UNITED NATIONS UNIVERSITY
GEOTHERMAL TRAINING PROGRAMME
Orkustofnun, Grensásvegur 9,
IS-108 Reykjavík, Iceland

Reports 2008
Number 28

ORIGIN OF GEOTHERMAL WATERS AND SUBSURFACE TEMPERATURE ESTIMATES IN THE SOUTHERN LOWLANDS OF ICELAND

Daniel Weldeyohannes Hailemichael
Ministry of Energy and Mines
Department of Mines, Geological Survey
P.O.Box 272, Asmara
ERITREA
whdani207@yahoo.com

ABSTRACT

Interpretation of the isotopic and chemical content of natural waters in the Southern Lowlands of Iceland reveals that the origin of the waters for the low-temperature geothermal systems in the area is related to their geographical and topographical positions relative to the sea and submergence of the lowlands at the end of the last glaciation. The low-temperature thermal waters that are located at relatively low altitudes are composed of present-day precipitation, seawater from the end of the last glaciation and also meteoric water from the same time.

Linear correlation between chloride and boron in spring waters from the Geysir high-temperature geothermal field indicate that warm spring waters are formed by the mixing of cold water and undegassed deep hot water. The same correlation also indicates mixing of cold ground and geothermal waters in the eastern and northwestern low-temperature thermal systems. All thermal waters have more negative δ^2H values than the local precipitation. Oxygen shift from the global meteoric line indicates strong (extensive) water-rock interaction for the non-mixed waters but is limited in the case of mixed waters.

Subsurface temperature estimates from silica and Na-K geothermometers indicate that they are unreliable in the cold surface waters and mixed waters from the Geysir area due to lack of equilibrium. The chalcedony and Na-K temperature estimates in the low-temperature systems are comparable but the Na-K geothermometer gives a higher estimate for temperatures of less than 100°C. The Na-K geothermometer gives lower temperature estimates for the un-mixed waters of the Geysir area, probably due to base-exchange reactions involving clays that remove K from the solution. Quartz equilibrium temperatures are, therefore, considered to be more reliable.

1. INTRODUCTION

The use of isotopes in geothermal investigations is based on the behaviour of the concentrations of the isotopes in the natural environments. Two opposing properties of isotopes have been exploited. Some isotopes have the tendency to vary in concentration as an effect of a fast, incomplete or uni-directional

process linked with temperature, water-rock interaction, steam separation, dilution or mixing. Other isotopes in water remain largely unaffected during the flow of this water from the source to the sampling point, making them suitable tracers (Nuti, 1991). The stable isotopes of hydrogen (^{2}H) and oxygen (^{18}O) are among the most common isotopic tools used to identify the origin of geothermal waters.

Conservative or highly mobile chemical elements are also used to obtain information about the origin of geothermal waters to evaluate the mixing of hot and cold waters in the up flow zones of geothermal systems and to assess other characteristics of such systems. B and Cl are among the most commonly used conservative elements in geothermal fluids (Arnórsson and Andrésdóttir, 1995 and references therein).

Geothermometers provide important information on the reservoir temperatures of geothermal systems. They are based on temperature dependent mineral equilibria. The information obtained from geothermometers is inexpensive and reliable. The quartz and Na-K geothermometers are the most commonly used chemical geothermometers.

This study presents geochemical evaluation of chemical and isotopic data from wells and springs in the Southern Lowlands of Iceland, covering a large low-temperature thermal area and the Geysir high-temperature area. The main focus is on the origin of water and subsurface temperature estimates by the silica and Na-K geothermometers.

2. GEOLOGICAL BACKGROUND

Iceland is located on the Mid-Atlantic Ridge, which separates the country into two major crustal plates, the North-American plate and the Eurasian plate. Being situated at the centre of a constructive plate boundary, Iceland is subjected to active volcanism and has formed by the piling up of volcanic material from volcanoes located in the NE-SW running axial rift zone that divides the country into two parts. The intense magmatism in Iceland relative to other parts of the Mid-Atlantic Ridge is due to its position above a mantle plume.

The youngest rocks are found within the rift zone and they become older both towards the east and west. This is so because as new crust forms at the plate boundary, older crust is pushed away from the rift zone. Therefore the oldest rocks, which are 16 million years old, are found in the easternmost and westernmost parts of the country.

The low-temperature area in the Southern Lowlands of Iceland is located east of the westernmost segment of the active volcanic and rifting zone and west of the eastern segment (Figure 1). The Geysir geothermal field occurs in the uppermost part of Southern Lowlands just outside the margin of the westernmost volcanic belt.

The bedrock in the Southern Lowlands is built up of interglacial basaltic lavas as well as hyaloclastite formations and pillow lavas, also of basaltic composition, which were formed by subglacial eruptions. A large part of the region was transgressed by the ocean at the end of the last glaciations and shallow marine sediments of variable thicknesses were deposited in some places (Norddahl, 1990). Thick, near shore clastic sediments from that period also cover the bedrock in the southern part of the Geysir geothermal field, forming extensive plains (Arnórsson, 1985). The hyaloclastites are often rich in tachylite glass and palagonite. Four domes of spherulitic rhyolite are exposed in the vicinity of the Geysir high-temperature field and pitchstone and tillite-like breccias are abundant in one of the domes, probably indicative of its subglacial extrusion (Arnórsson, 1985).

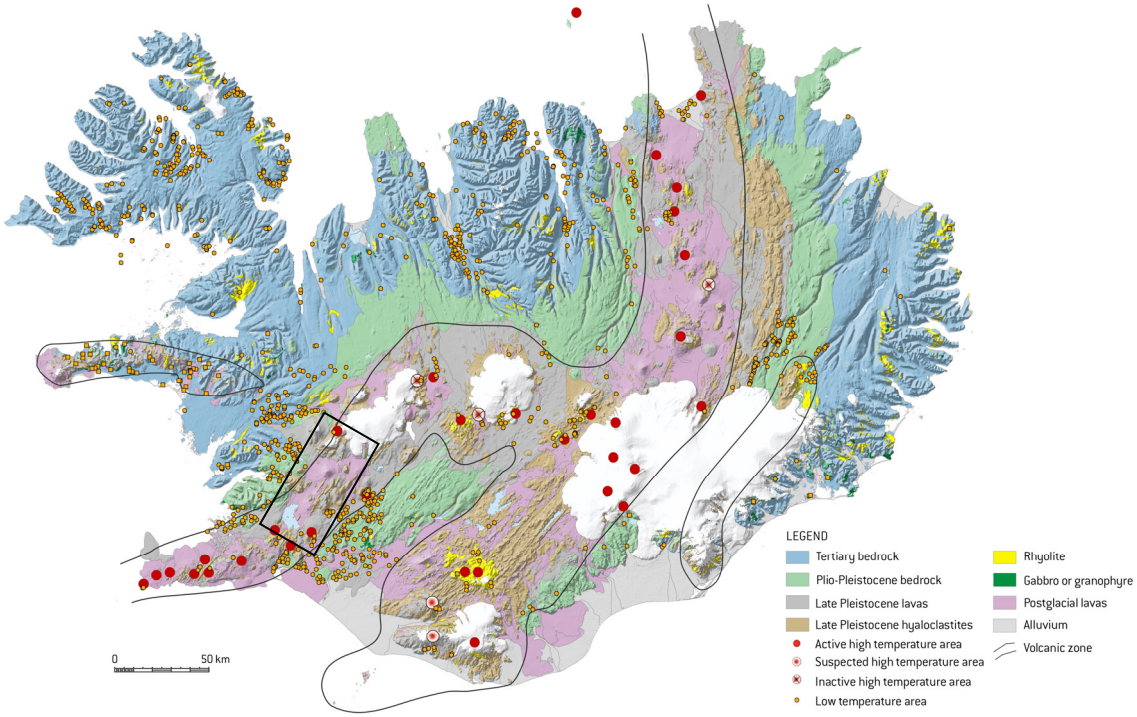

FIGURE 1: Geological, tectonic and geothermal locality map of Iceland and location of the study area (adopted from Jóhannesson and Saemundsson, 1999)

High-temperature geothermal fields in Iceland are typically associated with central volcanoes (Pálmason and Saemundsson, 1974), which are characterized by the abundance of silicic volcanics in addition to intrusions and a caldera structure. Geysir may also represent a central volcanic complex, although evidence is, admittedly, rather meagre (Arnórsson, 1985).

Some of the thermal springs in the Southern Lowlands are located on faults and dykes but a linear distribution along the faults is not very obvious (Arnórsson, 1970). In the Geysir field most of the geothermal activity is localized in an area a few hundred metres across, but surface manifestations, mostly in the form of warm springs, are spread over an area of about 6 × 0.5 km, which is elongated in the prevailing tectonic direction of the region, NNE-SSW.

3. DATA BASE AND DATA HANDLING

3.1 Data base

This study makes use of chemical and isotopic data of water samples from the Southern Lowlands low-temperature area, which were collected and analysed in the years 2002-2005, as well as data from the Geysir area from samples taken in 1979, 1982, and 2001. To better understand the nature of the geothermal waters, surface and non-thermal groundwaters were also collected from both areas. The data of the samples collected in 2002-2005 is from an unpublished database of the project "Vatnsbúskapur" and chemical data collected and analysed in 2001 is taken from the Institute of Earth Sciences, University of Iceland, also an unpublished database. Isotopic data used for Geysir, collected and analysed in 1979 and 1982, were taken from Arnórsson (1985).

3.2 Sampling and analysis

All samples were collected according to standard sampling procedures described by Arnórsson (2000) and Arnórsson et al. (2006). Samples for major cation analysis were filtered on site using a 0.2 µm

cellulose acetate membrane and a Teflon filter holder, and acidified with concentrated suprapure HNO_3 (E. Merck 100441), whereas samples for major anion analysis were only filtered. Samples for determination of pH and total carbonate carbon were cooled before collection into 300 ml glass bottles with air-tight caps. Major cations and anions were analysed using ICP-AES and IC, respectively. SO_4^{2-} was analysed using ICP-AES (as sulphur) and/or IC (ion chromatography). The IC data is preferred whenever both ICP-AES and IC analytical results were available, due to better precision. H_2S was determined on site by titration, with standard Hg-acetate solution. Total carbonate carbon was determined by alkalinity titration or IC.

Samples for the determination of the stable isotopes of hydrogen (δ^2H) and oxygen ($\delta^{18}O$) were cooled, filtered and stored in glass bottles with air-tight caps to avoid evaporation and exchange with the atmosphere. The isotopic ratios were determined using the Finnegan MAT 251 mass-spectrometer at the Science Institute, University of Iceland.

3.3 Isotopic composition of boiled aquifer water

Four of the samples from the low-temperature area were collected from boiling springs. The boiling will cause an enrichment of the heavy isotopes in the boiled water relative to the un-boiled deep water. The effects of boiling and steam loss were evaluated using:

$$\delta^2 H_d = \delta_{A,C} - Y_C \cdot \ln \alpha_{(A-B)C} \quad (1)$$

where the subscript d represents the un-boiled water; Y_C is the steam fraction formed by adiabatic boiling from the aquifer temperature to atmospheric pressure (100°C), and subscripts A and C represent the isotopic composition of water and steam, respectively, at sampling conditions and A-B the isotopic fractionation between the two phases,

For ^2H and ^{18}O, $10^3 \times \ln \alpha_{(A\text{-}B)C}$ is 27.8 and 5.24, respectively (Truesdell and Fournier, 1976). Y_C is given by:

$$Y_C = \frac{h^d - h^w}{h^w - h^l} \quad (2)$$

where h^d is the enthalpy of the un-boiled water and h^w and h^v the specific enthalpies of liquid water and vapour at sampling conditions, respectively.

The enthalpy h^d was derived using chalcedony temperatures with the aid of steam tables. Finally, δ^2H and $\delta^{18}O$ values for the un-boiled waters were obtained from the respective equations given by Arnórsson (2000).

3.4 Speciation calculations

Chemical analysis provides data on component concentrations. The WATCH chemical speciation program calculates individual species activities. Activity coefficients were obtained from the extended Debye-Hückel equation:

$$-\log \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + Ba_i \sqrt{I}} + B^{\bullet} I \quad (3)$$

where γ_i represents the activity coefficient of species i; A and B are temperature parameters dependent on the density and dielectric constant of water; a_i is the effective ionic diameter of ionic species i. $B^{\bullet}$

represents a deviation function describing the departure of the mean ionic activity coefficient of an electrolyte solution from that predicted by the Debye Hückel expression (Helgeson, 1969); and I stands for ionic strength given by:

$$I = \frac{1}{2}\sum m_i z_i^2 \quad (4)$$

where z_i is species charge; and m_i its concentration.

The thermodynamic database in the program for dissociational equilibria in version 2.1 of WATCH, used for the present study, are those given by Arnórsson et al. (1982) except for Al-, ferric-, and ferrous hydroxide complexes which are from Arnórsson and Andrésdóttir (1999), Diakonov and Tagirov (2002) and Arnórsson et al. (2002), respectively. Gas solubility constants are from Arnórsson et al. (1996). Al-Si dimer (Pokrovski et al., 1998) was also incorporated into the speciation calculations.

3.5 Calculation of species activities for derivation of geothermometer temperatures

The WATCH speciation program (Arnórsson et al., 1982), version 2.1 (Bjarnason, 1994) was used to calculate individual aqueous activities including those of $H_4SiO_4^o$, Na^+, and K^+. For hot springs with sub-boiling temperature and hot water wells, as well as non-thermal waters, the analysed compositions were used. For boiling springs, on the other hand, the analyzed spring water compositions were modified by taking into account steam and gas loss by boiling. In the case of the Geysir high-temperature area, it was assumed that the un-boiled aquifer water was at equilibrium with calcite and, by an iterative process, the extent of degassing of this water by its boiling was obtained. The boiling was taken to be adiabatic from the temperature of last equilibrium with quartz. For the boiling hot springs in the low-temperature areas, it was assumed that degassing due to boiling was 10% of maximum and chalcedony temperature was taken to represent the aquifer temperature. The extent of degassing of the boiling water affects the calculated value for the aquifer water pH and therefore the concentration of $H_4SiO_4^o$.

From the calculated $H_4SiO_4^o$ concentration in the water from hot water wells and sub-boiling hot springs, chalcedony and quartz equilibrium temperatures were calculated from the respective geothermometer equations of Fournier (1977) and Arnórsson (2000). The equation used to retrieve Na-K temperatures is that given by Arnórsson et al. (1998).

4. RELATIONSHIPS BETWEEN CHLORIDE AND BORON

Available literature agrees that Cl acts as incompatible in practically all natural water-rock environments, i.e. once in solution, it stays there both at ambient and elevated temperatures (Ellis, 1970). It is not adsorbed to any marked degree on mineral surfaces (Hem, 1970) and usually does not enter common rock-forming minerals due to the large size. High-temperature water-rock interaction experiments have shown that B in common types of igneous rocks is highly mobile and probably also incompatible. However, there is evidence that at temperatures below some 100-150°C, B is taken up from solution into secondary minerals, particularly illite and mica (Arnórsson and Andrésdóttir, 1995 and references therein). B concentrations in surface and non-thermal groundwaters are therefore either equal to or higher than in precipitation. The Cl/B ratios of water interacting with common types of igneous rocks are equal to or lower than that of sea water because the Cl/B ratio of such rocks is lower than that of seawater. The Cl/B ratios of natural waters in many of the Icelandic geothermal areas

display a gradual decrease from the Cl/B ratio in seawater, which is close to 4300, to that of basaltic rocks (approximately 15-50).

A linear relationship in a particular geothermal field between Cl and B indicates mixing of geothermal water with cold water. If mixing of geothermal water with cold water is responsible for variable Cl concentrations, it is expected that the intersection at 0 B of a line through the data points occurs at 2-20 ppm Cl as precipitation in Iceland contains Cl in that range as do non-thermal ground waters and surface waters (Arnórsson, 1985).

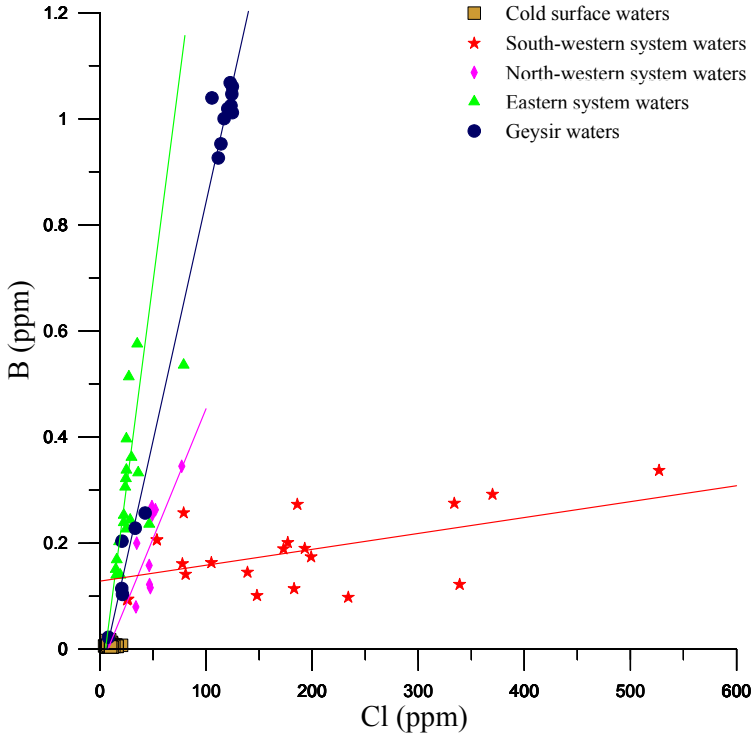

FIGURE 2: Cl-B relations of the natural waters of the Southern Lowlands; lines shown were obtained by linear regression of the respective data

A Cl-B plot (Figure 2) of the low-temperature thermal waters of the Southern Lowlands of Iceland depicts three distinct sets of data, possibly representing three different geothermal systems which can be referred to as southwestern, eastern and northwestern systems based on their geographic locations (Figure 3). The location of samples is seen in Figure 3.

The B and Cl concentrations of the southwestern system are in the ranges of 0.09-0.34 and 25-527 ppm, respectively, and the Cl/B weight ratios of the waters in this area are between 260 and 2279. These samples are close to the coast and lie in a relatively low lying area as compared to those in the northwestern and eastern systems. It was observed that the aqueous Cl concentrations of this area are generally much higher than in other systems. It was also noted that within this area the Cl and B concentrations correlate with distance from the sea and elevation. The variation in Cl concentrations with altitude is clear as relatively elevated areas have lower concentrations compared to waters on lower ground where B concentrations vary little but those of Cl much.

Thermal water samples from the eastern system contain the lowest Cl concentrations and relatively highest B concentrations, 15-79 and 0.14-0.57 ppm, respectively; Cl/B ratios (by weight) range from 53 to 197, i.e. they are comparable to the average ratio of basalt. These samples are from springs and drillholes located on relatively high ground. A good linear relationship is observed between Cl and B concentrations in waters from this area, which is considered to reflect a variable extent of interaction with basalt rather than mixing. Samples, which are farthest from the sea have higher boron concentrations, and are from higher temperature springs. Chloride concentrations are generally less than 30 ppm.

Cl and B concentrations in the northwestern low-temperature thermal waters of the Southern Lowlands are 8.9-77 and 0.018-0.345 ppm, respectively, and the Cl/B weight ratios are 174-509, higher than those of basalt but much lower than that of seawater. A linear relationship between Cl and B is observed for the system as for the eastern and southwestern systems. This system is relatively

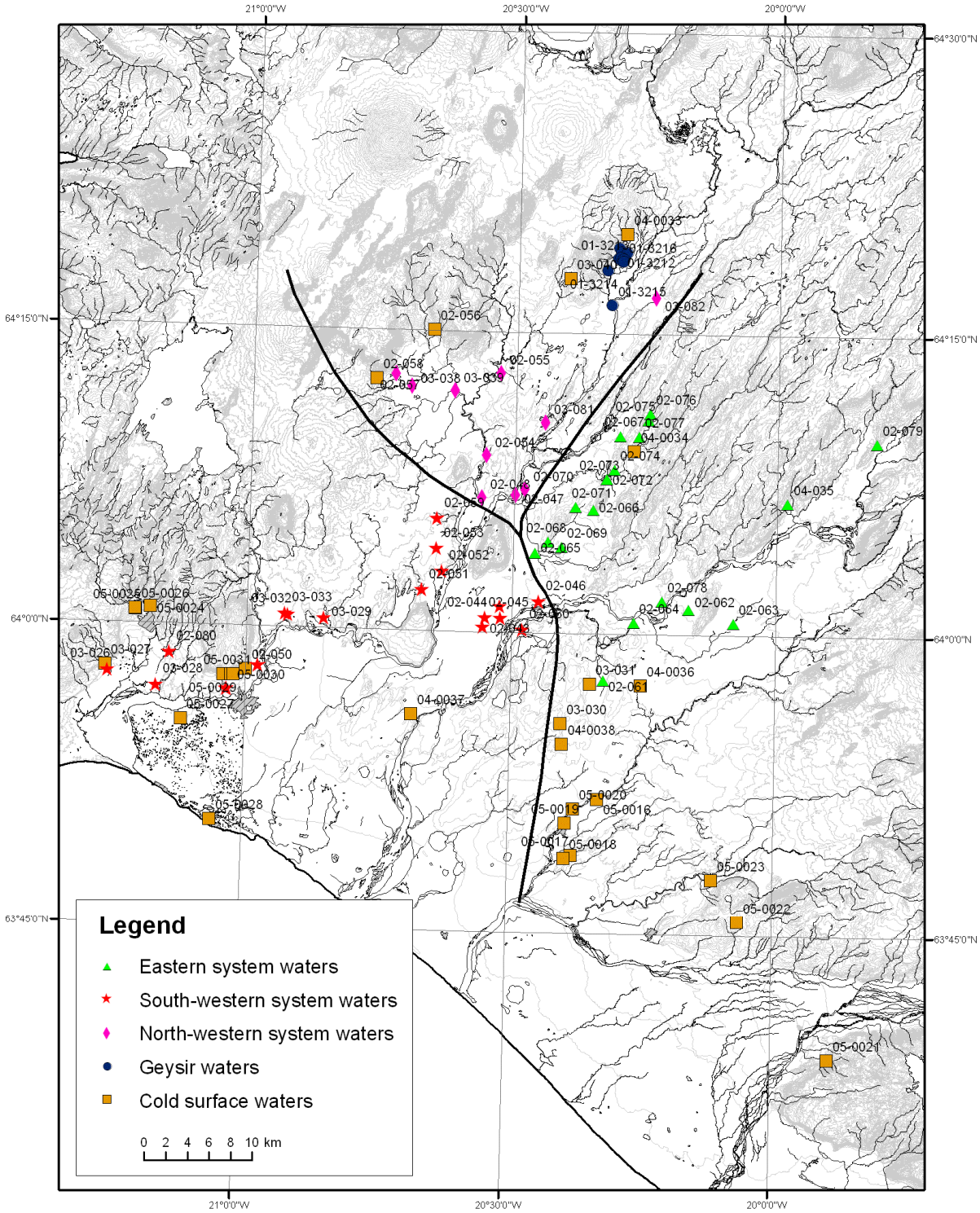

FIGURE 3: Location of samples and classification of low-temperature thermal waters into different systems

low lying compared to the eastern geothermal system but at higher elevation than the southwestern geothermal system.

Cold water samples from the whole Southern Lowlands area form a tight cluster on the Cl-B plot (Figure 2), the range of Cl and B being 4.4-20.3 and 0.004-0.017 ppm, respectively. The Cl/B ratio of these samples is 354-3012, a little lower than that of seawater.

The Geysir samples plot on a straight line forming two sets of points, one set close to the coldwater samples and another set displaying high B, 0.92-1.07 ppm, and Cl, 106-125 ppm. Cl/B ratios of the Geysir high-temperature geothermal area samples are 115-354. The samples plotted near the cold water samples; all represent warm water samples with measured temperatures of mostly less than 50°C, and Cl concentrations of <45 ppm. They possess the highest Cl/ B ratios. Unmixed waters in Geysir have Cl/B ratios similar to those of basalt, as do waters in the eastern low-temperature system. Other low-temperature systems have higher Cl/B ratios due to the presence of seawater.

Thermal waters from the three low-temperature geothermal systems contain higher Cl concentrations than surface waters and non-thermal groundwaters which contain similar Cl concentrations to rain water. The Cl/B weight ratios in the waters in the eastern system are similar to those of basalt, at least for the most reacted waters. In the southwestern and northwestern systems on the other hand, they are higher than that of the basaltic rocks. Possible explanations for the higher Cl/B ratios are either removal of B from solution or addition of Cl from other sources. It is known that B is not significantly removed from solution in the basaltic environment of Iceland. So, the cause likely is the addition of Cl from other sources. The most attractive explanation for the high Cl concentration and high Cl/B concentration ratios is seawater infiltration into the geothermal systems during the end of the last glaciations, some 10,000 years ago. This is supported by the strong decrease in Cl in geothermal waters on higher ground within the whole lowland area and their relative distances from the coast.

A linear Cl-B relationship in the Geysir high-temperature system indicates mixing of geothermal water with cold groundwaters. In the much larger southwestern and northwestern systems the same linear relationship is due to mixing of seawater with relatively much reacted geothermal water, but in the eastern system the cause of the observed linear Cl-B relationship is considered to be variable reaction of water of meteoric origin with basaltic rock of relatively homogeneous Cl and B content.

5. ORIGIN OF THE GEOTHERMAL WATERS

Knowledge of the origin of geothermal waters is very important in geothermal studies because it helps in discriminating the chemical properties of the thermal waters and also their sources of recharge. It is essential to determine the source of recharge of geothermal systems, especially those that are located in arid and semi-arid regions where precipitation is scarce and the lifetime of exploited geothermal systems may be highly dependent on the amount of water recharged into the system. Studies of stable isotopes play an important role in hydrogeological investigations of both thermal and non-thermal waters because the isotopes carry imprints of the origin of the waters.

5.1 Stable isotope content of thermal and non-thermal waters

Detailed deuterium distribution of mean annual precipitation of Iceland was produced by Árnason (1976), using analyses of local springs and streams. According to his results, the deuterium content of precipitation decreases with altitude and distance from the coast inland. This map (Figure 4) is useful for comparing the deuterium content of geothermal waters with local precipitation.

The δ^2H and $\delta^{18}O$ contents of the cold waters in the study area plot close to the global meteoric line (Figure 5). The observed small departure from the line is within the limits expected as a consequence of variability in air-moisture condensation processes due to the inland and altitude effect. The δ^2H content of these waters, together with their location, matches the deuterium map of Árnason (1976).

The geothermal waters have more negative δ^2H values than local precipitation and most of them display oxygen shifts doubtless caused by water-rock interaction. Some samples show small and probably insignificant negative oxygen shifts (Figure 5). The more negative δ^2H values for the

thermal waters indicate that the waters do not have local origin. Instead, they originate probably from far inland or contain older meteoric waters from Pre-Holocene times.

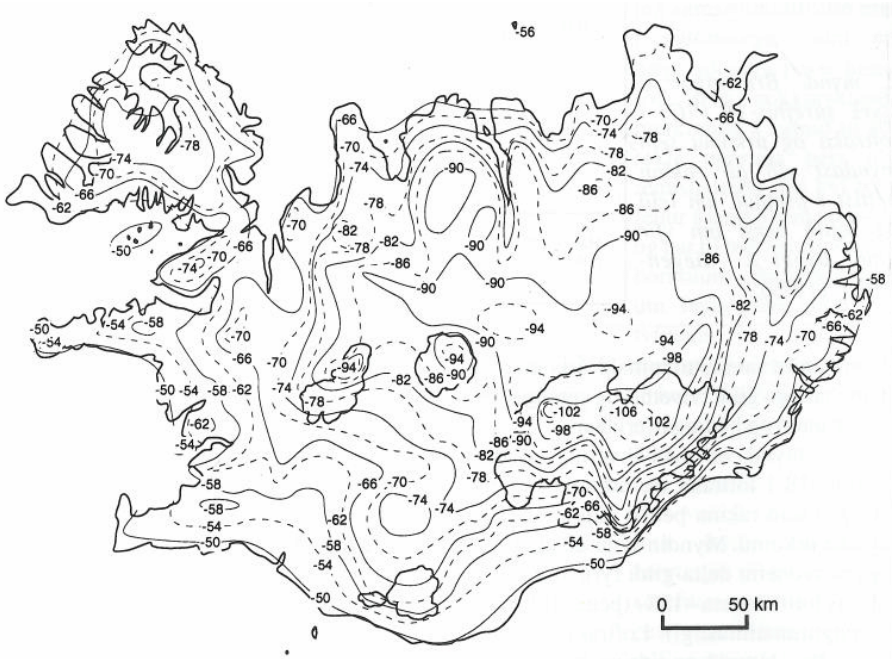

FIGURE 4: Deuterium content map of mean annual precipitation in Iceland (Árnason, 1976)

Three water samples from the southwestern low-temperature system and one sample from the eastern system are very low in δ^2H, less than -90‰. These samples also show large positive oxygen shifts. The same three samples from the southwestern system also have higher Cl concentrations and higher temperatures with two of them having also higher B concentration than the samples from similar locations. The more negative isotopic values indicate that these waters contain an old meteoric water component from the last glacial period when the precipitation at any location was more negative in δ^2H than the present precipitation due to the colder climate.

δ^2H - $\delta^{18}O$ relations of the Geysir waters show that the mixed waters plot at or near the global meteoric line with very little oxygen shift and they have relatively higher deuterium than the non-mixed waters. This relationship possibly implies that the mixed waters represent a mixture of cold groundwater and hot geothermal water with a high proportion of the cold groundwater component. One sample of the mixed waters is exceptionally low in deuterium, with δ^2H = -78.1‰. This sample is located at the southernmost part of the Geysir geothermal field; it is highly probable that the source water is from a river which originates farther inland, from the glaciers, which have more negative isotopic values.

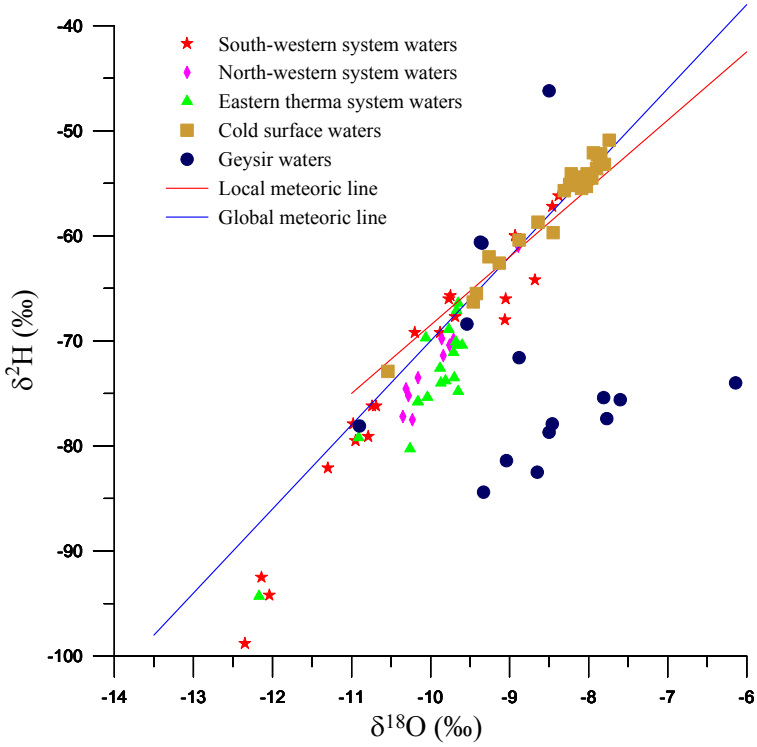

FIGURE 5: δ^2H - $\delta^{18}O$ relations of thermal and non-thermal waters from the Southern Lowlands

Figure 6 shows that δ^2H and Cl of waters from the southwest part of the Southern Lowlands are negatively correlated. A possible explanation for this is that these waters contain, in addition to the present-day precipitation, a component of very old water. This is a mixture of seawater which

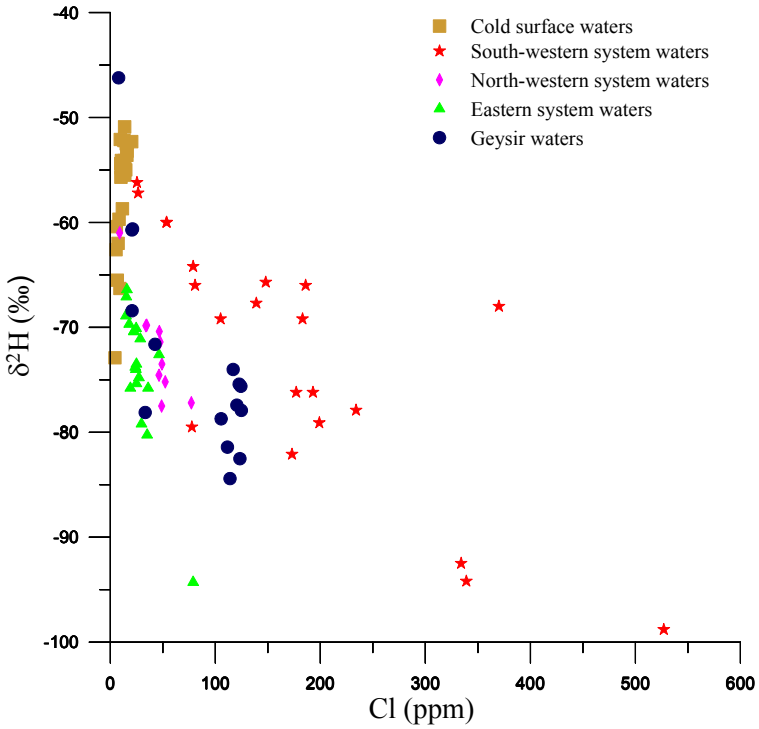

FIGURE 6: δ^2H-Cl relationship of the thermal and non-thermal waters from the Southern Lowlands

infiltrated the aquifers around the end of the last glaciation when the Southern Lowlands were mostly submerged, and meteoric water, also from that time, which is isotopically lighter than present-day precipitation due to the cold climate in Pre-Holocene times.

The northwestern system waters also show a slight negative correlation, which also implies that these waters contain a small component of these old waters, seawater and meteoric water, from the end of the last glaciation. They are though highly diluted by the present-day precipitation due to their distance from the ocean. Almost all the water in the hot springs is local present-day precipitation as seen when extrapolating the δ^2H-Cl relationship for each area to ~0 ppm Cl.

The eastern thermal waters on the other hand do not contain an old seawater component. They may be present-day precipitation in origin or contain an old fresh water component. If present-day precipitation is their origin, the more negative isotopic values show that the waters originate from higher inland, possibly from the glaciers.

5.2 Local meteoric line

Sveinbjörnsdóttir et al. (1995) studied the δ^2H - δ^{18}O relationships of cold groundwaters of Iceland and defined two different meteoric lines for the Icelandic groundwaters as:

$$\delta^2H = 6.5\ \delta^{18}O - 3.5 \quad (5)$$

when $\delta^{18}O \geq -10.5‰$ (and $\delta^2H \geq -76‰$)

and

$$\delta^2H = 8 \times \delta^{18}O + 11 \quad (6)$$

for lighter precipitation.

According to this classification, the groundwaters of the Southern Lowlands of Iceland should fit in the first group. However, the present data set fits best to the global meteoric line which is defined by $\delta^2H = 8\ \delta^{18}O + 10$ (Figure 5). The present data set was taken from a different part of the Southern Lowlands from the data set used to establish the local meteoric line by Sveinbjörnsdóttir et al., (1995).

5.3 Oxygen shift

Oxygen shift is the measure of deviation of samples from the local meteoric line in a δ^2H - $\delta^{18}O$ relation graph. This is readily observed in the plot in Figure 7. Oxygen shift ($\Delta^{18}O$) for the global meteoric line is given by:

$$\Delta^{18}O = \delta^{18}O_{sample} - \frac{\delta^{2}H_{sample} - 10}{8} \quad (7)$$

As discussed in Section 5.2, the present study uses the global meteoric line as the best fit line for cold groundwater samples in the Southern Lowlands of Iceland. We speak of oxygen shift but not of hydrogen because the amount of hydrogen in water flowing through rocks is expected to be much higher than that of the rocks. Therefore the effect of water-rock interaction on the concentration of hydrogen in the water is negligible. Relative to hydrogen, the amount of oxygen in rocks is much larger and as a result water-rock interaction affects the oxygen isotope content of the water significantly.

Oxygen shift is mainly caused by water-rock interaction. It is, therefore, natural that high-temperature thermal waters have highest oxygen shifts and non-thermal groundwaters and surface waters are expected to have low or no oxygen shift. This is so because interaction between water and rock is enhanced by increasing temperature. Underground residence time of natural waters in aquifers, before they come up to the surface as springs or from wells, is also important in determining the extent of water-rock interaction.

Cold groundwaters from the study area do not display a significant oxygen shift, the range being -0.21 to 0.26. This can be deduced from the δ^2H - $\delta^{18}O$ plot (Figure 5) and also in the temperature-oxygen shift plot (Figure 7).

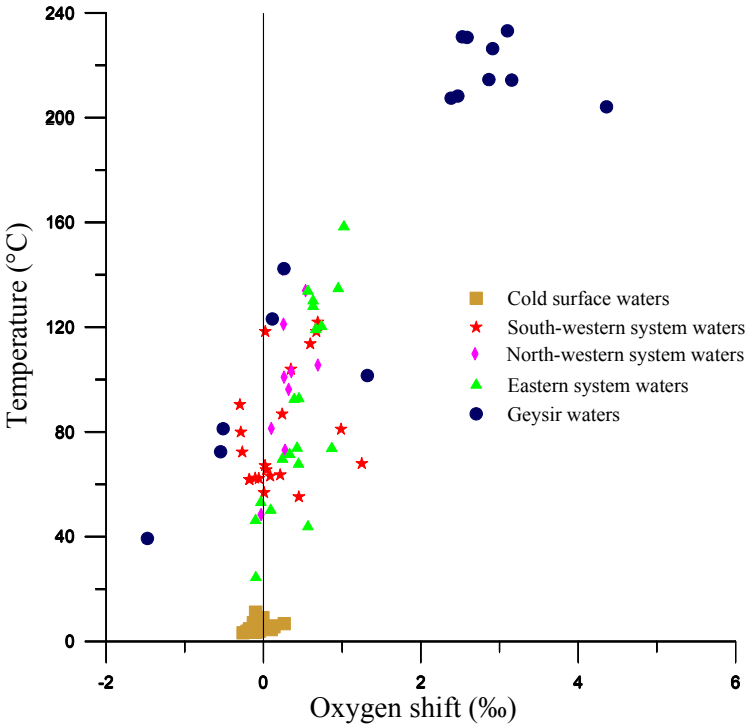

FIGURE 7: Temperature-oxygen shift plot of the thermal and non-thermal waters from the Southern Lowlands; measured temperature is used for the non-thermal waters and silica temperatures for the thermal waters

Waters from the southwestern thermal system show large differences in their behaviour with respect to their oxygen shift and δ^2H values. They show the highest and lowest δ^2H values and very high to no oxygen shift, between -0.3 and 1.25. Two sets of samples show relatively larger oxygen shift compared to the others, and each set is made of three geographically related samples within the main class. Five of the six samples from the two sample sets are relatively high in boron but with highly variable chloride concentrations. One set, samples 02-080, 03-028, and 03-026, which represents waters from the coastal area, are isotopically comparable with the local precipitation despite the oxygen shift. The oxygen shift in these samples could be associated with both long residence time and the temperature of the waters which lead to more water-rock interaction. Two of these samples, which show more oxygen shift, also have higher estimated silica temperature.

The Eastern thermal system waters show similar oxygen shifts, generally more than the waters from the rest of the low temperature thermal systems. Oxygen shift ranges between -0.1 and 1.02‰. The Northwestern thermal system waters are characterized by the lowest shifts, -0.015 to 0.708, relative to the rest of the low-temperature thermal system waters.

The differences in the oxygen shifts of the three low-temperature thermal systems may be linked with the reservoir temperature of the systems, the Eastern thermal system being the hottest but the Southwestern system being the lowest in temperature.

As discussed earlier, the Geysir geothermal system has two types of waters. This is clearly reflected in the δ^2H - $\delta^{18}O$ relationship graph (Figure 5) where the non-mixed waters show large oxygen shifts whereas the mixed waters show small oxygen shifts. The main reason for the oxygen shifts in this area is much water-rock interaction at the high temperatures existing at depth. Some samples show negative oxygen shifts. A possible explanation for this is the bubbling of CO_2 through the thermal waters which takes up ^{18}O and makes the water depleted in ^{18}O.

6. ESTIMATED SUBSURFACE TEMPERATURES

6.1 Theory of chemical geothermometry

Geothermometry is used to estimate the temperature at which a geological process takes or took place. In geothermal studies, geothermometry plays a very important role in all phases of development, exploration, development and exploitation.

During the exploration phase, geothermometry is used to estimate subsurface temperatures, i.e. temperatures expected to be encountered by drilling to the aquifer depth, using chemical and isotopic composition of hot spring and fumaroles discharges. In 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. It is also useful to assess chemical reactions occurring in the zone of depressurisation around wells that result from boiling or cooling due to the recharge of cold water. This provides important information at relatively low cost, if properly used, like most geochemical methods.

Geothermometers can be broadly classified as chemical and isotope geothermometers. Chemical geothermometers include solute and gas geothermometers. Chemical geothermometry is based on temperature dependent equilibria between minerals and geothermal solution and, in some cases, vapour. Isotopic geothermometers make use of the fractionation of isotopes of light elements between compounds which is quite significant and temperature dependent.

The application of chemical geothermometers to estimate subsurface temperatures or aquifer temperature is based on the basic assumption that temperature dependent chemical equilibria prevails in the source aquifer of the fluid in question. It also makes use of the major approximation that chemical reactions do not significantly modify the composition of the fluid as it ascends from the source aquifer to the point of sampling.

Water/solute geothermometers may be broadly classified into two groups: (1) those which are based on temperature-dependent variations in solubility of individual minerals, and (2) those which are based on temperature-dependent exchange reactions which fix the ratios of certain dissolved constituents (Fournier, 1989). In theory, any cation ratio and any uncharged aqueous species concentrations can be used as a geothermometer provided that overall equilibrium prevails (Arnórsson and Svavarsson, 1985).

Temperature equations for geothermometers have to be calibrated so that they can be utilized to determine aquifer temperatures with good confidence and this is done either on the basis of chemical thermodynamic data or empirically (geochemically). Chemical thermodynamic calibration is based on laboratory experiments for establishing equilibrium constant values for specific mineral-solution reactions on which the geothermometry equation is based. Empirical or geochemical calibration applies the correlation of specific aqueous component concentrations in well discharges with their aquifer temperatures (D´Amore and Arnórsson, 2000).

Silica and Na-K geothermometers are the most widely used chemical geothermometers and are applied in this study. Their temperature equations are described here.

6.1.1 Silica geothermometers

The concentration of the silica species $H_4SiO_4^o$ in geothermal systems is controlled by the solubility of quartz or its microcrystalline variety, chalcedony. The solubility of quartz appears to control dissolved silica concentration in high-temperature geothermal fluids with temperatures higher than 120-180°C (Fournier, 1991) but its microcrystalline variety, chalcedony at lower temperatures. Solubility graphs of the different silica polymorphs are presented in Figure 8 which shows the solubilities of quartz, chalcedony, opal and amorphous silica.

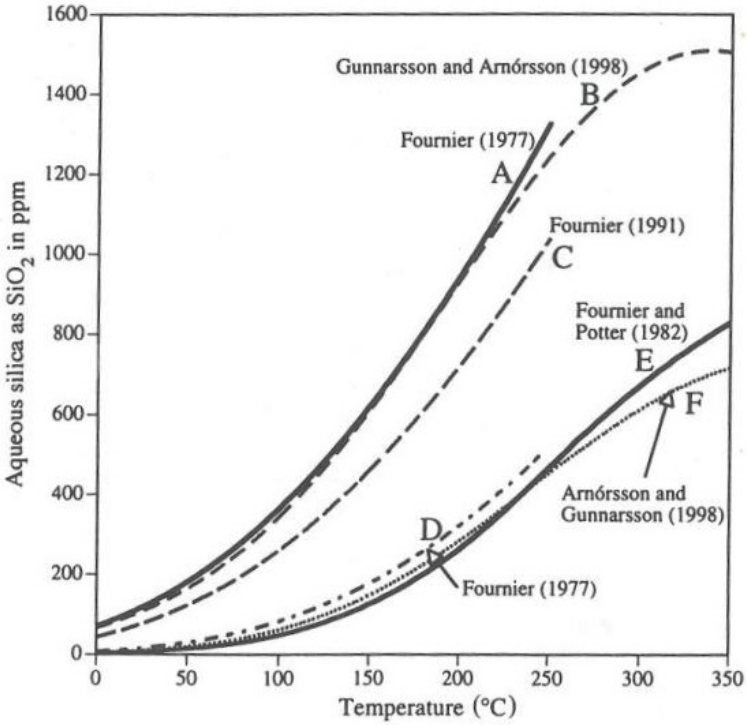

FIGURE 8: The solubility of quartz, chalcedony, opal and amorphous silica in water at 1 bar below 100°C and at the vapour pressure of the solution at higher temperatures, A and B are amorphous silica, C is opal, D is chalcedony, and E and F are quartz; sources of data are shown in the figure (D´Amore and Arnórsson, 2000)

The first silica geothermometer equation was presented by Morey et al. (1962). Fournier and Potter (1982) derived a polynomial equation for the quartz geothermometer that estimates temperature up to 330°C and which has been used quite extensively. Various silica geothermometer equations have been developed over the years to assess subsurface temperatures from the silica content of natural water in equilibrium with either quartz or chalcedony. Temperatures estimated by these geothermometers are referred to as quartz and chalcedony temperatures, respectively (Arnórsson, 2000). The quartz geothermometer is generally applied in high-temperature systems while the chalcedony geothermometer is used in low-temperature systems. Temperature equations for the silica geothermometers are theoretically calibrated from laboratory experiments.

The dissolution reactions for silica minerals are described as:

$$SiO_{2,solid} + 2H_2O_l = H_4SiO_4^o \quad (8)$$

$H_4SiO_4^o$ is a weak acid and dissociates, if the pH of the water is high enough, to yield $H_3SiO_4^-$:

$$H_4SiO_4^o = H^+ + H_3SiO_4^- \quad (9)$$

Analysis of silica in aqueous solution yields total silica concentration, generally expressed as ppm SiO_2, which includes both $H_4SiO_4^o$ and $H_3SiO_4^-$. The dissociation constant for silicic acid is about 10^{-10} at 25°C. Thus, at a pH of 10 ($H^+ = 10^{-10}$), the concentration of $H_4SiO_4^o$ equals that of ionized silica ($H_3SiO_4^-$):

$$\frac{K_{H_4SiO_4^o}}{(H)^+} = 1 + \frac{(H_3SiO_4^-)}{(H_4SiO_4^o)} \quad (10)$$

High pH waters, with pH in excess of 9, as measured at 25°C, contain a significant fraction (>10%) of silica in the form of $H_3SiO_4^-$ due to the dissociation of silicic acid increasing the solubility of silica in water in equilibrium with quartz or chalcedony. In calculating quartz or chalcedony equilibrium temperatures for such waters, the analyzed silica concentrations need to be corrected to retrieve the fraction in solution that occurs as $H_3SiO_4^-$ to avoid overestimation of reservoir temperatures. This can be done by simultaneously solving the following mass balance equation:

$$SiO_{2,analyzed} = [H_4SiO_4^o] + [H_3SiO_4^-] \quad (11)$$

with Equation 10 to yield:

$$[H_4SiO_4^o] = \frac{SiO_{2,analyzed}}{1 + \frac{K_{H_4SiO_4^o}}{(H)^+}} \quad (12)$$

The activity (parenthesis) is taken to be equal to concentration (brackets).

The temperature dependence of the dissociation constant for silicic acid is given by:

$$\log K_{H_4SiO_4^o} = -\frac{2549}{T} - 15.36 \cdot 10^{-6} \cdot T^2 \quad (13)$$

By calculating the value of this constant at the temperature at which the pH is measured, the concentration of $H_4SiO_4^o$, (unionized silica) can be retrieved from the measured pH and total silica concentration of the water with the aid of the third equation on this page. The value of silica (quartz or chalcedony) equilibrium temperature can then be obtained by inserting the value of unionized silica (as SiO_2.) into the respective silica geothermometer equation (Arnórsson et al., 1982).

The quartz geothermometer has been experimentally calibrated over a range of temperatures, from 0 to 500°C, and pressures of up to 1000 bars. It performs well up to 400°C, regardless of the fluid composition of the geothermal reservoirs (Pope et al., 1987). However, Verma (2000) criticized the use of the quartz geothermometer, especially its discrepancy at high temperatures arising from inconsistency between experimental solubility data. Some of the proposed silica geothermometer equations used to calculate aquifer temperatures are presented here below.

Fournier (1977) proposed the following equations applicable for temperatures 25-250°C. For waters equilibrated with quartz with no steam loss:

$$t^\circ C = \frac{1309}{5.19 - \log(SiO_2)} - 273.15 \quad (14)$$

where SiO_2 represents unionized silica as ppm SiO_2.

For silica concentrations in water initially in equilibrium with quartz after adiabatic boiling to 100°C Fournier (1977) used:

$$t^{\circ}C = \frac{1522}{5.75 - \log(SiO_2)} - 273.15 \quad (15)$$

Fournier and Potter (1982) presented the following geothermometry equation for quartz solubility which is applicable for temperatures 25-900°C:

$$t^{\circ}C = -42.2 + 0.28831 \cdot S - 3.6686 \cdot 10^{-4} \cdot S^2 + 3.1665 \cdot 10^{-7} \cdot S^3 + 77.034 \cdot \log S \quad (16)$$

where S denotes silica concentration as SiO_2 in ppm.

From this equation, Arnórsson (1985) derived the following equation, which describes silica concentrations in water initially in equilibrium with quartz after adiabatic boiling to 100°C:

$$t^{\circ}C = -53.5 + 0.11236 \cdot S - 0.5559 \cdot 10^{-4} \cdot S^2 + 0.1772 \cdot 10^{-7} \cdot S^3 + 88.390 \cdot \log S \quad (17)$$

Arnórsson et al. (1998) proposed the following two quartz geothermometer equations for temperatures 0-350°C:

$$t^{\circ}C = -53.5 + 0.36590 \cdot S - 5.3954 \cdot 10^{-4} \cdot S^2 + 5.5132 \cdot 10^{-7} \cdot S^3 + 74.360 \cdot \log S \quad (18)$$

$$t^{\circ}C = -66.9 + 0.13780 \cdot S - 4.9727 \cdot 10^{-5} \cdot S^2 + 1.0468 \cdot 10^{-8} \cdot S^3 + 87.841 \cdot \log S \quad (19)$$

Equation 18 represents quartz solubility and Equation 19 silica concentrations in water initially in equilibrium with quartz after adiabatic boiling to 100°C.

Equations 20 and 21 below for quartz solubility are from Verma and Santoyo (1997). They are valid in the temperature ranges and SiO_2 contents of 20-210°C and < 295 ppm and 210-310°C and ≥ 295 ppm, respectively:

$$t^{\circ}C = -44.119 + 0.24469 \cdot S - 1.7414 \cdot 10^{-4} \cdot S^2 + 79.305 \cdot \log S \quad (20)$$

$$t^{\circ}C = -140.82 + 0.223517 \cdot S \quad (21)$$

Fournier (1977) proposed the following chalcedony geothermometer equation:

$$t^{\circ}C = \frac{1032}{4.69 - \log S} - 273.15 \quad (22)$$

Arnórsson et al. (1983a) proposed a slightly different equation:

$$t^{\circ}C = \frac{1112}{4.91 - \log S} - 273.15 \quad (23)$$

In Equations 14-23, S refers to concentration of SiO_2 in ppm. Quartz geothermometer values in this study were applied only for the non-mixed waters of the Geysir high-temperature geothermal field. The geothermometer equations used were those of Fournier (1977).

Geothermal waters may boil in the upflow of geothermal systems if reservoir temperatures exceed 100°C. Boiling causes an increase in the concentrations of solutes in proportion to steam formation and an increase of the pH of the water because weak acids like H_2S and CO_2 are transferred into the steam phase. This may lead to an overestimation of quartz and chalcedony equilibrium temperatures. Therefore, it is advisable that geothermometry equations which are valid for steam loss by adiabatic boiling to 100°C should be utilized for boiling hot springs.

6.1.2 The Na-K geothermometer

As mentioned earlier, cation geothermometers are based on temperature-dependent exchange reactions, which fix the ratios of certain cations. The Na-K geothermometer is the most widely used cation geothermometer. Na/K ratios were first used to locate the major upflow zone of geothermal water in the Wairakei geothermal field in New Zealand (Ellis and Wilson, 1961), the lowest ratios being closest to the major upflow.

Most often the Na-K geothermometer has been calibrated geochemically (empirically) due to insufficient accuracy of available thermodynamic data or due to the involvement of other minerals than feldspars, which may control the Na/K ratio in aqueous solutions (D´ Amore and Arnórsson, 2000).

The Na-K geothermometer generally appears to take a longer time to attain chemical equilibrium than the silica geothermometer (Fournier, 1991). The Na-K geothermometer is, therefore, more applicable for deeper and possibly higher temperature parts of geothermal systems where waters reside for relatively longer periods of time. The use of this geothermometer for hot springs should be exercised with care because in hot spring waters, base-exchange reactions involving clays rather than feldspars may control the Na/K ratios.

The partitioning of sodium and potassium between alumina-silicates and aqueous solutions is temperature dependent. The reaction below describes the portioning between alkali-feldspars:

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+ \tag{24}$$

or

$$K_{\text{alkali-feldspar}} \cong \frac{(Na^+)}{(K^+)} \tag{25}$$

because both the feldspars are almost pure.

Efforts to establish Na-K geothermometry equations include, among many others, those of Truesdell (1976), Ellis and Mahon (1977), Arnórsson et al., (1983b), Giggenbach (1988), Arnórsson and Stefánsson (1999) and Fournier (1979). Some of them are based on experimental data, e.g. Arnórsson and Stefánsson (1999), others on empirical calibration, such as Truesdell (1976) and Arnórsson et al. (1983b). Below are shown some of the proposed Na-K geothermometry equations:

$$t^\circ C = \frac{856}{0.857 + \log(Na/K)} - 273.15 \tag{26}$$

$$t^\circ C = \frac{1217}{1.438 + \log(Na/K)} - 273.15 \tag{27}$$

$$t^\circ C = \frac{833}{0.780 + \log(Na/K)} - 273.15 \tag{28}$$

$$t^{\circ}C = \frac{933}{0.993 + \log(Na/K)} - 273.15 \quad (29)$$

$$t^{\circ}C = \frac{1319}{1.699 + \log(Na/K)} - 273.15 \quad (30)$$

$$t^{\circ}C = \frac{1178}{1.470 + \log(Na/K)} - 273.15 \quad (31)$$

$$t^{\circ}C = \frac{1390}{1.750 + \log(Na/K)} - 273.15 \quad (32)$$

$$t^{\circ}C = 733.6 - 770.551 \cdot Y + 378.189 \cdot Y^2 - 95.753 \cdot Y^3 + 9.544 \cdot Y^4 \quad (33)$$

In Equations 26-32, concentrations are in ppm but in Equation 33 Y refers to the logarithm of molal Na/K ratios. Equation 26 is from Truesdell (1976) and is applicable at temperatures between 100 and 275°C. Equations 27 and 28 are from Fournier (1979) and Tonani (1980), respectively. Equations 29 and 30 are from Arnórsson et al. (1983b) and are valid at temperatures of 25-250°C and 250-350°C, respectively. Equations 31 and 32 are from Nieva and Nieva (1987) and Giggenbach (1988), respectively. Equation 33 is from Arnórsson et al. (1998) and is applied to determine Na-K temperatures in this study.

6.2 Results

Subsurface temperature estimates in the high- and low-temperature areas of the Southern Lowlands, as estimated by the silica and Na-K geothermometers, are presented in Table 1. From these temperature estimates it can be concluded that both Na-K and silica geothermometers generally give comparable results for the low-temperature geothermal waters. Yet, as can be seen from Figure 9, Na-K temperatures tend to be higher in the low-temperature fields, when below ~100°C, than the chalcedony equilibrium temperatures. The reverse is the case for the Geysir high-temperature field. The samples which have higher silica equilibrium temperatures than Na-K temperatures are geographically related and are aligned north-northeast in the northwestern part of the eastern system.

As is clearly displayed in the Na-K versus silica temperature plot (Figure 9), non-thermal ground-water, surface waters and the mixed waters of Geysir area show unrealistic and non-comparable scattered temperature estimates. This is probably due to the lack of equilibrium in the non-thermal and mixed waters.

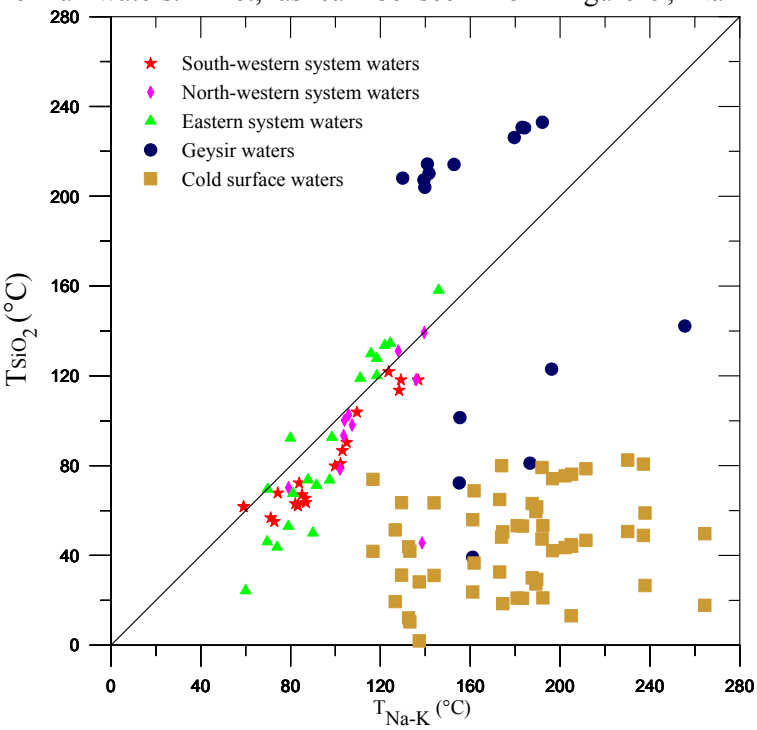

FIGURE 9: Silica and Na-K temperature relations of the Southern Lowlands thermal and non-thermal waters

TABLE 1: Estimated subsurface temperatures in the high and low-temperature areas of the Southern Lowlands in Iceland (* marks boiling springs)

Sample no.	Measured temp. (°C)	Na-K temp. (°C)	Chalcedony temp. (°C)
Southwestern geothermal waters			
02-041	69	74	68
02-042	69	82	63
02-043	64	137	118
02-044	69	88	64
02-045	74	87	65
02-046	68	85	67
02-049	55	59	62
02-051	80	129	118
02-052	48	102	81
02-053	79	110	104
02-059	81	103	87
02-060	62	71	57
02-080	82	128	114
03-026	120	124	122
03-028	60	73	55
03-029	74	84	72
03-032	84	105	90
03-033	72	99	80
04-031	60	83	62
04-032	60	83	62
Eastern geothermal waters			
02-061	51	60	24
02-062	57	79	53
02-063	55	74	44
02-064	60	70	46
02-065	60	81	68
02-066	62	80	92
02-067	94	122	134
02-068	64	92	71
02-069	61	88	74
02-071	82	98	93
02-072	95	111	119
02-073	100	118	128
02-074*	99	116	130
02-075	99	124	135
02-076*	98	146	158
02-077	98	11	120
02-078	63	90	50
02-079	68	97	74
04-035	52	70	70
Northwestern geothermal waters			
02-047	97	107	98
02-048	97	104	100
02-054	76	106	103
02-055*	99	140	139
02-057*	97	136	118
02-070	84	102	78
03-038	90	79	70

Sample no.	Measured temp. (°C)	Na-K temp. (°C)	Chalcedony temp. (°C)
03-039	88	104	93
03-081	133	128	131
03-082	23	139	46
Geysir high-temperature field			
01-3201*	87	192	233
01-3202*	88	183	231
01-3203*	98	184	230
01-3204*	93	141	214
01-3205*	88	139	207
01-3206*	99	140	204
01-3207*	95	180	226
01-3208	30	187	81
01-3209	39	155	101
01-3210	26	155	72
01-3211	20	161	39
01-3212*	98	130	208
01-3213	86	153	214
01-3214	65	256	142
01-3215	48	196	123
01-3216*	98	142	210

Un-mixed waters from the Geysir high-temperature field show higher silica (quartz) temperatures compared to Na-K temperatures, shown in two sets of reservoir temperature estimates. These two sets of temperature estimates have quartz temperatures in the range between 208-215°C, and 226-233°C, and Na-K temperatures between 130-153°C and 180-192°C, respectively. These sets of temperatures could possibly be associated with the presence of two aquifers with different temperatures within the same system. The difference in the temperature estimates by the two geothermo-meters is probably due to removal of K from solution into clay minerals. In this case the quartz geothermometer is considered to be reliable.

Relationships between measured temperatures and calculated silica equilibrium temperatures show that some of the low-temperature geothermal waters have lower estimated silica temperatures than the measured temperatures (Figure 10) but others have indicated temperatures which are up to 60°C higher than the measured spring temperatures. The results shown in Figure 10 also indicate that there is no silica equilibrium in cold surface waters. Some waters from the eastern thermal system consistently indicate chalcedony equilibrium temperatures of 120-140°C. In the rest of the thermal systems,

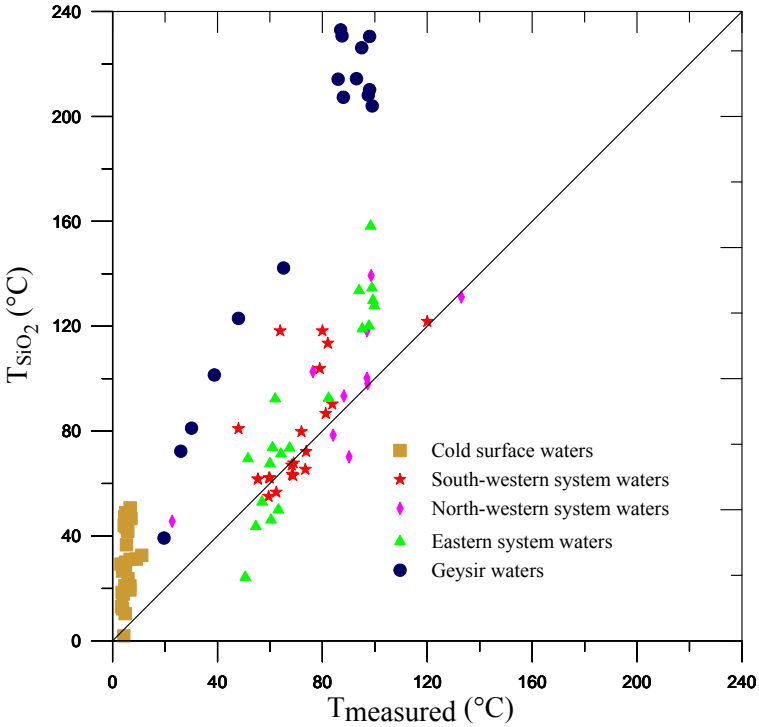

FIGURE 10: Estimated silica and measured temperature relations of the thermal and non-thermal waters from the Southern Lowlands

chalcedony equilibrium temperatures are variable.

Five samples from the eastern thermal system waters have measured temperatures higher than the silica (chalcedony) temperatures (Figure 10). All of these five samples have pH greater than or equal to 10 (10.00-10.45). The reason for such low chalcedony temperatures is possibly because the high pH conditions inhibit saturation with respect to chalcedony.

7. CONCLUSIONS

Data on Cl and B indicate that the low-temperature activity in the Southern Lowlands of Iceland may be divided into three geographic geothermal systems, here named the southwestern, northwestern and eastern systems. These systems are closely linked with elevation and distance from the ocean. Waters in the southwestern and northwestern systems have considerably higher Cl/B ratios than basalt and relatively high Cl concentrations, in particular the southwestern system, which is closer to the coast. Both the southwestern and the northwestern systems were transgressed by the ocean at the end of the last glaciation. It is considered that seawater infiltrated the bedrock at this time and that a small component of this old seawater is still present in the geothermal waters of these two systems, explaining the high Cl concentration and the high Cl/B ratios of the waters. The eastern system, which is more elevated than the other two systems, has lower Cl concentrations and Cl/B ratios that are similar to that of basalt, at least for the most reacted waters. It is considered that the geothermal waters of this system do not contain a seawater component and the origin of the Cl and B in the water is largely from the basalt with which it has reacted but also the Cl and B in the parent precipitation.

Boiling hot spring waters from the Geysir field have Cl/B ratios, which are very similar to those of basalt. It is considered that the source of these two elements in the waters is for the most part the rock with which they have reacted. Only a small fraction is derived from the parent precipitation. Warm spring waters from the Geysir high-temperature field originate by dilution of the hot reservoir water with cold water. Their Cl/B ratios are intermediate between those of seawater and highly reacted geothermal water. The cold waters have high Cl/B ratios; slightly lower than that of seawater, i.e. local precipitation.

The δ^2H values of the geothermal waters, both in the low-temperature areas and the Geysir high-temperature area, are more negative than those of local precipitation. Some of the geothermal waters in the southwestern system have values as low as the lowest δ^2H values in precipitation in Iceland today. These highly negative values may be due to the presence in the waters of an ice-age component. During the last glacial period in Iceland, precipitation at any particular locality was more negative than today's precipitation. Geothermal waters with more negative δ^2H values than local precipitation may contain a component of ice-age water, or represent precipitation during post-glacial periods when the climate in Iceland was cooler than today. Alternatively, these waters may represent precipitation that fell inland at higher elevation relative to the respective hot springs.

The δ^2H and Cl are negatively correlated in the southwestern and northwestern systems. The correlation is slight in the northwestern system. This is because the waters in the northwestern system largely contain present-day precipitation but a very small fraction of old water. The geothermal waters that have similar δ^2H values as the lowest in today´s precipitation in Iceland are those, which have higher Cl concentration indicating that these waters also contain an ice-age meteoric water component.

Geothermal waters from the high- and low-temperature systems in the Southern Lowlands show oxygen shifts. Non-mixed waters from the Geysir field show larger oxygen shifts, 2.39-4.36‰, than the mixed waters. The eastern system waters show generally larger oxygen shifts than the southwestern and northwestern systems. The smallest and the largest oxygen shifts were observed in the southwestern system. Some of the mixed waters show negative oxygen shifts. Oxygen shift is

caused by water-rock interaction, which is influenced by the temperature and underground residence time of the geothermal water. The large oxygen shifts in the non-mixed Geysir waters are, therefore, caused by water-rock interaction at high temperatures. The same reasoning applies to variations in the oxygen shift in the low-temperature fields. This means higher temperature conditions prevail in the eastern system followed by the northwestern system, in a general sense. The negative shifts in the mixed waters are considered due to the bubbling of CO_2 through the geothermal waters, which takes up ^{18}O and makes the water depleted in this isotope.

Geothermal waters in the Southern Lowlands, with the exception of the mixed waters of the Geysir area, equilibrated at temperatures similar to or higher than those measured in discharges. The silica and Na-K temperatures show comparable results for the low-temperature systems. Yet, Na-K temperatures tend to be higher at temperatures below 100°C and some waters from the southwestern system show much higher Na-K temperatures than chalcedony temperatures. Some waters from the eastern system, which show much lower chalcedony temperatures than Na-K temperatures, also show lower chalcedony temperatures than measured temperatures. These waters have highest pH ($\geq$ 10) of the low-temperature system waters. The reason for such a low chalcedony temperature is thought to be due to lack of chalcedony saturation at the high pH conditions.

The mixed waters and cold surface waters show unrealistic and non-comparable chalcedony and Na-K temperature estimates due to lack of equilibrium.

Boiling spring waters in the Geysir area yield higher quartz than Na-K temperatures. The cause is considered to be the removal of K from solution into clay minerals. Therefore, quartz temperatures are more reliable than Na-K temperatures in this area. The temperature relationships in the Geysir area show that there are two sets of equilibrium temperatures, possibly indicating the existence of two aquifers.

ACKNOWLEDGEMENTS

I would like to extend my hearty gratitude to the staff of the United Nations University Geothermal Training Programme, Dr. Ingvar Birgir Fridleifsson, director, and Mr. Lúdvík S. Georgsson, deputy director, for giving me the chance to attend this training, for the continuous care they provided throughout the training period and for their interest and willingness to share their priceless knowledge on geothermal energy, Mrs. Dorthe H. Holm for being always there ready to help whenever needed, Ms. Thórhildur Ísberg for all the administrative assistance she provided me with, starting from when I was home and ever since, and also Mr. Markús A. Wilde for his readiness to help me with everything I asked. I thank the UNU-GTP and especially the Government of Iceland for providing me with the necessary funds and facilities for the training. I sincerely thank my supervisor Dr. Stefan Arnórsson for his professional guidance in carrying out this study. My appreciation is extended to all instructors, staff of the Icelandic Geosurvey (ISOR) and National Energy Authority (Orkustofnun).

I would like to extend my gratitude to the Department of Mines, Ministry of Energy and Mines of the State of Eritrea, for allowing me to attend this training course. My special thanks go to Mr. Alem Kibreab, director of the Department of Mines, for his continuous support and encouragement.

I am pleased to thank my beloved wife, Miriam, for standing by my side during the time when my presence was essential to her and for being able to take care of our new born twins. Lastly, I would like to thank all friends and family members for their support. Praise to the almighty God.

REFERENCES

Árnason, B., 1976: *Groundwater systems in Iceland traced by deuterium*. Soc. Sci. Islandica, 42, Reykjavík, 236 pp.

Arnórsson, S., 1970: Underground systems in hydrothermal areas in Iceland as deduced from silica content of the thermal water. *Geothermics, 2*, 536-541.

Arnórsson, S., 1985: The use of mixing models and chemical geothermometers for estimating underground temperature in geothermal systems. *J. Volc. Geotherm. Res., 23,* 299-335.

Arnórsson, S. (ed.), 2000: *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 351 pp.

Arnórsson, S., and Andrésdóttir A., 1995: Processes controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim. Cosmochim. Acta, 59*, 4125-4146.

Arnórsson, S., and Andrésdóttir, A., 1999: The dissociation constants of Al-hydroxy complexes at 0-350°C and P_{sat}. *Proceedings of the 5th International Symposium on the Geochemistry of the Earth´s Surface*, *Rotterdam, Balkema,* 425-428.

Arnórsson, S., Andrésdóttir, A., Gunnarsson, I., and Stefánsson, A., 1998: New calibration for the quartz and Na/K geothermometers – valid in the range 0-350°C (in Icelandic). *Proceedings of the Geoscience Society of Iceland Annual Meeting, April,* 42-43.

Arnórsson, S., Bjarnason, J.Ö., Giroud, N., Gunnarsson, I., and Stefánsson, A., 2006: Sampling and analysis of geothermal fluids. *Geofluids, 6, 203-216*.

Arnórsson, S., Geirsson, K., Andrésdóttir, A., and Sigurdsson, S., 1996: *Compilation and evaluation of thermodynamic data on aqueous species and dissociational equilibria in aqueous solutions. I. The solubilities of CO_2, H_2S, H_2, CH_4, N_2, O_2 and Ar in pure water.* University of Iceland, Science Institute, report RH-17-96, 20 pp.

Arnórsson, S., Gunnlaugsson, E., and Svavarsson, H., 1983a: The chemistry of geothermal waters in Iceland II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta*, *47*, 547-566.

Arnórsson, S., Gunnlaugsson, E., and Svavarsson, H., 1983b: The chemistry of geothermal waters in Iceland III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta, 47*, 567-577.

Arnórsson, S., Sigurdsson, S., and Svavarsson, H., 1982: The chemistry of geothermal waters in Iceland I. Calculation of aqueous speciation from 0°C to 370°C. *Geochim. Cosmochim. Acta, 46,* 1513-1532.

Arnórsson, S., and Stefánsson, A., 1999: Assessment of feldspar solubility constants in water in the range 0-350°C at P_{sat}. *Am. J. Sci., 299,* 173-209.

Arnórsson, S., Stefánsson, A., Gunnarsson, I., Andrésdóttir, A., and Sveinbjörnsdóttir, A.E., 2002: Major element chemistry of surface and ground waters in basaltic terrain, N-Iceland. I. Primary mineral saturation. *Geochim. Cosmochim. Acta, 66,* 4015-4046.

Arnórsson, S., and Svavarsson, H., 1985: Application of chemical geothermometry to geothermal exploration and development. *Geoth. Res. Council, Trans., 9-1*, 293-298.

Bjarnason, J.Ö., 1994: *The speciation program WATCH, version 2.1.* Orkustofnun, Reykjavík, 7 pp.

D'Amore, F., and Arnórsson, S., 2000: Geothermometry. In: Arnórsson, S.(ed.), *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 152-199.

Diakonov I., and Tagirov B.R., 2002: Iron (III) speciation in aqueous solutions: Part 2. Thermodynamic properties of $Fe(OH)^{+2}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3^{0}$ species and solubilities of iron (III) oxides, and hydroxides. *In preparation.*

Ellis, A.J., 1970: Quantitative interpretation of chemical characteristics of hydrothermal systems. *Geothermics, 2*, 516-527.

Ellis, A.J., and Mahon, W.A.J., 1977: *Chemistry and geothermal systems.* Academic Press, New York, 392 pp.

Ellis, A.J., and Wilson, S.H., 1961: The geochemistry of alkali metal ions in the Wairakei hydrothermal system, *N.Z.J. Geol. & Geophys., 3*, 593-617.

Fournier, R.O., 1977: Chemical geothermometers and mixing model for geothermal systems. *Geothermics, 5,* 41-50.

Fournier, R.O., 1979: A revised equation for Na-K geothermometer. *Geoth. Res. Council, Trans., 3,* 221-224.

Fournier, R.O., 1989: *Lectures on geochemical interpretation of hydrothermal waters*. UNU-GTP, Iceland, report 10, 73 pp.

Fournier, R.O., 1991: Water geothermometers applied to geothermal energy. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 37-69.

Fournier, R.O., and Potter, R.W., 1982: An equation correlating the solubility of quartz in water from 25° to 900°C at pressures up to 10,000 bars. *Geochim. Cosmochim. Acta, 46*, 1969-1973.

Giggenbach, W.F., 1988: Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta, 52*, 2749-2765.

Helgeson, H.C., 1969: Thermodynamic of complex dissociation in aqueous solution at elevated temperatures and pressures. *Am. J. Sci., 267,* 729-804.

Hem, J. D., 1970: Study and interpretation of the chemical characteristics of natural water. *U.S. Geol. Survey, water supply paper 1473.*

Jóhannesson H., and Saemundsson, K., 1999. *Geological map of Iceland 1:1.000.000*. Icelandic Institute of Natural History.

Morey, G.W., Fournier, R.O., and Rowe, J.J., 1962: The solubility of quartz in water in the temperature interval from 29 to 300°C. *Geochim. Cosmochim. Acta, 26,* 1029-1043.

Nieva, D., and Nieva, R., 1987: Developments in geothermal energy in Mexico, part 12-A: Cationic composition geothermometer for prospection of geothermal resources. *Heat Recovery Systems and CHP, 7,* 243-258.

Norddahl, H., 1990: Late Weichselian and Early Holocene deglaciation history of Iceland. *Jökull, 40,* 27-50.

Nuti, S., 1991: Isotope techniques in geothermal studies. In: D´Amore (coordinator), *Applications of geochemistry in geothermal reservoir development.* UNITAR/UNDP publication, Rome, 215-251.

Pálmason, G., and Saemundsson K., 1974: Iceland in relation to the Mid-Atlantic Ridge. *Annual Review Earth Planet. Sci., 2,* 25-50.

Pokrovski, G.S., Schott, J., Salvi, S., Gout, R., and Kubicki, J.D., 1998: Structure and stability of aluminium-silica complexes in neutral to basic solution. Experimental study and molecular orbital calculations. *Mineralogical Magazine, 62A,* 1194-1195.

Pope, L.A., Hajash, A., and Popp, R.K., 1987: An experimental investigation of the quartz, Na-K, Na-K-Ca geothermometers and the effect of fluid composition. *J. Volcanol. Geotherm. Res., 31*, 151-161.

Sveinbjörnsdóttir, Á.E., Johnsen, S., and Arnórsson, S., 1995: The use of stable isotopes of oxygen and hydrogen in geothermal studies in Iceland. *Proceedings of the World Geothermal Congress, 1995, Florence, Italy, 2,* 1043-1048.

Tonani, F., 1980: Some remarks on the application of geochemical techniques in geothermal exploration. *Proceedings, Adv. Eur. Geoth. Res., 2nd Symposium, Strasbourg*, 428-443.

Truesdell, A.H., 1976: Summary of section III - geochemical techniques in exploration. *Proceedings of the 2nd UN Symposium on the Development and Use of Geothermal Resources, San Francisco, 1,* liii-lxxix.

Truesdell, A.H., and Fournier, R.O., 1976: Calculations of deep temperatures in geothermal systems from the chemistry of boiling spring waters of mixed origin. *Proceedings of 2nd UN Symposium on the Development and Use of Geothermal Resources, San Francisco, 1,* 837-844.

Verma, M.P., 2000: Chemical thermodynamics of silica: a critique on its geothermometer. *Geothermics, 29*, 323-346.

Verma, S.P., and Santayo, E., 1997: New improved equations for Na/K, Na/Li and SiO_2 geothermometers by outlier detection and rejection. *J. Volcanol. Geotherm. Res., 79*, 9-23.