 1: A ternary Cl-SO<sub>4</sub>-HCO<sub>3</sub> diagram showing the characteristics of waters from different Ugandan geothermal systems

and HCO<sub>3</sub><sup>-</sup> concentrations depend on pH and CO<sub>2</sub> concentration because of equilibrium between the fluid and calcite, F<sup>-</sup> and SO<sub>4</sub><sup>-2</sup> concentrations are related to that of Ca<sup>+2</sup>, limited by solubility of fluorite and anhydrite and temperature and salinity dependent silicate equilibria control a very low Mg<sup>+2</sup> 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.

### 3. TRACING THE ORIGIN AND FLOW IN GEOTHERMAL SYSTEMS

Stable isotopes and conservative constituents making use of ratios, e.g. Br/Cl, B/Cl and/or ternary diagrams, e.g. Cl-Li-B, 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<sub>4</sub><sup>-2</sup>-HCO<sub>3</sub><sup>-</sup> give an insight into the origin of the constituents of the water.

#### 3.1 The use of stable isotopes

In sea water δD and δ<sup>18</sup>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).

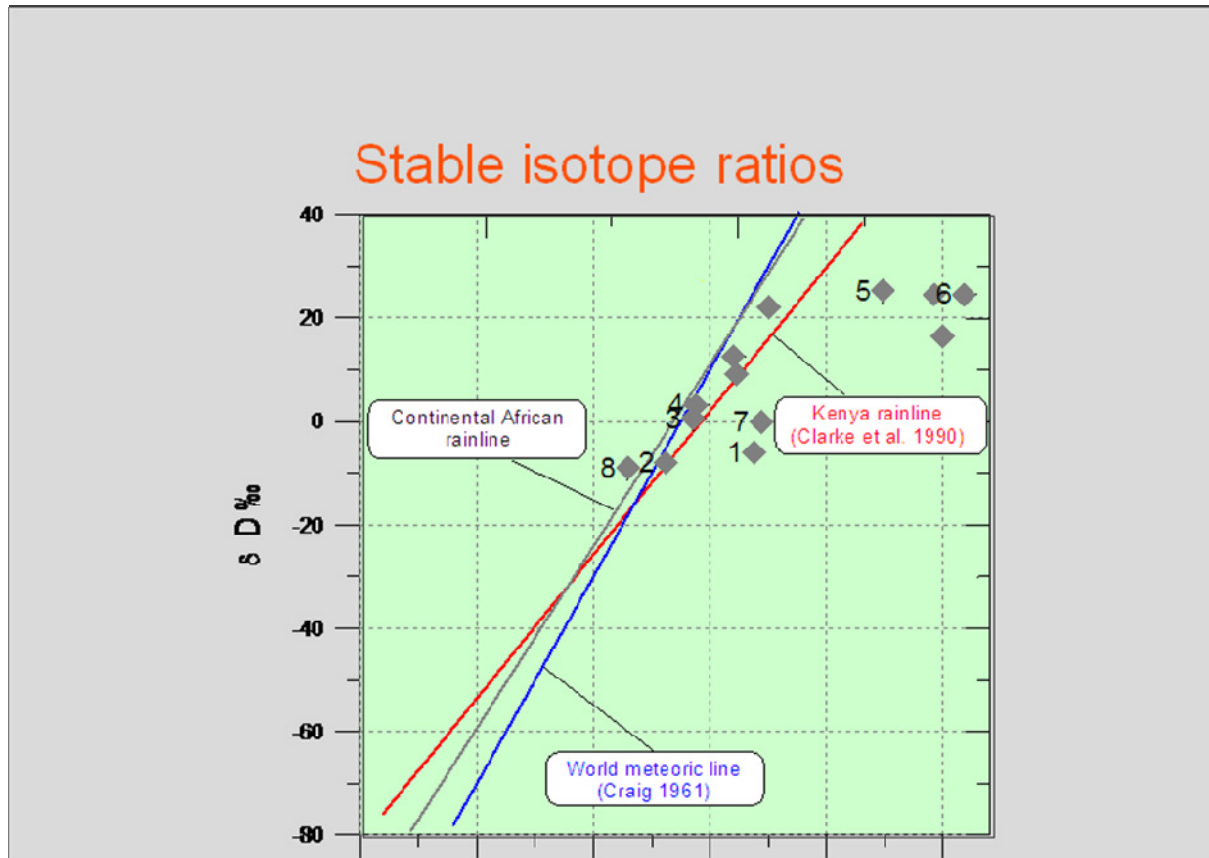


FIGURE 2: World meteoric line, Continental African rainline, Kenya rainline. Samples from Ugandan areas plotted and show variation. The oxygen isotope shift is probably due to poor permeability

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  $\delta D$  and  $\delta^{18}O$  applies all over the world although deviations are known and local lines have been described. However 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  $^3\text{H}$  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  $\approx 2000$  TU from the nineteen fifties to 1963/1964 but is down to  $\approx 10$  TU at present. For older waters dating with  $^{14}\text{C}$  with a half life of 5730 years has been used. It is present in atmospheric  $\text{CO}_2$ , 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  $^{14}\text{C}$  content is often presented as % modern carbon (pMC), grown in in 1950. Fallout  $^{14}\text{C}$  (in  $\text{CO}_2$ ) 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
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  $\text{CO}_2$  of different origins are -10 - -1‰ in magmatic gases, -2 - +2‰ in gas derived from marine limestone, <-20‰ for  $\text{CO}_2$  of organic origin and -5 - -8 ‰ in atmospheric  $\text{CO}_2$ . Sulphur isotope ratio ( $\delta^{34}\text{S}$ ) for  $\text{H}_2\text{S}$  leached from rock is <0‰, of magmatic origin  $\approx 0$ ‰ and of marine origin >0‰. Hydrogen isotope ratio ( $\delta\text{D}$ ) in  $\text{H}_2$  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 -10‰ in hydrocarbons of inorganic origin. Nitrogen is usually of atmospheric origin with  $\delta^{15}\text{N} \approx 0$ ‰.

## 4. GEOTHERMOMETRY

Many reactions in geothermal systems are temperature dependent but their kinetics are not fast at lower temperatures so that their equilibrium characteristics are preserved even though the waters rise to the surface and cool down. Thus the concentrations of surface geothermal fluids may be determined and, as a result subsurface temperature may be determined as well. Reactions in the liquid phase and in the vapour phase as well as isotope exchange reactions in both phases have been used this way for geothermometry. Geothermometers may be univariant, e.g.  $\text{SiO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$  with the disadvantage of sensitivity to secondary changes such as dilution, steam loss and condensation. They may be global involving the assumption that a number of constituents is simultaneously at equilibrium and that their present concentrations can be used to obtain the equilibrium temperature and thus depend on analytical reliability and thermodynamic data. Thirdly, equimolar and equicoulombic ratios, e.g. Na/K,  $\text{CO}_2/\text{H}_2$  can be used for geothermometry. Such geothermometers overcome the disadvantage of univariant geothermometers but equilibrium and rate conditions limit their value. Combinations of alkali and alkaline earth metal concentrations may as well as providing subsurface temperatures be used to

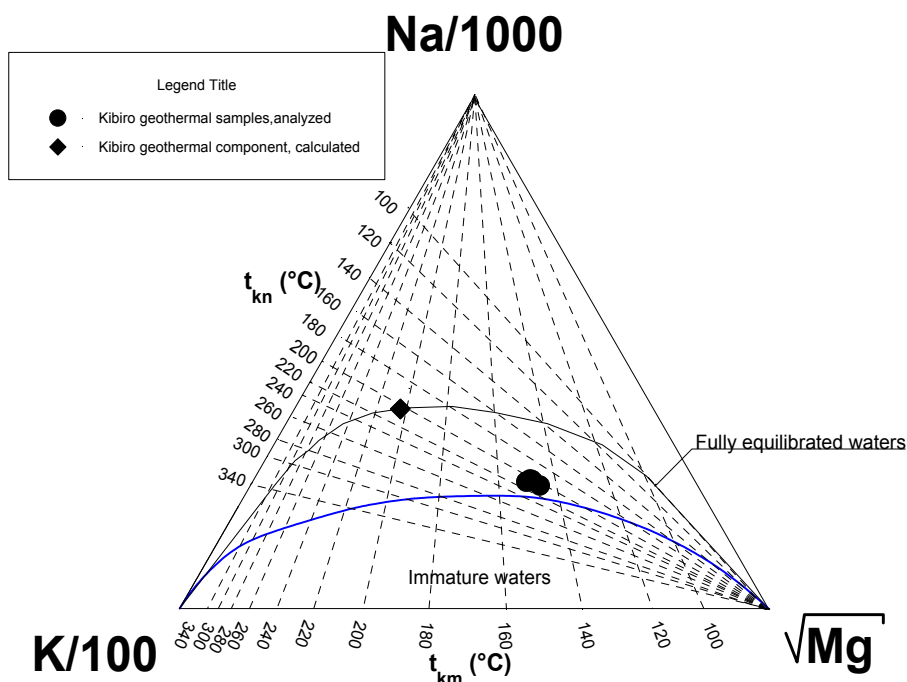


FIGURE 3: Na-K-Mg triangular diagram, showing examples from Kibiro, Uganda

evaluate whether the water is at equilibrium with the prevalent alteration minerals in the rock, e.g. by using the Na-K-Mg diagram shown in Figure 3 (Giggenbach 1991). The points in the diagram are from the Kibiro area, Uganda, and the partially equilibrated waters represent a mixture of the geothermal component and local groundwater whereas the fully equilibrated water represents the geothermal component. For equilibrium calculations which are needed to obtain temperatures from global geothermometers speciation programs such as WATCH (Bjarnason 1994) and SOLVEQ (Reed and Spycher 1989) are used. An example is shown in Figure 3 in which the temperature of well 4 in Námafjall, Iceland has been estimated by calculating  $\log(Q/K)$  where Q is the activity quotient but K is the equilibrium constant over a range of temperatures. The saturation temperature and therefore the equilibrium subsurface temperature corresponds to  $\log(Q/K) = 0$  and this is found at about 160°C in the present example.

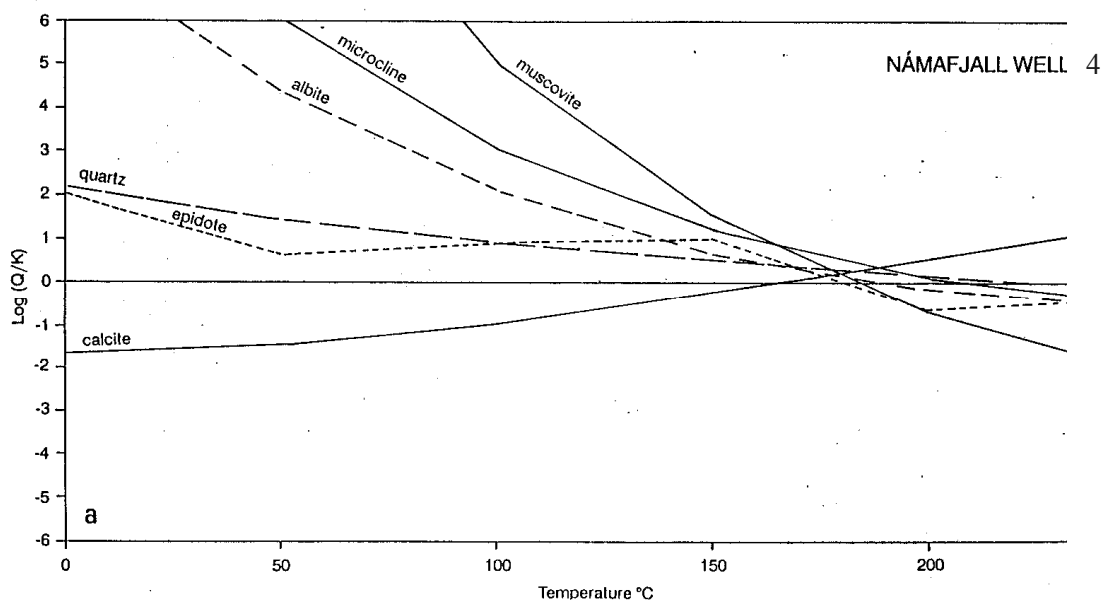


FIGURE 4: A  $\log(Q/K)$  diagram for probable alteration minerals in well 4, Námafjall, Iceland (Tole et al. 1993)

## 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, calcite 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.

Silica deposits 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.

Flashing causes CO<sub>2</sub> 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.

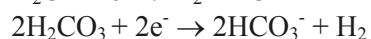
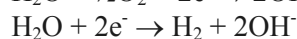
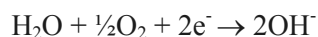
### 5.2 Corrosion

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<sub>2</sub> at low temperatures; H<sup>+</sup> (pH) but low pH favours the first two cathodic half-reactions; Cl<sup>-</sup> which gives Fe<sup>+2</sup> + Cl<sup>-</sup> ⇌ FeCl<sup>+</sup> thus favouring the first anodic half-reaction; CO<sub>2</sub> which controls pH and favours the last cathodic half-reaction. H<sub>2</sub>S attacks Cu, Ni, Zn and Pb. H<sub>2</sub>S, CO<sub>3</sub><sup>-2</sup> and SiO<sub>2</sub> 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.

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