



## GEOCHEMICAL AND ISOTOPIC STUDIES OF NATURAL WATERS FROM THE TRÖLLASKAGI AREA, N-ICELAND

**Özge Can Ataş**

Kocaeli University

Engineering Faculty, Geological Engineering Deptm.

41040 İzmit

TURKEY

*ozgecan@kou.edu.tr*

### ABSTRACT

The objective of this study is to compile all existing geochemical and isotopic data of the waters in the Tröllaskagi area, N-Iceland. The waters were classified, reservoir temperatures evaluated, mixing processes studied and the origin and movement of the waters determined. From the ternary plots, the waters can be classified as cold groundwaters, volcanic waters and a combination of the two, with the exception of Hrísey which plots close to mature waters. The plots also suggest that all the waters originate from old systems. Most of the geothermal waters seem to have equilibrated with respect to specific minerals. Subsurface temperature prediction, using the chalcedony geothermometer with correction for dissociated silicic acid, is in the range 42-103°C. The chalcedony mixing model shows that the geothermal waters are not mixed and their subsurface temperatures range from 50 to 143°C. Both the binary plots and the Schoeller diagram suggest the absence of mixing except for the Hrísey waters, which seem to have mixed with sea water. Stable isotopes of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  have been used in the study area to trace and determine the origin and movement of groundwater. The thermal waters in the Tröllaskagi area are more depleted than the local precipitation and in some cases more depleted than any precipitation on Iceland today. The isotopic values of the thermal waters found within the Tröllaskagi peninsula suggest a different origin for the different sites. It is possible to trace the origins of the thermal waters in Siglufjörður and Ólafsfjörður to the mountainous areas south of the thermal sites using isotopes, whereas the thermal waters in Dalvík and points further to the south are more depleted than any precipitation on the Tröllaskagi peninsula today.

### 1. INTRODUCTION

Iceland straddles the Mid-Atlantic Ridge, a divergent plate boundary between the European and American plates evidenced in a zone of active rifting and volcanism. The rifting is followed by continuous volcanic eruptions along the divergent plates where new crust, pre-dominantly of basaltic composition, is formed as the older rocks in East and West Iceland move away from each other at a rate of 2 cm/year.

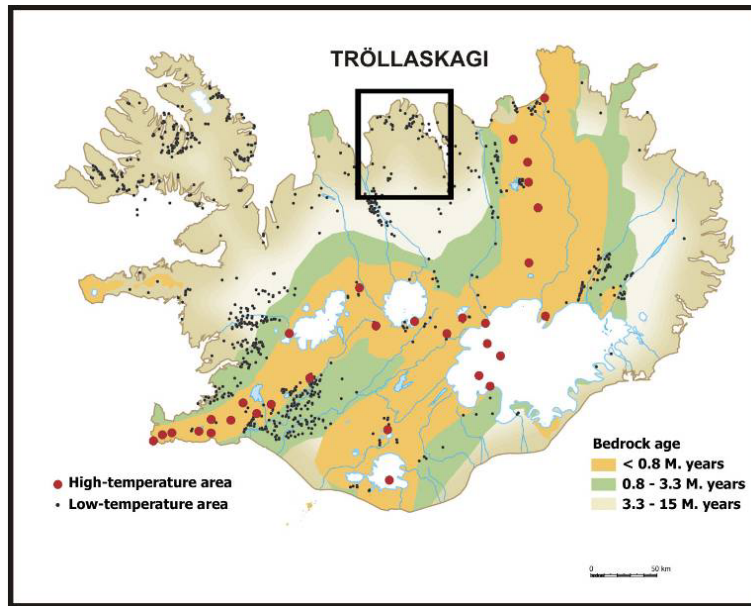


FIGURE 1: The main geological features and locations of geothermal areas in Iceland; the study area in N-Iceland is also shown

The active geothermal areas in Iceland (Figure 1) are distinguished as low-temperature areas and high temperature areas (Bödvarsson and Pálmason, 1961). More than 200 volcanoes are located within the active volcanic zone running through the country from the southwest to the northeast. In this volcanic zone there are at least 20 high-temperature areas containing steam fields with underground temperatures reaching 250°C within 1000 m depth. These areas are directly linked to active volcanic systems. About 250 separate low-temperature areas with temperatures not exceeding 150°C in the uppermost 1000 m are found, mostly in the areas flanking the active zone.

Geochemistry is extensively applied to all phases involved in geothermal exploration and development. Management of geochemical studies of geothermal fluids requires an expert with background knowledge in chemistry or geology. Geochemistry is also a major tool for monitoring studies. During the exploration phase, the task of the geochemist is largely twofold:

- To estimate subsurface temperatures by using isotope and chemical geothermometers as well as mixing models;
- To identify the source of the water, largely by using isotopic techniques.

The main objective of the present study is to compile all existing geochemical and isotopic data from this area. More specifically the objectives are:

- To evaluate reservoir temperatures and equilibrium conditions using chalcedony geothermometers and equilibrium calculations;
- To evaluate the effects of mixing processes;
- To interpret the stable isotopic composition of the natural waters; and
- To determine the origin and movement of the fluids.

## 2. GEOLOGICAL SETTING

The study area, usually called Tröllaskagi, is a high mountainous peninsula between the fjords Skagafjörður and Eyjafjörður and located in northern Iceland (Figure 2). Topographically the area is characterized by glacial erosion, its most prominent feature being the Valley of Skagafjörður. The mountains on either side of the Skagafjörður valley reach an elevation of 900-1300 m a.s.l. Glacially eroded valleys extend from the main valley into the mountains on either side and into the interior highland plateau north of Hofsjökull which is at an elevation of 700-900 m a.s.l.

The rocks within the study area are a monotonous pile of Tertiary quartz to olivine normative tholeiite flood basalts which are compositionally rather similar to normal MORB. The lavas generally dip a few degrees to the southwest (Saemundsson et al., 1980). The total thickness of the succession is ~7

km with the oldest lavas 11-12 m.y. old (Jóhannesson, 1991). Quaternary basalt lavas and hyaloclastites overlie the Tertiary formations at the head of the Skagafjörður valley system and in the interior highlands. The upper part of the Tertiary flood basalts in the mountains on either side of the Skagafjörður Valley is unaltered and free from vesicle minerals.

In outcrops down in the valley the basalts are also quite fresh but partly vesicle filled. The vesicle minerals include chalcedony, calcite and small crystals of the low-temperature (<100°C) zeolites, chabazite, thomsonite and stilbite. The sparse vesicle fillings and the small size of their crystals indicate that the exposed flood basalts in Skagafjörður have never been deeply buried (Walker, 1960; Neuhoﬀ et al., 1999). The present flat tops of the mountains on the east side of the Skagafjörður Valley are considered to be close to the original lava plateau surface (Jóhannesson, 1991).

In the oldest exposed rocks in the area, near Siglufjörður (Figure 2), the degree of alteration and the extent of vesicle fillings are more extensive than in younger rocks further south (Indridason, 2002). This is in line with observations elsewhere in Iceland that the degree of alteration is mostly determined by depth of burial (Walker, 1960; Neuhoﬀ et al., 1999). The extent of alteration of these oldest rocks is considered to be similar to that found at 1-2 km depth in the main geothermal area in central Skagafjörður.

A zone of recent fracturing extends N15°E from the active volcanic belt in central Iceland across the central part of the Valley of Skagafjörður and into the mountains to the east of the valley and the Skagafjörður fjord (Figure 2). In several places these fractures run through ground moraines resting upon the bedrock, indicating movement in Postglacial times.

Thermal and non-thermal springs occur in very many places on low ground in the study area. Their temperatures range from 2° to 90°C. The thermal springs are concentrated where the recent fracture zone cuts across the Skagafjörður Valley (Arnórsson and Gíslason, 1990). The young faults and fractures represent permeability anomalies. The largest non-thermal springs occur at the heads of the valleys which penetrate the interior plateau (Hjartarson et al., 1998).

Data available on permeability from testing of 1-3 km deep wells in the valley of Eyjafjörður, ~50km to the east of Skagafjörður (Figure 2) give a good idea of what the regional bedrock permeability may be in Skagafjörður. The two valleys intersect the same flood basalt succession which has a similar history in both valleys subsequent to formation with respect to tectonics, burial and secondary mineralization. According to Björnsson et al. (1990), the regional permeability in these formations lies in the range of  $0.4 \times 10^{-15}$ - $10^{-14}$  m<sup>2</sup>. These numbers are considered to be applicable to the lava succession underlying the Valley of Skagafjörður, but in rocks forming the higher mountains and the interior plateau north of the ice cap of Hofsjökull permeability will be higher, probably by one to two orders of magnitude as deduced from data presented by Saemundsson and Fridleifsson (1980) on drillholes sunk into Tertiary and Quaternary basalts in Iceland.

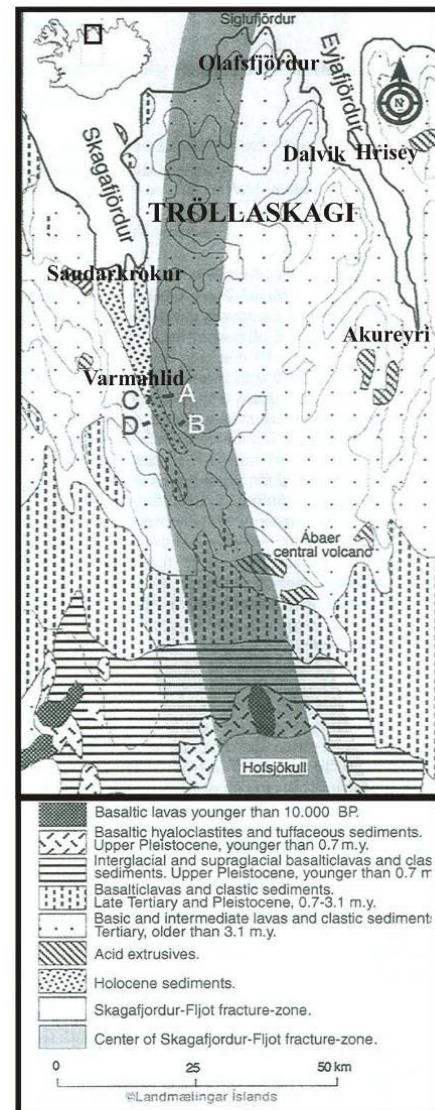


FIGURE 2: General geological map of the study area

### 3. METHODOLOGY

#### 3.1 Chemical features of the fluid

##### 3.1.1 Cl-SO<sub>4</sub>-HCO<sub>3</sub> triangular diagram

The Cl-SO<sub>4</sub>-HCO<sub>3</sub> ternary diagram is one of the diagrams used for classification of natural waters (Giggenbach, 1988). It helps to discern immature unstable waters and gives an initial indication of mixing relationships or geographical groupings. The diagram distinguishes several types of thermal water including immature waters, peripheral waters, volcanic waters and steam-heated waters. It gives a preliminary statistical evaluation of groupings and trends. The position of a data point in such a triangular or trilinear plot is simply obtained by first forming the sum  $S$  of all three constituents involved (in mg/kg):

$$S = C_{Cl} + C_{SO_4} + C_{HCO_3} \quad (1)$$

Then the percentage of each of the three anions can be calculated as:

$$Cl (\%) = 100C_{Cl}/S, \quad SO_4 (\%) = 100C_{SO_4}/S, \quad HCO_3 (\%) = 100C_{HCO_3}/S \quad (2)$$

##### 3.1.2 The Cl-Li-B triangular diagram

The Cl-Li-B triangular diagram is useful for evaluating the origin of geothermal fluids. Among rock derived constituents, lithium is least affected by secondary processes, so it can be used as a tracer for deep rock dissolution and as a reference for evaluating the possible origin of the main two conservative constituents of thermal waters, Cl and B. Once added, Li remains largely in solution. It is, however, striking that both Cl and B are added to the Li containing solutions in proportions close to those in crustal rocks. At high temperatures Cl occurs largely as HCl and B as H<sub>3</sub>BO<sub>3</sub>. Both are volatile and can be mobilized by high-temperature steam. At lower temperatures the acidity of HCl increases rapidly, and it is soon converted by reaction with the rock to the less volatile NaCl. B remains in its volatile form to be carried in the vapour phase even at lower temperatures. The B content of thermal fluids probably reflects, to some degree, the maturity of a geothermal system. Due to its volatility, B is likely to escape during the early heating up stages. Fluids from older hydrothermal systems can be expected to be depleted of the element.

The position of a data point on the diagram is calculated by:

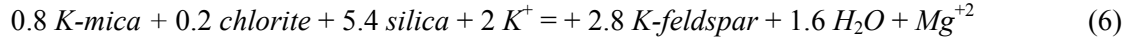
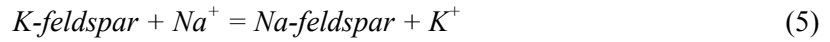
$$S = C_{Cl}/100 + C_{Li} + C_B/4 \quad (3)$$

$$\%Cl = C_{Cl}/S \quad \%Li = 100 C_{Li} \quad \%B = 25 C_B/S \quad (4)$$

##### 3.1.3 Na-K-Mg triangular diagram

The Na-K-Mg diagram is used to classify waters into fully equilibrated, partially equilibrated and immature waters. It can be used to predict the equilibrium temperature and also the suitability of thermal waters for the application of ionic solute geothermometers. It is based on the temperature dependence of the full equilibrium assemblage of potassium and sodium minerals that are expected to form after isochemical recrystallization of average crustal rock under conditions of geothermal interest (Giggenbach, 1988).

It is essentially based on the temperature dependence of the two reactions:



Na, K and Mg concentrations of waters in equilibrium with this assemblage are accessible to rigorous evaluation. The coordinates of a point on the diagram are calculated by

$$S = C_{Na} / 1000 + C_K / 100 + \sqrt{C_{Mg}} \quad (7)$$

$$\%Na = C_{Na} / 10S \quad \%K = C_K / S \quad \%Mg = \sqrt{C_{Mg}} / S \quad (8)$$

### 3.2 Geothermometers

#### 3.2.1 General background

Geothermometers constitute a very important tool for estimating original subsurface temperatures below the zone of cooling. Geothermal waters from the deep reservoir may be cooled during upflow to the surface, either by conduction, when travelling through cooler rocks, or by boiling, when the hydrostatic pressure decreases.

Geothermometers have been classified into three groups (D'Amore and Arnórsson, 2000);

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

Geothermometers are generally derived from the van't Hoff equation, and express the temperature dependency of equilibrium constants:

$$t(^{\circ}C) = \frac{a}{b + \log(K)} - 273 \quad (9)$$

where  $a$  and  $b$  are constants that describe the linear relationship between  $\log(K)$  and  $1000/T$ , where  $T$  is the absolute temperature in K. The quantity  $K$  depends on the reaction used for the geothermometer under consideration ( $K_{SiO_2}$  for all silica geothermometers,  $K_{Na/K}$  for all Na-K geothermometers, etc.).

Many water geothermometers were developed from the mid-1960's to the mid-1980's. The most important ones are the silica (quartz and chalcedony), Na/K and Na-K-Ca geothermometers. Two approaches, theoretical and empirical, have been used to calibrate the water geothermometers. When applied to the same geothermal fluid, the different geothermometers frequently yield appreciably different reservoir temperatures due to a lack of equilibrium between the solution and the hydrothermal minerals, or as a result of reactions, mixing or degassing during up-flow. In order to get reasonable results, the validity of the assumptions of specific solution/mineral equilibria, and some of the physical and chemical processes involved, should be taken into account.

For this study only water or solute geothermometers were used, particularly the chalcedony geothermometer, which may be distorted because of high pH which leads to the dissociation of silicic acid.

### 3.2.2 Chalcedony geothermometer

This geothermometer is based on the solubility of chalcedony. Fournier (1991) suggested that there is ambiguity in the use of silica geothermometers at temperatures below 180°C as chalcedony appears to control dissolved silica in some places and quartz in others. Chalcedony is a very fine-grained variety of quartz, which is probably not a separate mineral but a mixture of quartz and moganite and, with time, it probably all changes to quartz (Gislason et al., 1997). Temperature, time and fluid composition all affect different crystalline forms of silica. Thus, in some places (old systems), where water has been in contact with rock at a given temperature for a relatively long time, quartz may control dissolved silica at temperatures down to 100°C. In other places (young systems), chalcedony may control dissolved silica at temperatures up to 180°C. The chalcedony geothermometer in a condition of maximum steam loss, presented by Arnórsson et al. (1983a), is:

$$t(^{\circ}\text{C}) = \frac{1264}{5.31 - \log \text{SiO}_2} - 273.15 \quad (10)$$

and without steam loss:

$$t(^{\circ}\text{C}) = \frac{1112}{4.91 - \log \text{SiO}_2} - 273.15 \quad (11)$$

Another function for the chalcedony geothermometer was obtained by Fournier (1977):

$$t(^{\circ}\text{C}) = \frac{1032}{4.69 - \log S} - 273.15 \quad (12)$$

### 3.3 Mineral-solution equilibria

The thermodynamic properties of minerals and species change with temperature and pressure. The effect of temperature is much greater than the effect of pressure in the temperature range from 0 to 350°C and pressure range from 1 to 200 bar, so that the effect of pressure on mineral-solution equilibrium can be neglected. One of the assumptions for the chemical geothermometers presented above is that there is equilibrium between the fluid and the minerals in the reservoir. A geothermal system is characterized by a flow of fluid through a body of rock. This fluid will react with the rock chemically and, as is the case with any chemical reaction, change the system towards equilibrium. The equilibrium state for a given reaction of mineral and solution in a geothermal system can be evaluated by the ratio of the equilibrium constant ( $K$ ) for the given reaction to the reaction quotient ( $Q$ ) (Arnórsson, 2000).

Calculations of chemical equilibrium have been applied to geothermal investigations for over 30 years (Helgeson, 1969, Reed and Spycher, 1984). Using the activities of aqueous species calculated for homogeneous equilibrium at a series of temperatures, it is possible to compute the degree of super- or undersaturation of the aqueous phase with minerals at each temperature. This is expressed for a mineral  $k$  in terms of  $\log (Q/K)_k$ ,

$$\log (Q/K)_k = \log \prod_{i,k}^i a_{i,k}^{v_{i,k}} - \log K_k \quad (13)$$

where  $K_k$  = Equilibrium constant for mineral  $k$ ;  
 $a_{i,k}$  = The activity;  
 $v_{i,k}$  = Stoichiometric coefficient of component species  $i$  in the equilibrium mass action expression for mineral  $k$ , written with the mineral on the left hand side.

Using the results of the aqueous speciation calculations, the saturation indices (*SI*) for minerals in aqueous solutions at different temperatures were computed as:

$$SI = \log \frac{Q}{K} = \log Q - \log K, \quad (14)$$

where  $\frac{Q}{K}$  = The calculated ion activity product (IAP); and  
 $K$  = The equilibrium constant.

The *SI* value for each mineral is a measure of the saturation state of the water phase with respect to the mineral phase. Values of *SI* greater than, equal to, and less than zero represent supersaturation, equilibrium and undersaturation, respectively, for the mineral phase with respect to the aqueous solution. If *SI* for calcite is higher than 0, the water can deposit calcite; if *SI* = 0 the solution is in equilibrium with calcite and will neither deposit nor dissolve calcite; and if *SI* is lower than 0, the water does not have a calcite deposition potential.

Equilibrium constants for mineral dissolution often vary strongly with temperature. Therefore, if the *SI*s with respect to several minerals converge to zero at a particular temperature, that temperature is taken to be the reservoir temperature. The computer program WATCH (Arnórsson et al., 1983b; Bjarnason, 1994) has been developed to calculate the aqueous speciation of geothermal waters.

### 3.4 Mixing models

The thermal waters ascending from a geothermal reservoir may be cooled by mixing with cold, shallow waters, which tends to occur where there is a change in rock permeability. The pressure potential in the upflow zones of many geothermal systems is commonly lower than in the enveloping cold groundwater bodies. When this is the case, cold water tends to enter the geothermal system and mix with the rising hot water. Since cold waters are mostly lower in dissolved solids than geothermal waters, mixing is often referred to as dilution with respect to conservative components. However, mixing can upset chemical equilibria between water and rock minerals, thus causing a tendency for the water to change composition after mixing with respect to reactive chemical components, which may yield misleading results for geothermometers (Arnórsson, 2000).

It is necessary to establish that the sampled and analysed waters are truly mixed before applying mixing models to estimate reservoir temperatures. Recognition of mixed water on the basis of the chemical composition of a single sample is generally not convincing, so that the mixing process has to be identified and quantified by the consideration of samples from many springs or wells and surface waters.

Linear relationships between the concentrations of conservative components, e.g. between Cl and B or Cl and  $\delta D$ , are generally considered to constitute the best evidence for mixing. Sometimes the near linear relationships between Cl and  $\delta^{18}O$  or chloride and silica have been observed for variably mixed waters in some geothermal fields. Such relationships imply that  $\delta^{18}O$  and silica behave as conservative components after mixing (Arnórsson, 2000).

At present, a few mixing models for geothermal and cold water are applied to estimate subsurface temperatures in geothermal systems, employing the mixing of two components of quite different composition in such a way that the concentrations of reactive constituents do not change much after mixing has occurred. Sometimes, mixing at deep levels in geothermal reservoirs is likely to be completely masked in reactive constituent condensation through re-equilibration of these constituents subsequent to mixing, in which case the application of geothermometers is appropriate to estimate

subsurface temperature of the mixed fluid rather than mixing models for the temperature of the original geothermal fluid.

The three mixing models that are most commonly used to unravel mixing processes in a geothermal system are:

- The silica-enthalpy mixing model;
- The chloride-enthalpy mixing model;
- The silica-carbonate mixing model.

In addition, binary plots of chemical constituents, such as the linear pattern of a binary plot of chloride versus boron or  $\delta^{18}\text{O}$  values are taken to be convincing evidence for mixing (Arnórsson, 1991).

### 3.4.1 Schoeller diagrams

Schoeller diagrams are used to classify water types. They may also be used to show changes over time for the different water types. The log concentrations of fluid constituents from a number of analyses are connected with a line. Because logarithmic values are used, a wide range of concentrations can be shown. The effect of mixing with dilute water (as well as gain or loss of steam) is to move the connecting line vertically without changing its shape (Truesdell, 1991). Different water types will be displayed by crossing lines.

Slopes of lines between constituents represent concentration ratios. These diagrams show the effect of mixing on a number of constituents. When many analyses are shown, individual patterns may be lost, but the mixing patterns will remain clear.

### 3.4.2 Cl-B ratio

The Cl/B ratio is a convenient tool for distinguishing between aquifer systems, as neither Cl nor B participates in any important mineral/solute equilibria. Boiling and cooling of the geothermal water should, thus, not change the relative concentrations of the elements (Kristmannsdóttir and Johnsen, 1982). The distribution of B and Cl in Icelandic water is determined by its essentially incompatible behaviour and supply from four sources. These sources are (1) the atmosphere, i.e., seawater spray and aerosols incorporated into the precipitation, (2) the soil and rock with which the water interacts, (3) seawater that has percolated into the bedrock, and (4) magma intrusions. Most geothermal waters contain B and Cl within 0.05-1 and 10-100 ppm, respectively. These rather low values are attributed to the low content of B and Cl, which are 0.1-6.6 and 75-750 ppm, respectively, in the basaltic rock. B and Cl concentrations generally increase with water temperature. The Cl/B ratio in seawater is 4350 and a little lower in surface water and groundwater in Iceland. In Icelandic basalt this ratio is much lower, or in the range 25-50. The Cl/B ratio in geothermal water decreases with increased temperature and approaches that of the rock. The reason is that with higher water temperature, the leaching of Cl and B from the rock becomes faster, and because of the low Cl content in Icelandic basalt, the B enrichment is greater (Arnórsson and Andrésdóttir, 1995). Hence, a study of this ratio can yield valuable information on the origin of the water.

### 3.4.3 The silica-enthalpy mixing model

The silica-enthalpy mixing model proposed by Fournier (1977) may be used as an aid to evaluate subsurface temperatures. It is based on the solubility of silica as described in Figure 3.

In this model, the dissolved silica concentration of a mixed water and a silica-enthalpy diagram may be used to determine the temperature of the hot-water component (Figure 3). A straight line drawn from a point representing a non-thermal component of the mixed water (point-A) through a mixed-water warm spring (point B) to the intersection with the quartz solubility curve gives the initial silica



concentration and enthalpy of the hot water component (point C). The original temperature of the hot water component is then obtained from steam tables (Keenan et al., 1969).

In this procedure it is assumed that any steam that forms adiabatically does not separate from the residual liquid water before mixing with the cold water component. In the case where steam is lost before mixing takes place, for instance at atmospheric pressure, point D is the intersection of the line A-B and a vertical line representing the enthalpy of water at 100°C, the temperature to which it boils and at which it is assumed to mix. A horizontal line drawn from point D to the intersection with the maximum steam loss curve gives the initial enthalpy of the hot water component (point E). The initial dissolved silica is shown by point F. Therefore, the assumption of mixing after maximum steam loss gives minimum temperatures, while the assumption of mixing without steam loss gives maximum temperatures.

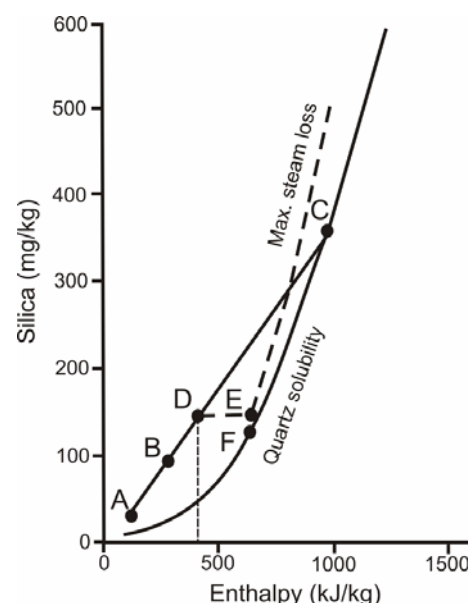


FIGURE 3: Silica-enthalpy diagram illustrating use in calculating silica mixing model temperatures

#### 4. CHEMICAL COMPOSITION OF THE THERMAL FLUID

##### 4.1 Sampling and analysis

In this study, the geothermal water samples were collected from 19 wells and 9 cold water samples were collected from springs and rivers. The samples were collected between 1994 and 1999. All the sampling and analyses were carried out by ISOR (Iceland Geosurvey). After collection, the samples were treated and a summary of the methods used is listed in Table 1. The analytical methods used are listed in Table 2. The results of the chemical analyses are in Table 3.

TABLE 1: Sample preparation methods

Treatment	Container	Specification	To determine
None; amber glass bottle with ground glass stopper	250-300 ml glass	Ru	pH, CO <sub>2</sub> , H <sub>2</sub> S (if not in field), conductivity
None	200 ml plastic	Ru	Mg, SiO <sub>2</sub> if < 100 ppm
Dilution; 50 ml of sample added to 50 ml of distilled, deionised water	3x100 ml plastic	Rd (1:1)	SiO <sub>2</sub> if > 100 ppm
Filtration	200 ml plastic	Fu	Anions
Filtration; 0.8 ml conc. HNO <sub>3</sub> (Suprapur) added to 200 ml sample	200 ml plastic	Fu	Cations
Filtration; 2 ml 0.2 M ZnAc <sub>2</sub> added to sample in 100 ml volumetric glass flask and ≥ 10 ml to ≥ 500 ml bottle containing ≥ 25 mg SO <sub>4</sub> to precipitate sulphide	100 ml, > 500 ml plastic	Fp; Fpi	SO <sub>4</sub>
Filtration; 160 ml and 2 1000 ml amber glass bottles	60 ml, 1000 ml glass	Fui, Fuc, Fut	<sup>2</sup> H, <sup>18</sup> O, <sup>3</sup> H, <sup>13</sup> C

Fp - Filtered, precipitated;

Fu - Filtered, untreated spectroscopy;

Fui- Filtered, untreated for <sup>2</sup>H and <sup>18</sup>O in water;

Rd - Raw, diluted;

Fpi - Filtered, precipitated for <sup>34</sup>S and <sup>18</sup>O in SO<sub>4</sub>;

Fuc- Filtered, untreated for <sup>13</sup>C;

Fut- Filtered, untreated for tritium;

Ru - Raw, untreated.

TABLE 2: Analytical methods used for the constituents determination

Constituent	Sample fraction	Method	Detection limit (mg/l)
pH	Ru	pH-meter	-
CO <sub>2</sub>	Ru	Electrometric titration	1.0
H <sub>2</sub> S	Ru	Titrimetric method	0.04
SiO <sub>2</sub>	Rd	Spectrophotometer	0.5
F	Fu	Selective electrode	-
Cl	Fu	Selective electrode	0.025
SO <sub>4</sub>	Fu/Fp	Selective electrode	0.020
B	Fu	Spectrophotometer	0.005
Na	Fa	AAS DA	0.01
K	Fa	AAS DA	0.01
Mg	Fa	AAS DA	0.01
Ca	Fa	AAS DA	0.01
Al	Fa	AAS GF	0.01
Fe	Fa	AAS GF	0.0001
TDS	Fu	Gravimetric	2.5

Ru - Raw, untreated;

Rd - Raw, diluted

Fu - Filtered, untreated spectroscopy

Fp - Filtered, precipitated

AAS - Atomic absorption

Fa - Filtered, (0.2  $\mu$ , 0.45  $\mu$ m) acidified

DA - Direct aspiration

GF- Graphite furnace

## 4.2 Classification of fluids

**Cl-SO<sub>4</sub>-HCO<sub>3</sub> triangular diagram.** Figure 4 shows that all cold waters have a high HCO<sub>3</sub> relative to Cl and SO<sub>4</sub> as does typical cold groundwater in Iceland. All hot water samples with the exception of well Hrísey-10, plot between volcanic and cold groundwaters suggesting that their origin is a combination of groundwater and volcanic water. The water sample from Hrísey-10 has high Cl relative to SO<sub>4</sub> and HCO<sub>3</sub> and plots close to mature waters, but this is because of the effect of sea water since it is close to the sea.

**Cl-Li-B triangular diagram.** All the samples have high Cl relative to Li and B suggesting that the samples originate from old systems (Figure 5).

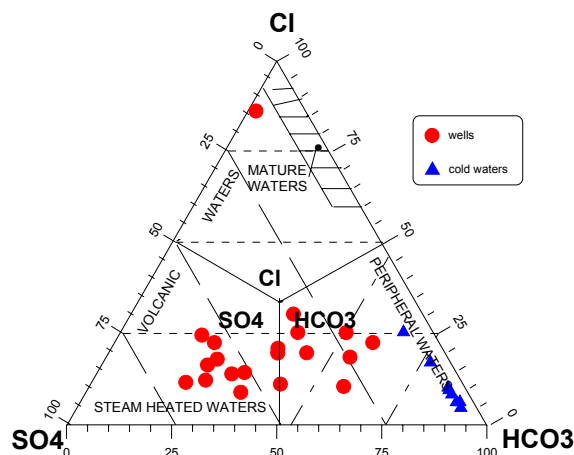


FIGURE 4: Cl-SO<sub>4</sub>-HCO<sub>3</sub> classification diagram of Giggenbach (1991) for the fluids of the Tröllaskagi area

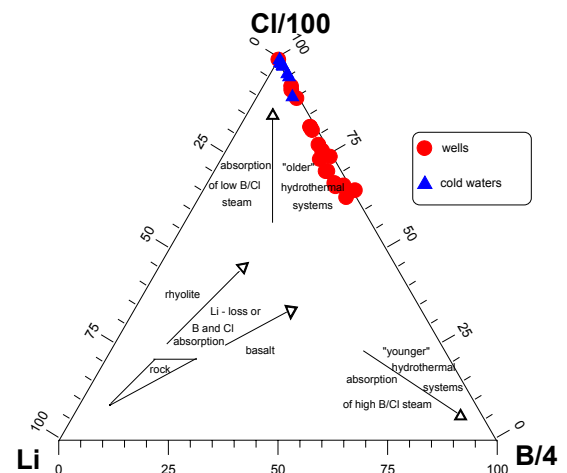


FIGURE 5: Cl-Li-B diagram of Giggenbach (1991) for the fluids of Tröllaskagi

TABLE 3: Chemical analysis results

Sample no.	Location <sup>a</sup>	Type	Temp. (°C)	pH	T/pH (°C)	SiO <sub>2</sub> (ppm)	B <sup>d</sup> (ppb)	Na (ppm)	K <sup>f</sup> (ppm)	Ca (ppm)	Mg (ppm)	Fe <sup>d</sup> (ppb)	Al <sup>d</sup> (ppb)	CO <sub>2</sub> <sup>e</sup> (ppm)	H <sub>2</sub> S (ppm)	SO <sub>4</sub> (ppm)	Cl (ppm)	F (ppm)	Li (ppb)
02-033	GYN-7	well	60.5	9.87	21	75.5	217.0	45.9	0.66	2.45	<0.0010	1.7	40.9	16.4	0.053	33.00	11.30	0.60	3.89
02-083	Sigluþfjörður, 11	well	71.6	9.91	18	96.1	29.2	43.3	0.87	1.47	0.0040	3.9	74.3	17.6	<0.03	9.44	9.04	0.38	1.34
02-084	Ólafsfjörður, 4	well	67.0	10.14	23	78.1	37.2	38.2	0.74	2.48	0.0010	0.6	91.5	11.7	<0.03	6.03	8.57	0.17	1.18
02-085	Ólafsfjörður, 12	well	56.3	10.11	23	65.9	22.4	34.1	0.69	1.82	0.0010	1.4	99.7	13.1	<0.03	4.40	7.55	0.11	0.72
02-086	Dalvík, 10	well	64.5	10.17	23	85.8	79.8	48.6	0.81	1.93	0.0040	0.7	77.8	13.8	0.060	13.20	9.26	0.50	2.17
02-087	Árskógsströnd, 29	well	73.4	10.07	23	102.0	150.0	54.7	1.17	2.02	0.0060	<0.4	68.3	14.8	0.170	15.50	13.90	0.94	4.25
02-088	Hrisey, 10	well	76.7	9.26	23	58.9	88.4	236.2	4.53	90.23	0.0470	1.0	14.6	3.2	0.040	60.10	500.00	0.26	15.00
04-025	Sigluþfjörður,	spring	5.2	6.75	20.6	14.1	3.40	8.0	0.30	5.35	1.9509	4.5	4.0	21.2	0.000	2.61	12.40	0.04	0.08
05-004	GYN-7	well	61	9.85	21.3	76.6	210.67	49.4	0.54	2.60	0.0009	2.3	44.5	25.1	0.07	33.40	10.80	0.58	3.17
05-005	Glerá	river	1.1	7.5	23.6	17.6	5.98	6.4	0.49	6.53	2.1947	18.8	1.5	25.5	0.06	1.67	9.04	0.07	0.31
00-47	Reykir RH-02	well	60.6	10.04	21.7	93.7	0.43	54.9	0.55	2.54	0.0030	8.4	38.2	16.4	0.06	17.90	19.90	1.40	7.93
02-030	L <sub>-</sub> 10	well	104.1	9.73	20	124.1	243.0	55.1	1.41	2.06	<0.0010	1.6	164	43.7	0.205	28.10	13.30	0.78	7.93
02-031	Vagfir	spring	4.0	6.97	21	20.4	10.4	5.0	1.02	6.28	2.6378	5.8	7.4	32.4	-	1.54	5.64	0.05	0.09
02-032	HJ-19	well	85.7	10.07	20	114.2	194.0	55.5	1.06	1.79	0.0012	3.0	129	12.9	0.289	17.60	10.90	1.77	6.14
02-034	RNW-7	well	75.7	9.77	20	87.0	252.0	53.4	1.05	3.65	<0.0010	1.1	78.3	14.7	0.069	47.20	11.70	0.57	5.45
02-035	HN-10	well	83.4	9.79	21	70.6	142.0	45.6	0.84	3.45	0.0014	5.2	142	18.2	-	37.30	8.07	0.50	4.55
02-036	BN-1	well	92.1	9.75	20	92.1	179.0	54.2	1.23	4.32	0.0022	2.5	191	12.9	0.073	54.20	11.90	0.59	6.42
02-037	LI-5	well	94.4	9.72	20	97.4	157.0	52.4	1.19	2.85	<0.0010	1.7	131	17.0	0.066	39.80	12.50	0.38	6.73
02-038	TN-4	well	81.4	9.82	20	89.5	188.0	56.0	0.89	3.71	<0.0010	0.6	94.9	14.5	0.056	47.60	15.80	0.44	4.83
02-039	Gleráðalslindir	spring	3.1	7.60	21	16.8	6.9	4.3	0.55	7.11	1.1048	0.7	0.3	23.0	-	0.73	3.13	0.04	0.05
02-040	Hesjuvallalindir	spring	2.9	8.60	21	16.5	2.0	4.5	2.90	4.84	0.7283	1.0	2.2	16.5	-	0.74	2.26	0.04	0.04
03-042	Gardsá	river	18.8	9.74	22.7	56.4	257	53.6	0.46	5.08	0.0075	10.9	4.59	17.1	-	49.90	19.00	0.37	3.34
03-043	Grisarárlindir	spring	2.8	7.76	21.4	24.6	9.18	3.4	0.77	5.42	1.3853	0.8	1.19	21.8	-	0.88	2.39	0.04	0.54
03-044	Selbót undir Haus	spring	4.0	7.54	23.2	18.0	5.06	8.1	<0.50	5.16	1.3339	1.6	2.57	25.9	-	1.27	5.08	0.05	0.08
03-045	Borhola ofan Ö	well	5.4	7.43	23.7	18.5	3.76	8.1	<0.50	5.29	1.3776	1.3	1.69	26.1	-	1.24	5.45	0.05	0.07
03-096	Varmahlid, 3	well	91.0	9.53	22.7	121.6	407	76.4	1.82	1.68	0.0028	0.8	71	35.0	-	47.90	27.50	2.17	16.50
03-097	Sauðárkrökur, 12	well	70.6	9.86	22.6	69.0	186	58.2	0.80	3.64	0.0017	0.7	69.5	11.4	-	46.00	23.00	1.44	5.41
03-098	Sauðárkrökur, 13	well	68.8	9.93	22.6	68.6	150	53.8	0.73	3.25	0.0017	1	63.8	12.0	-	38.40	18.40	1.46	4.26

**Na-K-Mg ternary diagram**

is used to evaluate equilibrium between the hot waters and rocks at depth and to estimate reservoir temperature. Figure 6 shows the equilibrium state of the well waters. It also shows that all the geothermal fluids plot above the equilibrium line obtained from Arnórsson et al. (1983a) Na-K relationship, which means that they are equilibrating with different minerals.

**4.3 Geothermometry**

The temperature estimates using the chalcedony geothermometers are listed in Table 4. An attempt to correct the dissociation of silicic acid at high pH observed for these samples yields, in many instances, chalcedony temperatures that are lower than the measured values and cannot be considered correct. As has been shown by Fleming and Crerar (1982) there is a variation in published values for the dissociation constant of silicic acid and it seems that the value used by WATCH may be somewhat high. Using a lower but still plausible value brings most of the values in line with the measured values and thus suggests that most of these samples are unmixed geothermal waters in equilibrium with the rock.

This is clearly seen in Figure 7 where the points should plot on the line  $\Delta T = 0$  for low-enthalpy fields, but do not because of the difference between the measured and calculated chalcedony values.

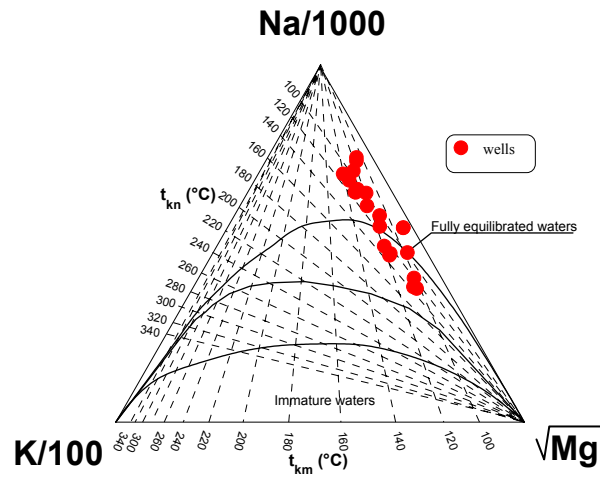


FIGURE 6: Na-K-Mg equilibrium diagram of Arnórsson et al. (1983a) for the fluids of Tröllaskagi area

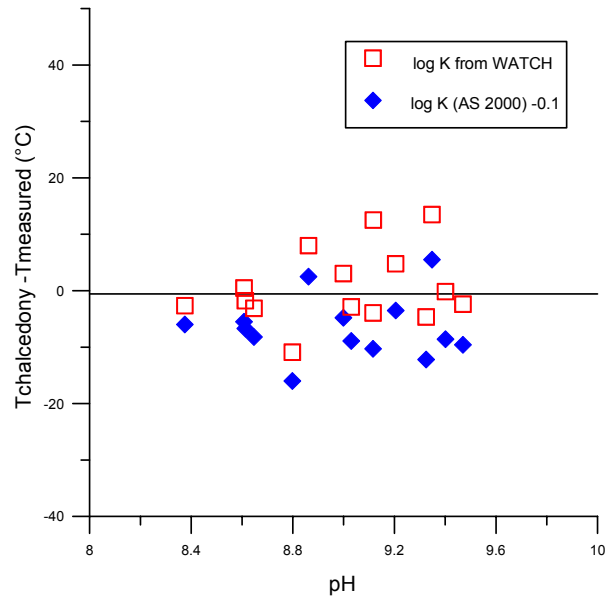


FIGURE 7: The difference between the calculated temperature and the observed temperature as a function of in situ pH

TABLE 4: Results of different chalcedony geothermometers from wells in the Tröllaskagi area

Sample no.	Location	pH	T <sub>meas</sub> (°C)	T <sub>chal</sub> <sup>1</sup> (°C)	T <sub>chal</sub> <sup>2</sup> (°C)	T <sub>chal</sub> <sup>3</sup> (°C)
02-033	GYN-7	9.87	60.5	65.5	93.56	93.84
02-083	Siglufjörður, 11	9.91	71.6	80	106.74	108.04
02-084	Ólafsfjörður, 4	10.14	67.0	49.2	95.39	95.77
02-085	Ólafsfjörður, 12	10.11	56.3	42	86.56	86.29
02-086	Dalvík, 10	10.17	64.5	51.6	100.43	101.24
02-087	Árskógsströnd, 29	10.07	73.4	67.9	110.13	111.72
02-088	Hrisey, 10	9.26	76.7	69.4	81.02	80.29
05-004	GYN-7	9.85	61	65.5	94.37	94.66
00-47	Reykir RH-02	10.04	60.6	67.1	105.31	106.50
02-030	L <sub>-</sub> 10	9.73	104.1	88.7	121.69	124.35
02-032	HJ-19	10.07	85.7	78.5	116.68	118.90
02-034	RNW-7	9.77	75.7	78.5	101.22	102.06
02-035	HN-10	9.79	83.4	58.6	90.10	90.08
02-036	BN-1	9.75	92.1	79.9	104.32	105.46
02-037	LJ-5	9.72	94.4	83	107.48	108.87
02-038	TN-4	9.82	81.4	76.1	102.74	103.74
03-096	Varmahlíð, 3	9.53	91.0	103.1	120.47	123.00
03-097	Saudárkrókur, 12	9.86	70.6	57.4	88.94	88.81
03-098	Saudárkrókur, 13	9.93	68.8	53.6	88.63	88.49

1) Fournier (1977) with correction for dissociated silicic acid;

2) Arnórsson et al. (1983a);

3) Fournier (1977).

#### 4.4 Solution-mineral equilibria

The log ( $Q/K$ ) diagram can be calculated by computer programs like WATCH and SOLVEQ. In the present study the WATCH program was used to prepare log ( $Q/K$ ) diagrams for the temperature range 20-120°C. The plausible alteration minerals in the system were selected with reference to some

TABLE 5: Temperature estimates from log  $Q/K$  plots

Sample no.	T <sub>meas</sub> (°C)	Range of estimate for subsurface temps. (°C)
02-033	60.5	80
02-083	71.6	90
02-084	67.0	80
02-085	56.3	70
02-086	64.5	70-80
02-087	73.4	80
02-088	76.7	80
05-004	61	90
00-47	60.6	70
02-030	104.1	100-110
02-032	85.7	80-90
02-034	75.7	80-90
02-035	83.4	90
02-036	92.1	90-100
02-037	94.4	100
02-038	81.4	80
03-096	91.0	100
03-097	70.6	70-80
03-098	68.8	70-80

available records of alteration minerals in the feed zones of the wells. Laumontite, albite-low, calcite, microcline, muscovite and chalcedony were selected to calculate the equilibrium state for hot water from wells. The calculated saturation index ( $SI = \log Q/\log K$ ) vs. temperature for water from wells are shown in Figure 8. The temperature where a  $SI$ -curve intersects the zero line represents the equilibrium temperature for each mineral. If the  $SI$ -curves for most of the minerals cross the equilibrium line at the same temperature, it is interpreted as being the reservoir temperature. The estimated temperatures from the plots are summarized in Table 5.

Figure 8 shows that equilibrium lines for a group of minerals converge close to the measured temperature. In all 19 graphs a clear temperature-rock equilibrium is reached between all the minerals and the thermal fluid. Chalcedony and calcite intersect the  $SI = 0$  line close to the measured temperature (Table 5). Other minerals found in cuttings show

equilibrium temperatures in the range from 80 to 120°C. The fact that the measured and calculated temperatures are similar, further suggests that the fields are low-temperature fields.

#### 4.5 Mixing models

In this study, a Schoeller diagram, some binary plots and the silica enthalpy model were applied to estimate mixing processes. The main components of thermal, cold and mixed waters from the study area are plotted in a Schoeller diagram (Figure 9). The figure shows that the Mg concentration for thermal samples is very low suggesting that there is no mixing except possibly for well Hrisey 10, where mixing with sea water is also suggested by the high chloride concentration. The diagram also shows that the groundwater originates from precipitation and has passed through similar rock types. This confirms that the water comes from the same lithology and similar aquifers (Connolly et al., 1990).

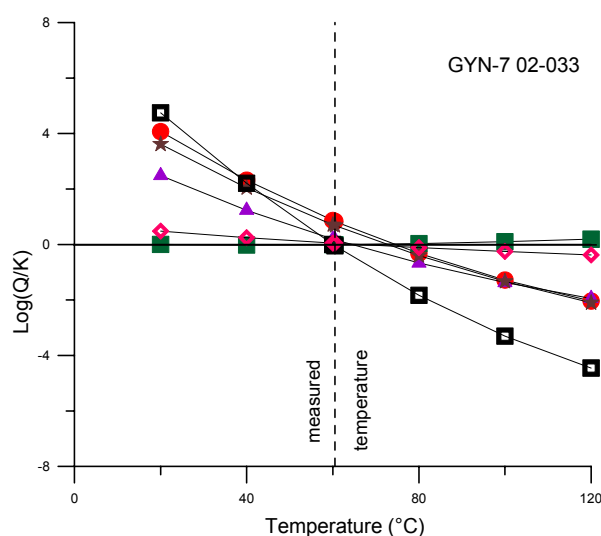


FIGURE 8: Saturation index diagram (log  $Q/K$ ) vs. temperature for the 14 wells from the Tröllaskagi area

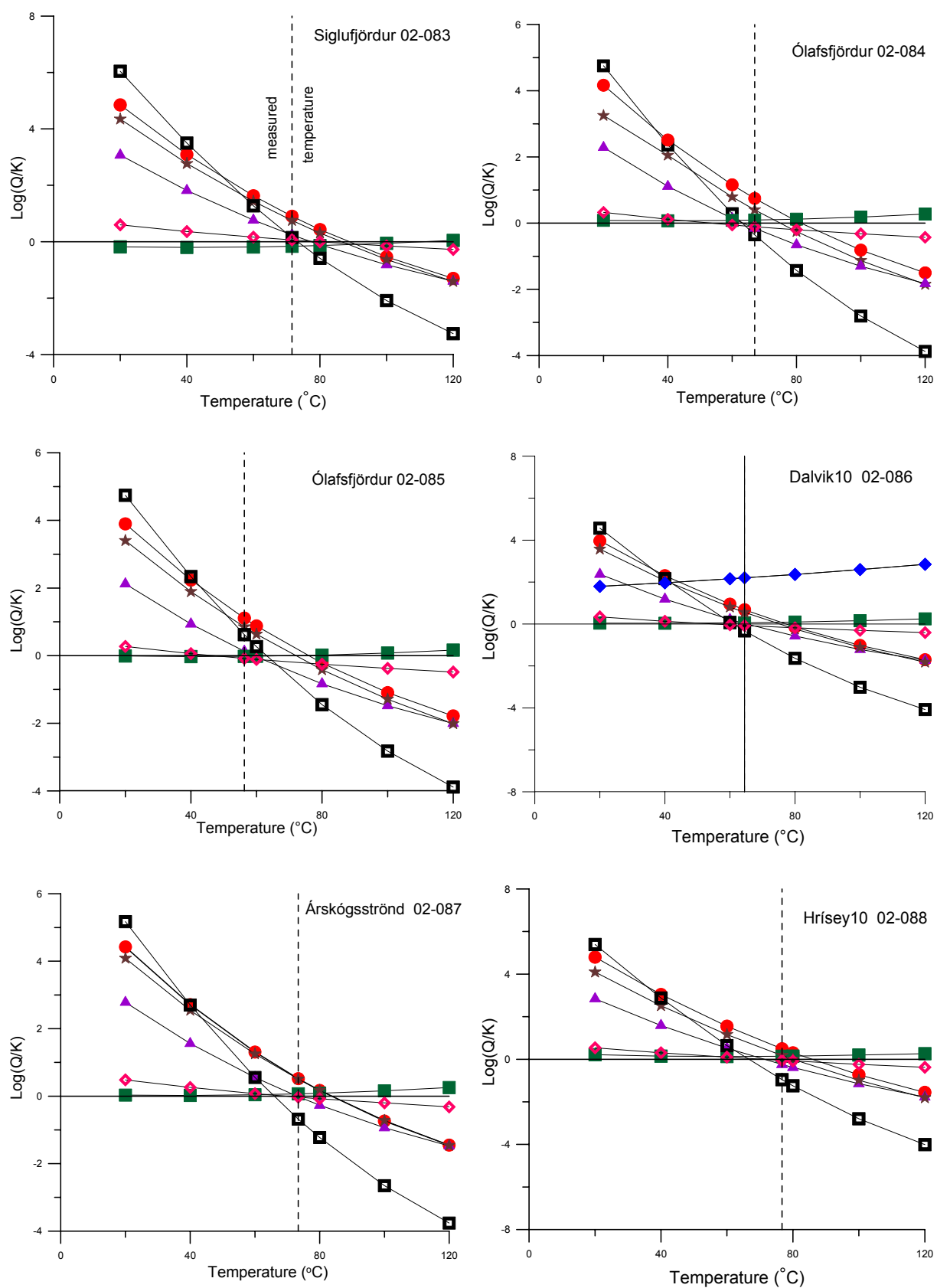


FIGURE 8 Continued: Saturation index diagram ( $\log Q/K$ ) vs. temperature for the 14 wells from the Tröllaskagi area

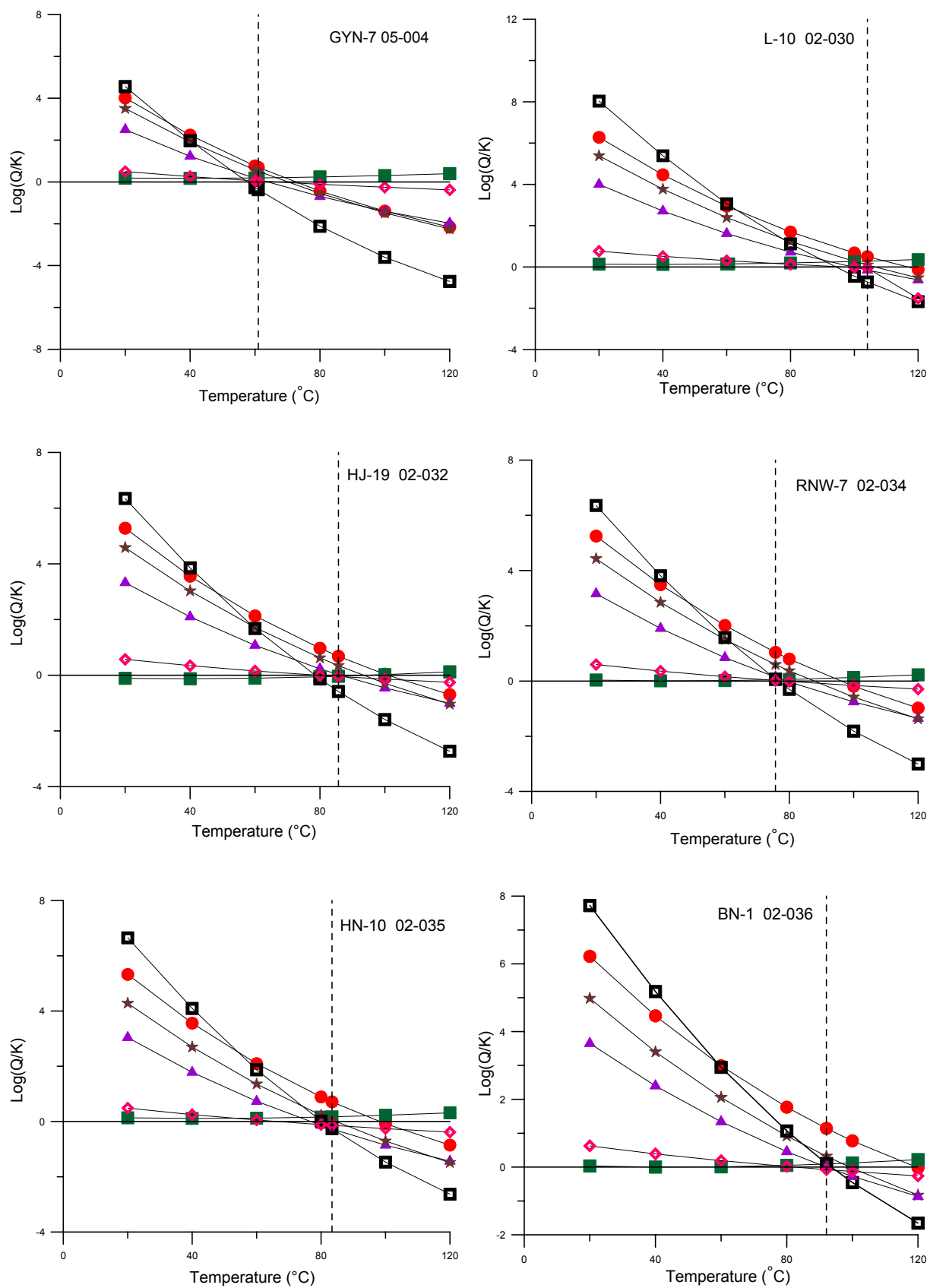


FIGURE 8 Continued: Saturation index diagram ( $\log Q/K$ ) vs. temperature for the 14 wells from the Tröllaskagi area

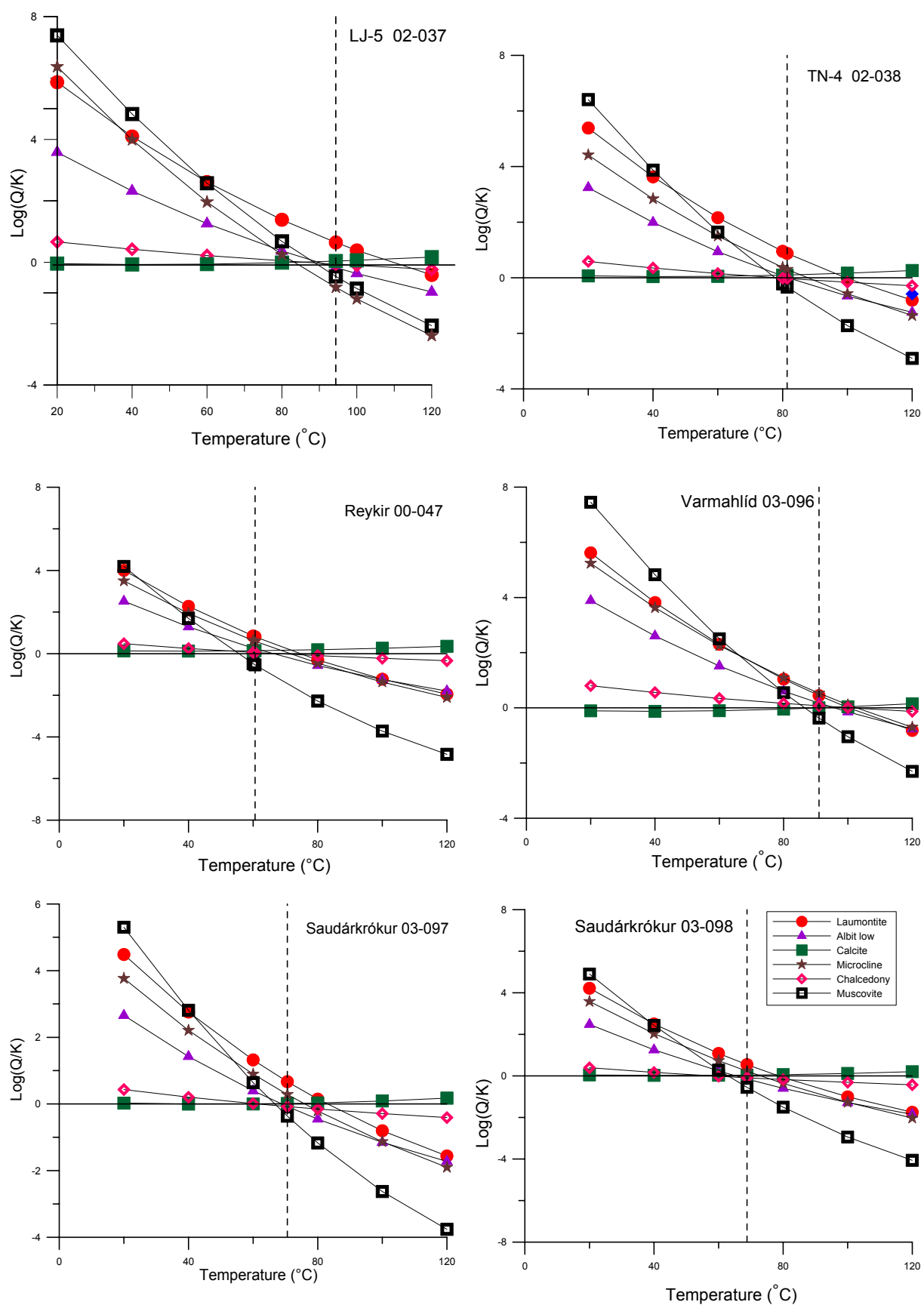


FIGURE 8 Continued: Saturation index diagram ( $\log Q/K$ ) vs. temperature for the 14 wells from the Tröllaskagi area



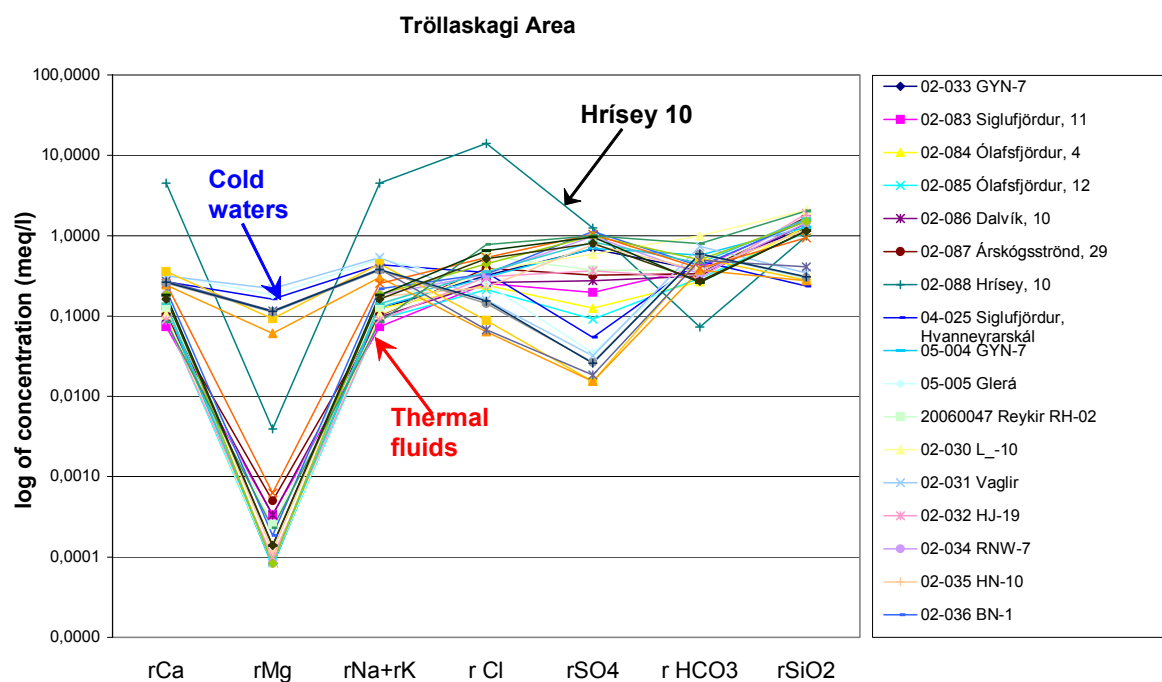


FIGURE 9: Schoeller diagram for the samples from the Tröllaskagi area

The silica-enthalpy mixing model was applied to the samples from the study area (Figure 10). Here, it is assumed that no steam loss occurred before mixing, and also that chalcedony controls the solubility of silica in the hot water component. The temperatures estimated are in the range of 50-143°C and the model also suggests the absence of mixing.

Cl is a conservative component in geothermal fluids. The concentration of Cl increases continually during progressive rock dissolution. Figure 11 shows the Cl concentration in relation to some other constituents. The data in Figure 11 do not seem to indicate mixing.

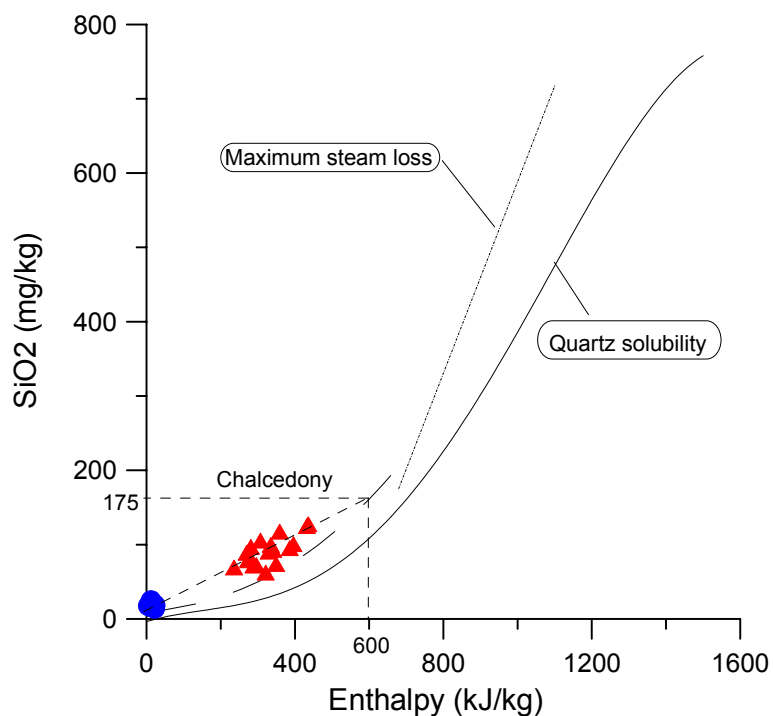


FIGURE 10: Silica-enthalpy mixing model

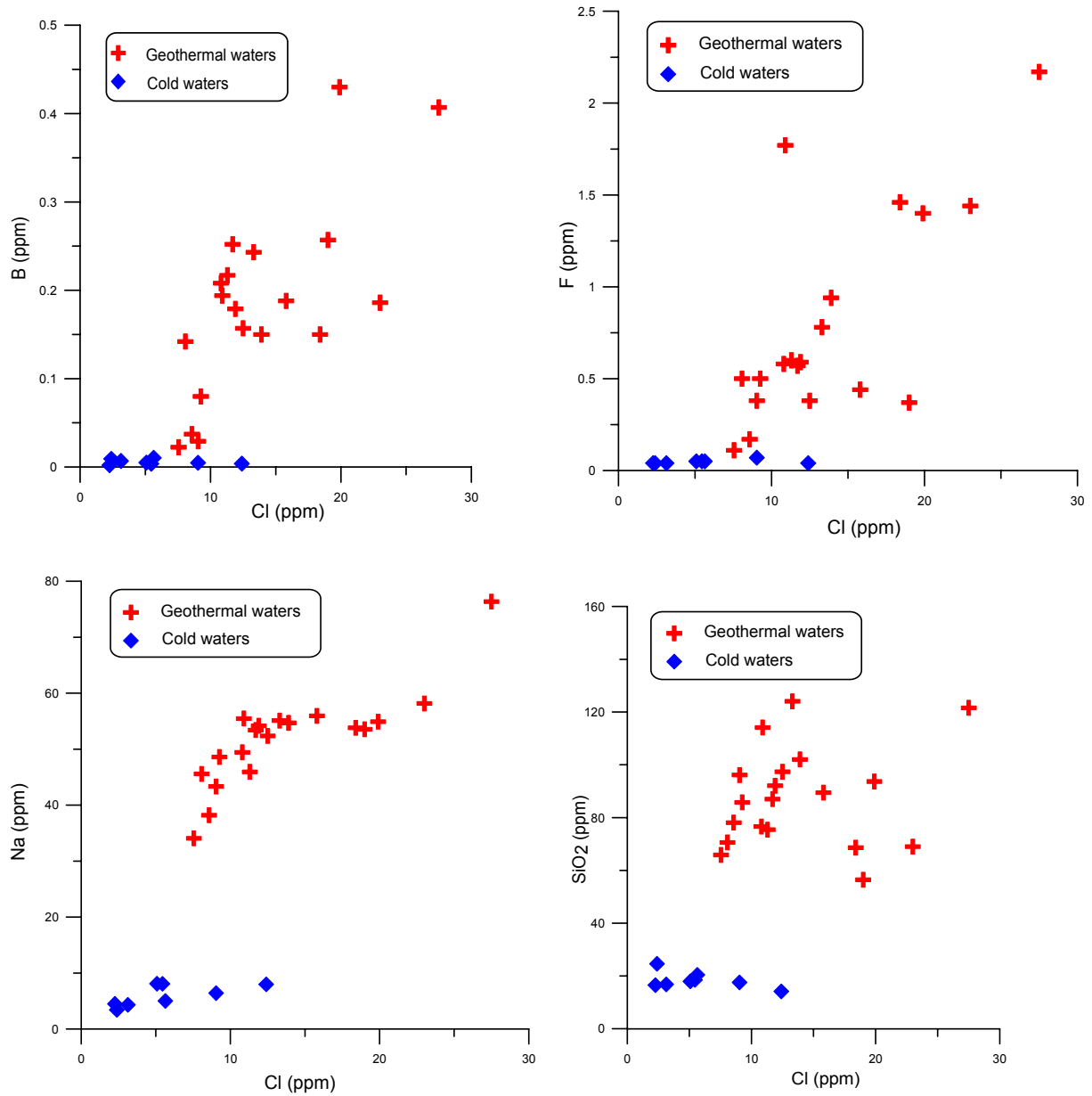


FIGURE 11: Relationship between Cl and some other constituents

## 5. ISOTOPIC COMPOSITION OF NATURAL WATERS

### 5.1 Background

Isotopes have become an essential part of studies of major geothermal development. Their use and interpretation are strengthened if complemented and combined with chemical techniques. Isotopes have been found useful at various stages in geothermal exploration and development.

Geothermal fluids originate mainly from meteoric water (Craig, 1963). Metamorphic and magmatic sources of water in geothermal systems have also been suggested. Craig (1961) observed that the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in precipitation are linearly related by:

$$\delta D = 8 \delta^{18}O + 10 \quad (15)$$

$\delta D$  and  $\delta^{18}O$  represent:

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \quad (16)$$

where  $R$  = The isotopic ratio (e.g.  $D/H$  or  $^{18}O/^{16}O$ ) of the sample or the standard.

The standard that has been used for measuring  $\delta$ -values for the isotopes of oxygen and hydrogen is the Standard Mean Ocean Water (SMOW). By definition, SMOW has  $\delta^{18}O = 0$  and  $\delta D = 0$ . The line defined by Equation 15 is termed the “World Meteoric Water Line” (WMWL) or “Global Meteoric Water Line” (GMWL), and it is based on precipitation data from locations around the globe. The relationship provides a useful reference for geothermal studies in helping to identify recharge areas of geothermal systems. Local meteoric waters in different parts of the world can, however, have different isotopic signatures. The slope and intercept of any “Local Meteoric Water Line” can be significantly different from the “Global Meteoric Water Line”.

An important aspect of geothermal investigations is to determine the recharge to the geothermal systems. Craig (1963) established the isotopic characteristics ( $\delta^2H$ ) and ( $\delta^{18}O$ ) of precipitation relating to latitude and altitude as well as to continental effects. Samples from higher latitudes and elevation or those collected further inland were progressively lighter (more negative isotopic values). This is due to preferential removal of the heavier isotopes from the precipitating clouds as demonstrated in Figure 12.

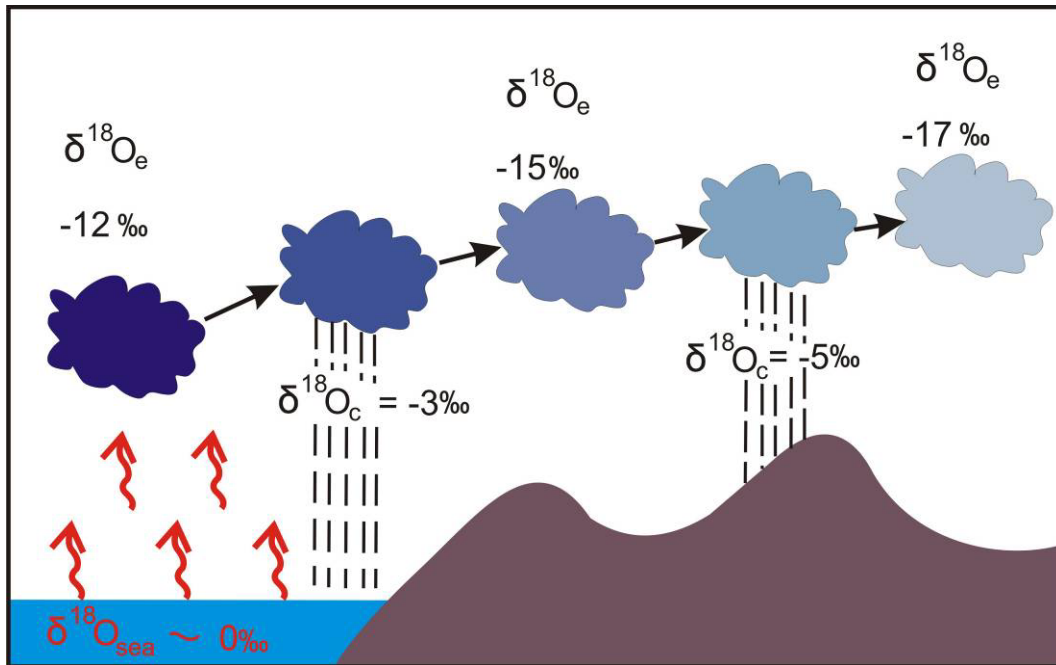


FIGURE 12: Changes in the content of  $\delta^{18}O$  in air moisture and precipitation that forms when the moisture condensates stepwise as it travels inland (Siegenthaler, 1979)

Figure 13 shows a detailed map of the deuterium content of the mean annual precipitation in Iceland, as estimated from local springs and streams (Árnason, 1976; 1977). It shows well how the deuterium values generally decrease from the coastal areas inland due to the combined effects of altitude and distance from the coast (source). The map has been used extensively to trace the origin of groundwater, including geothermal water. From investigations of stable isotopes in ice cores from

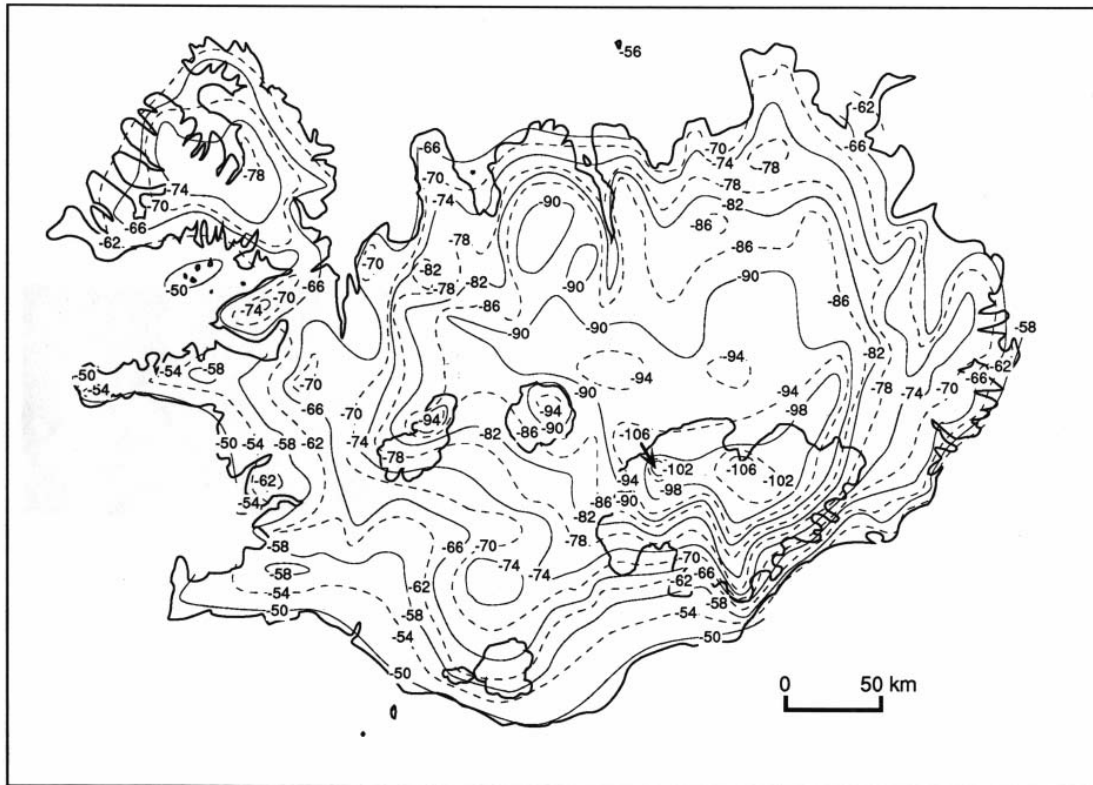


FIGURE 13: Map showing the distribution of deuterium in precipitation in Iceland (Árnason 1976)

Greenland it is possible to conclude that the isotopic content of the precipitation at any particular locality has not changed much during the last 8,000 years. However during glacial time the isotopic composition of precipitation was much lighter due to the cold climate. As groundwater can originate from different climate regimes, the deuterium map of the present day precipitation should be used with care to obtain information on the recharge areas to geothermal systems.

Since 1986 extensive oxygen and hydrogen isotope analyses have been carried out on natural waters in Iceland and the relationship between the isotope ratios studied. A new  $\delta^{18}\text{O}$  -  $\delta\text{D}$  relationship of Icelandic cold groundwater has been defined,  $\delta\text{D} = 6.5 \times \delta^{18}\text{O} - 3.5$  when  $\delta^{18}\text{O}$  is  $\geq -10.5\text{‰}$  ( $\delta\text{D} \geq -76\text{‰}$ ) and as  $\delta\text{D} = 8 \times \delta^{18}\text{O} + 11$  for lighter precipitation (Sveinbjörnsdóttir et al., 1995).

Craig et al. (1956) showed that waters in many geothermal fields possess stable isotope content similar to that of the local precipitation, thus indicating that meteoric water is the dominant source of supply of most geothermal waters. In other geothermal systems, as in almost all of the Icelandic ones, the isotopic content of the geothermal waters is somewhat lower (more negative) than that of the local precipitation. However, the  $\delta^{18}\text{O}$ -  $\delta\text{D}$  relationship of these waters indicates that they are of meteoric origin. The difference between the isotopic values of the geothermal waters and those of the local precipitation was considered by Árnason (1976) to indicate that the recharge areas to the geothermal systems lie farther inland at a higher elevation.

There are some subsurface processes which can change the original isotopic characteristics of geothermal waters. Isotopic exchange at high temperature between the water and the rock minerals can lead to an increase in the  $^{18}\text{O}$  content of the water and a subsequent decrease in the  $^{18}\text{O}$  content of the rock. This causes the "oxygen isotope shift" in the  $\delta\text{D}$ - $\delta^{18}\text{O}$  diagram, towards less negative values of  $\delta^{18}\text{O}$  (Ellis and Mahon, 1977). Reaction of rocks with seawater or reservoir water at low to intermediate temperatures can cause a less common shift of  $\delta^{18}\text{O}$  away from the meteoric water line towards more negative values (Nicholson, 1993) (Figure 14).

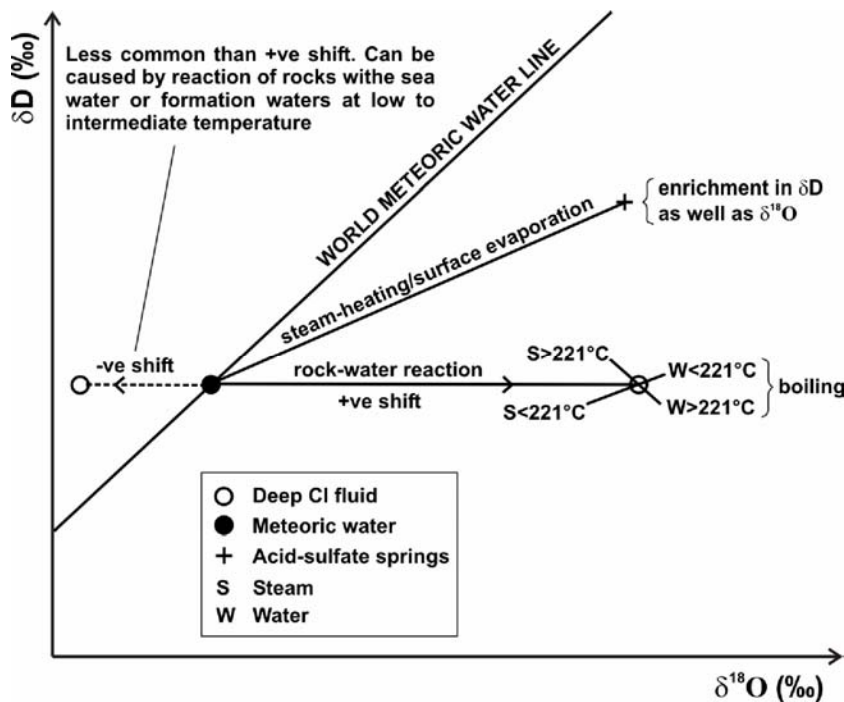


FIGURE 14: Schematic trends in isotopic signatures of meteoric water and geothermal fluids with active processes (from Nicholson, 1993)

Generally, no corresponding shift is seen in the  $\delta D$  value, because there is little hydrogen in the rocks. However, in systems where a large proportion of clay and micaceous minerals occur in the rock, some exchange of deuterium with hydrous minerals does happen, making possible a slight “deuterium shift” (Ellis and Mahon, 1977). Mixing with meteoric water can change the isotopic composition of geothermal fluids. The  $^{18}O$  and D isotopes can provide an indication of boiling as well as mixing processes in the geothermal system. They are also useful in reservoir monitoring during exploitation.

Data on permeability and temperature in deep wells in several low-temperature geothermal systems in Iceland indicate that these systems are transient and represent groundwater convection in young fractures (Björnsson, 1980; Bödvarsson, 1982; Arnórsson and Gíslason, 1990; Björnsson et al., 1990). Thus, the heat source to the system is local and the hot rock is made permeable by active fracturing. This contradicts the old model of the low-temperature geothermal systems (Einarsson, 1942; Árnason, 1976) which suggests that the systems withdraw water from a deep groundwater current driven by the hydraulic gradient from the highlands towards the coasts.

## 5.2 Analytical methods

In this study 140 cold surface and spring water samples and 40 geothermal water samples were selected in N-Iceland. All the sampling and analyses were carried out by the Science Institute, University of Iceland. Stable isotope analyses for oxygen and hydrogen were analysed on a Finnegan MAT 251 mass spectrometer at the Science Institute, University of Iceland. The results are defined in the conventional  $\delta$  notation in ‰, relative to the standard VSMOW for oxygen and hydrogen.

Oxygen was extracted from the water by equilibrating 5 ml of degassed water with a small amount of  $CO_2$  gas in a sealed tube for 3 hours, in a shaking water bath at  $20.0^\circ C$  (Epstein and Mayeda, 1953). The measurements were subsequently corrected for the  $CO_2$  gas which was also used as a secondary reference standard. Hydrogen was extracted from the water by a variant of the method by Coleman et al. (1982). Degassed water 2  $\mu l$  was reduced with 15 mg of zinc metal in a sealed quartz tube at about  $450^\circ C$  for ten minutes. The zinc pellets were then heated up to  $700^\circ C$  in order to transfer the rest of the zinc to the walls of the sample tubes by evaporation and condensation. Then the samples were kept at  $450^\circ C$  for 20 minutes. Since 1998, hydrogen has been extracted from water by the same principles as oxygen, where 2 ml of degassed water is equilibrated with a small amount of  $H_2$  gas in a shaking water bath at  $20^\circ C$ . Pt catalyst is used to enhance the isotopic exchange between the  $H_2$ -gas and the water sample (Horita, 1988). The accuracy of the measurements, at the 95% confidence level, is 0.04‰ for  $\delta^{18}O$  and 1.0‰ for  $\delta D$ .



### 5.3 Results

In this study, isotopic results of 140 cold surface and spring water samples and 40 thermal water samples have been compiled (Appendix I). The sample locations are shown in Figure 15. All surface waters were collected from springs, rivers and streams ranging in temperature from 1.1 to 18.8°C, whereas the geothermal waters were collected from wells. Their temperatures ranged from 26 to 104.1°C.

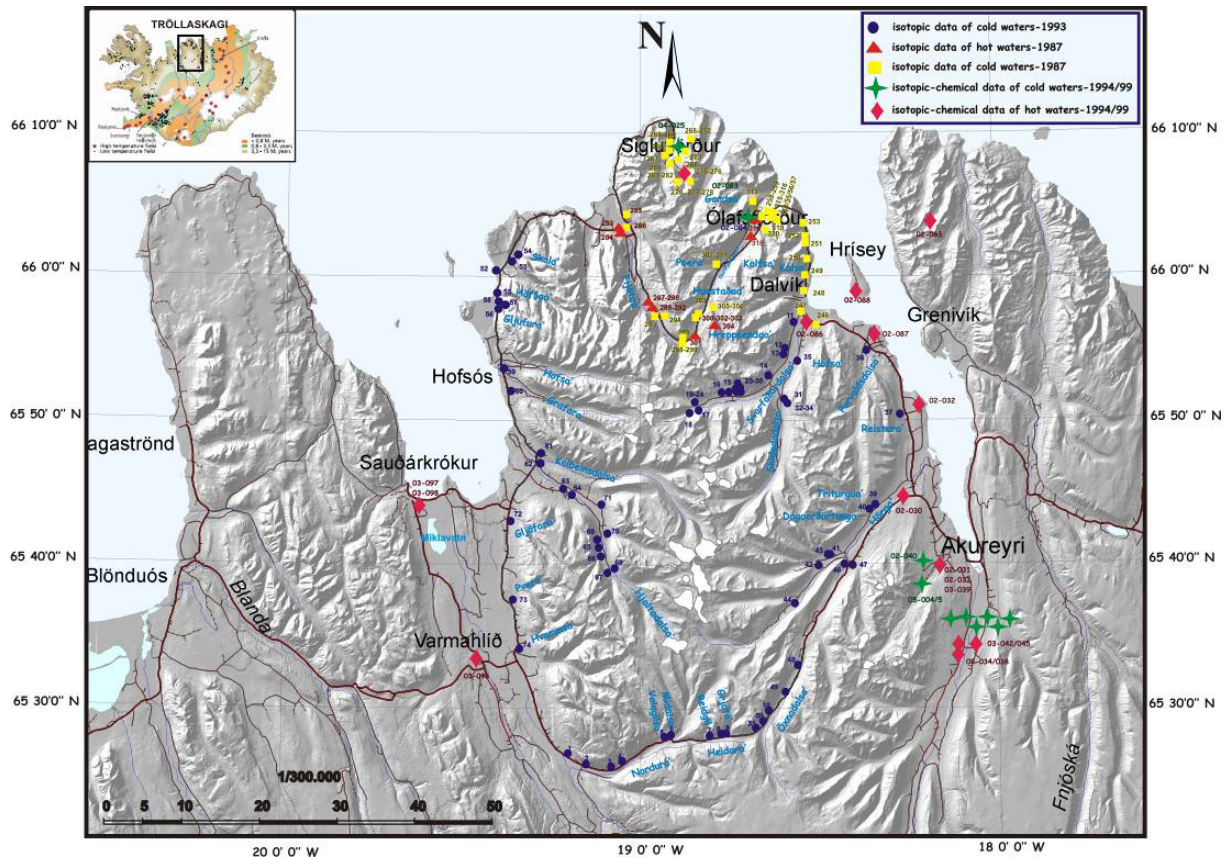


FIGURE 15: Map of the Tröllaskagi area showing chemical and isotopic samples locations

#### 5.3.1 Cold water

The results for the cold surface water samples were plotted on a map using the ArcGIS program. Figure 16 shows the  $\delta^{18}\text{O}$  contour map drawn to determine the origin and movement of the fluids of the Tröllaskagi area.

Figure 16 is based on 140 surface samples, which are thought to represent the isotopic value of the local mean annual precipitation. The map shows well how the surface waters generally become depleted in  $^{18}\text{O}$  with distance from the northern coast. As shown in the figure the most enriched  $^{18}\text{O}$  sample has a  $\delta^{18}\text{O}$  value of -7.7 ‰, and the most depleted value is -13.6‰ found in the mountainous area in the southern part of Tröllaskagi. This range is due to the combined effects of altitude and distance from the coast. The  $\delta\text{D}$  isotopes show the same pattern and range from -53‰ to -99‰.

Figure 17 shows the  $\delta^{18}\text{O}$ -  $\delta\text{D}$  relationship of the natural cold waters within the studied area. It demonstrates that the cold waters follow the two meteoric water lines that have been defined for Iceland (Sveinbjörnsdóttir et al., 1995).

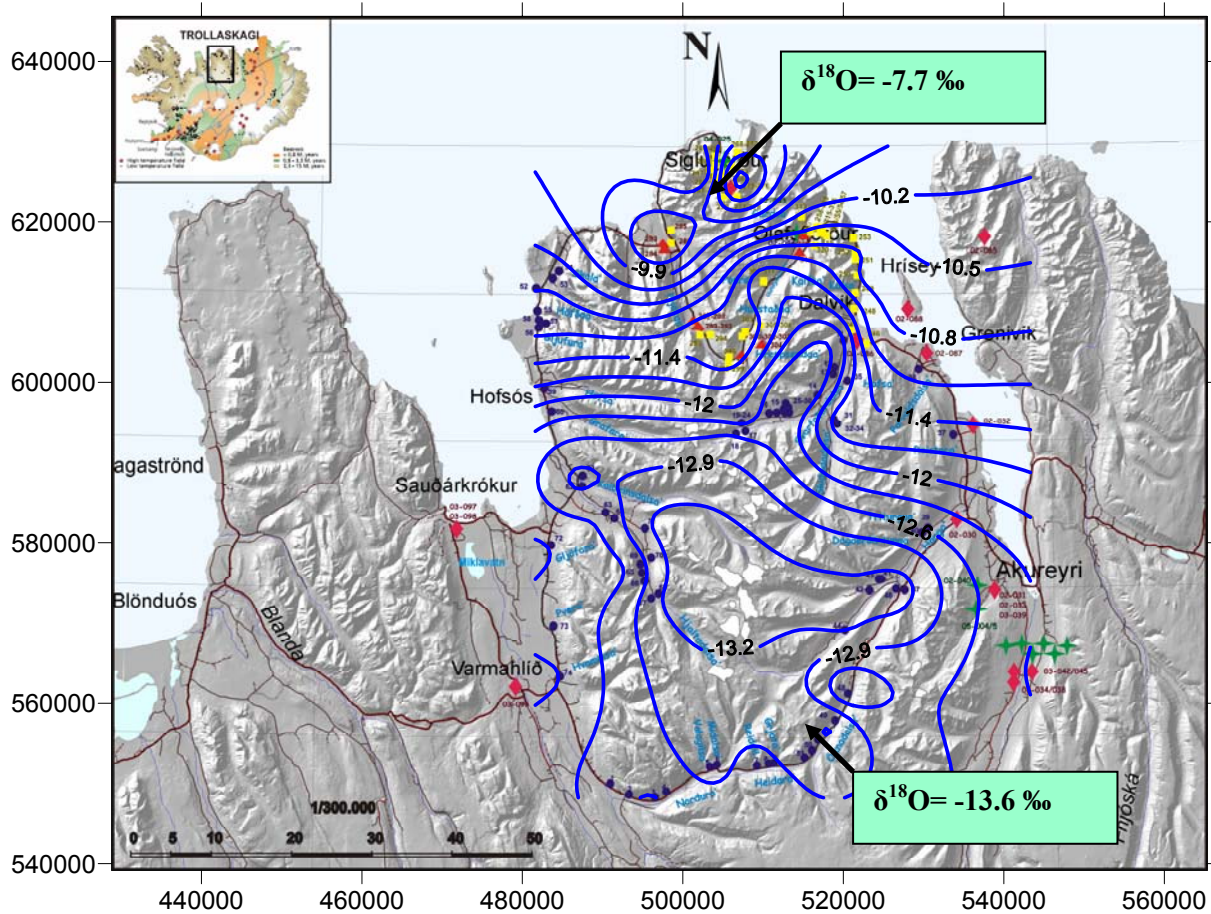


FIGURE 16: Map showing the distribution of  $\delta^{18}\text{O}$  in surface waters in the studied area

### 5.3.2 The thermal water

The hot water samples were collected in several places within the peninsula of Tröllaskagi and also from thermal areas both west (Varmahlíð and Saudárkrókur), east (Hrísey) and south (Akureyri) of the peninsula, as shown in Figure 15. The isotopic values of the thermal waters are very distinct for each area as also seen in Figure 17, where the relation between  $\delta^{18}\text{O}$ - $\delta\text{D}$  is shown. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the geothermal waters within the Tröllaskagi area are generally lower (more negative) than the local cold springs and surface waters. Figure 17 shows that the isotopic values of the thermal water in the Siglufjörður and Ólafsfjörður areas do not differ from the cold water in Tröllaskagi, although they are more depleted than the local precipitation in the respective areas. The average difference between the isotopic composition of the thermal water and local precipitation is about 2‰ in oxygen and about 16‰ in deuterium. The isotopic values for the thermal water in Dalvík ( $\delta^{18}\text{O} = -14.9\text{‰}$ ,  $\delta\text{D} = -104\text{‰}$ ), Árskógaströnd ( $\delta^{18}\text{O} = -14.95\text{‰}$ ,  $\delta\text{D} = -109\text{‰}$ ), HJ-19 ( $\delta^{18}\text{O} = -14.17\text{‰}$ ,  $\delta\text{D} = -101\text{‰}$ ) and L-10 ( $\delta^{18}\text{O} = -13.99\text{‰}$ ,  $\delta\text{D} = -101.1\text{‰}$ ) are more depleted than any surface water in the peninsula of Tröllaskagi (Figure 17).

The samples from Akureyri and Saudárkrókur are similar in their isotopic composition, with  $\delta^{18}\text{O}$  around -13‰ and  $\delta\text{D}$  around -100‰. These samples were also considerably lighter than the local precipitation. The thermal water in Hrísey ( $\delta^{18}\text{O} = -14.85\text{‰}$ ,  $\delta\text{D} = -109.2\text{‰}$ ) was the most depleted in the area together with the sample from Árskógsströnd and in fact they were more depleted than any precipitation on Iceland today.

The thermal water in Varmahlid was considerably more depleted in deuterium than the thermal water in Saudárkrókur, which is situated only about 40 km north of Varmahlid. Their oxygen isotopic values were, however, quite similar, as an oxygen shift of about 1,0 ‰ was observed for the thermal water in Varmahlid (Figure 17). Oxygen shift was not observed for any of the other thermal waters within the studied area despite the fact that some of the waters had similar temperatures as the Varmahlid waters (around 90°C) and some were even warmer (up to 104°C).

Figure 18 shows the relationship between the isotopic values and the water temperature. It demonstrates that the isotopic values for each thermal area was relatively constant despite considerable range in temperature. We see for example in Siglufjörður that the temperature ranged from 20 to about 70°C, whereas the  $\delta^{18}\text{O}$  was consistently around -13‰.

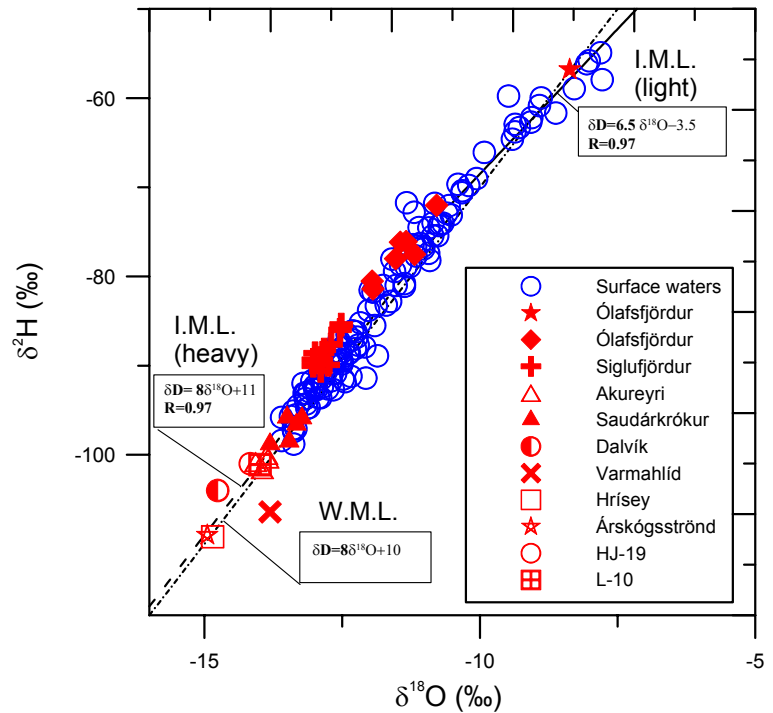


FIGURE 17: The relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in cold and geothermal waters in the Tröllaskagi area

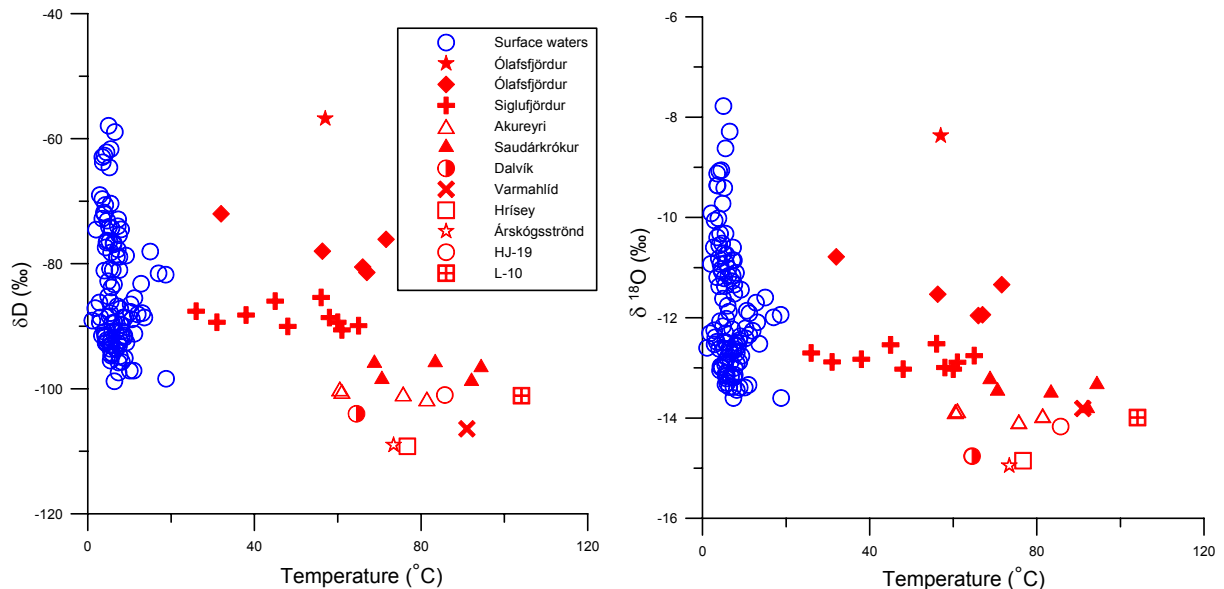


FIGURE 18: Relationship between the isotopic values and the water temperature

#### 5.4 The origin of the thermal waters

Based on the isotopic results the origin of the thermal water in the Siglufjörður area can be traced up to the mountainous areas in the southern part of Tröllaskagi, where present day precipitation has similar isotopic values as the thermal waters. With the same method, the origin of the thermal water in Ólafsfjörður can be traced to the mountainous areas southwest of Dalvík as indicated by the red arrows on Figure 19.



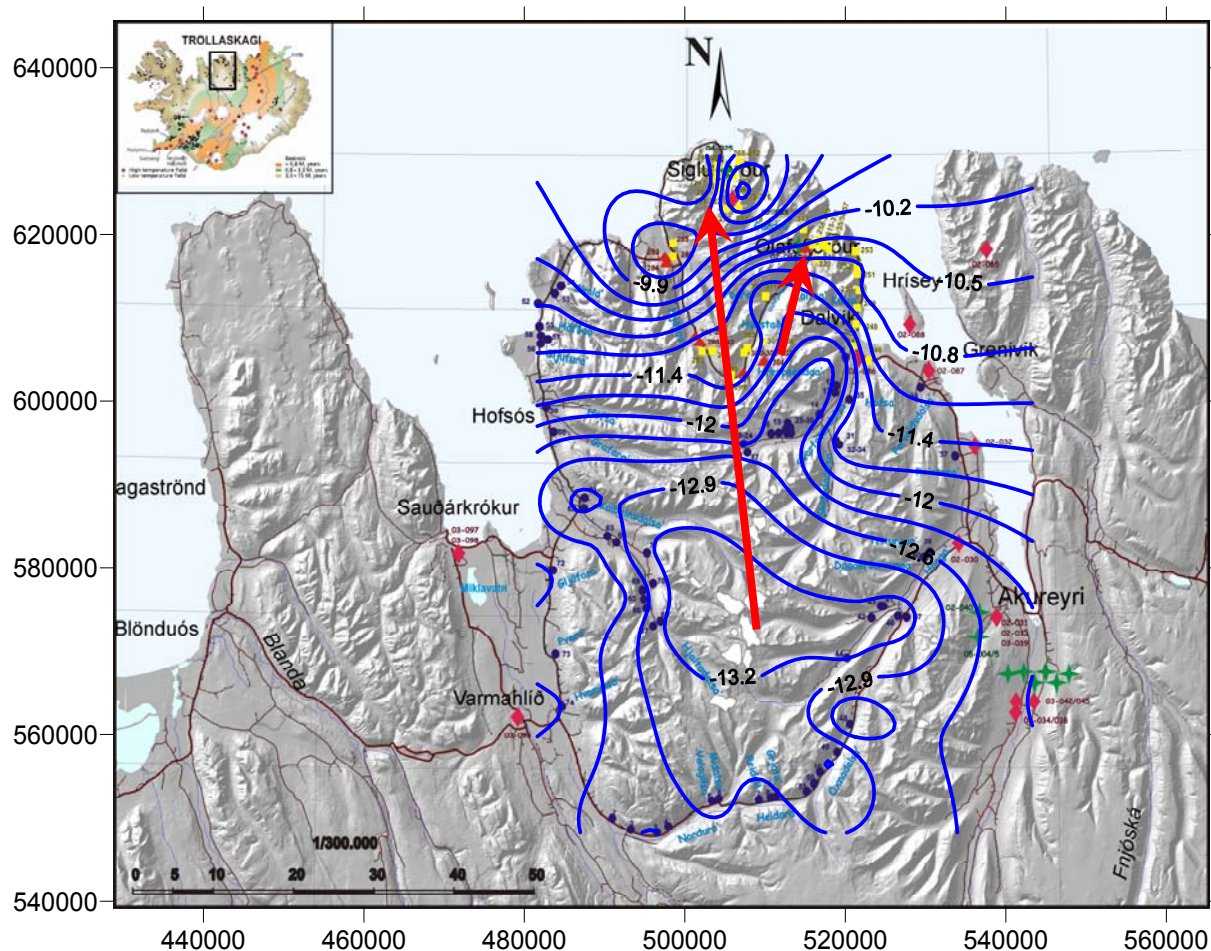


FIGURE 19: Subsurface flow of water from recharge areas to geothermal fields

The isotopic composition of the thermal water in Dalvík is more depleted than any of the present surface water in Tröllaskagi and, therefore, its origin cannot be traced to any place within the peninsula. The same holds for the samples from the western edge of the Tröllaskagi peninsula between Dalvík and Akureyri (Árskógsströnd L-10 and HJ-19).

The isotopic composition of the thermal waters in Dalvík, Árskógsströnd and of the island of Hrísey show very depleted samples. The most possible explanation is that they contain a small component of groundwater of a pre-Holocene age, from the last glaciation, when the precipitation was more depleted due to the cold climate at that time. This may also be true for the sample from well HJ-19. Earlier studies have shown that the thermal water in Skagafjörður (Varmahlíð) has a component of a pre-Holocene water (Sveinbjörnsdóttir et al., 2001).

The thermal water in the Akureyri area to the southeast of the Tröllaskagi peninsula is considerably more depleted than the local precipitation, the difference being about 1.2‰ in oxygen and about 10‰ in deuterium. It is suggested that the origin of the thermal water is in the interior highlands south of the area, where precipitation has similar isotopic values as the thermal water.

## 6. CONCLUSIONS

The following are the main conclusions of this study:

- The waters in the Tröllaskagi area can be classified as cold groundwaters, volcanic waters and a combination of the two, with the exception of Hrisey which plots close to mature waters. The ternary plots also suggest that all the waters originate from old systems.
- Most of the geothermal waters seem to have equilibrated with respect to specific minerals.
- The subsurface prediction using the chalcedony geothermometer, with correction for dissociated silicic acid (Fournier, 1977). is in the range 42-103°C. The temperatures obtained from chalcedony geothermometers and log  $Q/K$  are very close to the measured temperatures which are then interpreted as the reservoir temperatures. A temperature range 50-120°C is inferred from the chalcedony mixing model. The model also suggests the absence of mixing which is consistent with the binary plots. The Schoeller diagram also suggests the absence of mixing except for Hrisey waters, which seem to be mixed with sea water.
- The stable isotopes  $\delta^{18}\text{O}$  and  $\delta\text{D}$  were used in the study area to trace and determine the origin and movement of groundwater. The thermal waters in the Tröllaskagi area are more depleted than the local precipitation and in some cases more depleted than any precipitation on Iceland today.
- The isotopic values for the thermal waters found within the Tröllaskagi peninsula suggest different origins for the different sites. It is possible, based on isotopes, to trace the origin of the thermal waters in Siglufjörður and Ólafsfjörður to the mountainous areas south of the thermal sites. The isotopic composition of the thermal waters in Dalvík and within the thermal areas located on the western edge of the Tröllaskagi peninsula between Dalvík and Akureyri (i.e. Árskógsströnd, L-10 and HJ-19) show more depleted samples than any of the present surface waters in Tröllaskagi and therefore their origin cannot be traced to any place within the Tröllaskagi peninsula.
- The thermal water in the island of Hrisey just west of Dalvík is more depleted than any precipitation in Iceland today and therefore probably has an old water component from the last glaciation, when precipitation was more depleted than today due to the cold climate. This is also the most likely explanation for the depleted waters in Dalvík and Árskógsströnd, south of Dalvík. Recharge into convecting geothermal systems may be of water of variable age and with different  $\delta\text{D}$  values. When there is a component of "ice age water" present, the resulting geothermal water will be both isotopically light and sometimes relatively saline, due to the influx of seawater into the bedrock of flat lying coastal areas which were submerged around the end of the last glaciation.
- Earlier studies have shown that the thermal water in Skagafjörður has a component of a pre-Holocene water. The oxygen shift observed for the Varmahlíð water, which reflects extensive water-rock interaction, is consistent with the presence an "old" water component in this water.

## ACKNOWLEDGMENTS

I am deeply grateful to the United Nations University and the Government of Iceland for having awarded me the opportunity of attending the Geothermal Training Programme. I would like to especially express my gratitude to Dr. Ingvar B. Fridleifsson, Director of UNU-GTP, for selecting me for this very special programme. My deepest thanks go also to Mr. Lúdvík S. Georgsson, Deputy Director of the UNU-GTP, for his helpful guidance, and Mrs Guðrún Bjarnadóttir and Miss Thórhildur Ísberg for their efficient help and kindness during the whole training. And I would like to thank Dr. Suzan Pasvanoğlu for recommending that I attend this course.

My special regards go also to my supervisor, Dr. Árný Erla Sveinbjörnsdóttir. It has been an honour to be under her guidance and to share her experience and knowledge during the realization of the

project. I am grateful to Dr. Halldór Ármannsson for his kind and critical comments. I also express my appreciation to Mrs. Guðrún S. Jónsdóttir for her help in ArcGIS applications, and to all the lecturers and staff members at Orkustofnun and ISOR-Iceland Geosurvey, for their comprehensive presentations and willingness to share their knowledge and experience.

I also thank the UNU fellows of 2006 and, especially, my flatmates Wang Wei and Irada Ibahimova for their unforgettable friendship. Thanks also go to my colleagues from the Department of Geology, Kocaeli University. I owe special thanks to Prof. Dr. Selçuk Tokel for his help and support.

Finally, my deepest thanks go to my family and friends for their moral support during the six month absence.

## REFERENCES

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

Árnason, B., 1977: Hydrothermal systems in Iceland traced by deuterium. *Geothermics*, 5, 125-151.

Arnórsson, S., 1991: Geochemistry and geothermal resources in Iceland, In: D'Amore, F. (co-ordinator), *Applications of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 145-196.

Arnórsson, S., 2000: Mineral saturation. In: Arnórsson, S. (ed.), *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 241- 266.

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 Gislason, S., 1990: On the origin of low-temperature geothermal activity in Iceland (in Icelandic with an English summary). *Náttúrufræðingurinn*, 60, 39-56.

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

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

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

Björnsson, A., Axelsson, G., and Flóvenz, Ó.G., 1990: The nature of hot spring systems in Iceland. *Náttúrufræðingurinn*, 60-1, (in Icelandic with English summary), 15-38.

Björnsson, S., 1980: Heat, groundwater and geothermal systems (in Icelandic with an English summary). *Náttúrufræðingurinn*, 50, 271-293.

Bödvarsson, G., 1982: Glaciation and geothermal processes. *Jökull*, 32, 21-28.

Bödvarsson, G., and Pálmason, G., 1961: Exploration of subsurface temperatures in Iceland. *Jökull*,

11, 39-48.

Coleman, M.L., Shepard, T.J., Durham, J.J., Rouse, J.E., and Moore, G.R., 1982: Reduction of water with zinc for hydrogen isotope determination. *Anal. Chem.*, 54, 993-995.

Connolly, A., Walther, L., Baadsgaard, H., and Longstaff, F., 1990: Origin evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Applied Geochemistry*, 5, 397-413.

Craig, H., 1961: Isotope variations in meteoric water. *Science* 153, 10702-10703.

Craig, H., 1963: The isotopic geochemistry of water and carbon in geothermal areas. In: Tongiorgi, E. (ed.), *Nuclear geology on geothermal areas*. Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, 17-53.

Craig, H., Boato, G., and White, D.E., 1956: Isotope geochemistry of thermal waters. In: *Proceedings of the 2<sup>nd</sup> Conference on Nuclear Processes in Geologic Settings*, National Academy of Sciences-National Research Council, paper 400, 29-38.

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.

Einarsson, T., 1942: Über das Wesen der heissen Quellen Islands mit einer Übersicht die Tektonik des mittleren Nord-Islands. *Soc. Sci. Islandica*, 26, 91 pp.

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

Epstein, S. and Mayeda, T.K., 1953: Variation of  $^{18}\text{O}$  content of waters from natural sources. *Geochim. Cosmochim. Acta*, 4, 213-224.

Fleming, B.A., and Crerar, D.A., 1982: Silicic acid ionization and calculation of silica solubility at elevated temperature and pH. *Geothermics*, 11, 15-29.

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

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.

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

Gíslason, S.R., Heaney, P.J., Oelkers, E.H., and Schott, J. 1997: Kinetic and thermodynamic properties of moganite, a novel silica polymorph. *Geochim. Cosmochim. Acta*, 61, 1193-1204.

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

Hjartarson, A., Fridleifsson, G., and Hafstad, Th.H., 1998: *Bedrock in the Skagafjörður valleys and tunnel locations*. Orkustofnun, Reykjavík, report OS-97020, 55 pp.

Horita, J., 1988: Hydrogen isotope analysis of natural waters using an H<sub>2</sub>-water equilibration method: A special indication to brines. *Chemical Geology (Isotope Geoscience Section)*, 72, 89-94.

Indridason, H.D., 2002: *Geology of the Siglufjörður area*. Univ. of Iceland, Reykjavík, unpubl. M.Sc. thesis.

Jóhannesson, H., 1991: The mountains west of Eyjafjörður, In: *The Icelandic Tourist Association yearbook 1991* (in Icelandic). The Icelandic Tourist Association, Reykjavík, 246 pp.

Keenan, J.H., Keyes, F.G. Hill, P.G. and Moore, J.G., 1969: *Steam tables. Thermodynamic properties of water, including vapour, liquid and solid phases* (international edition - metric units). John Wiley and Sons, NY, 162 pp.

Kristmannsdóttir, H., and Johnsen, S., 1982: Chemistry and stable isotope composition of geothermal waters in the Eyjafjörður region, North Iceland. *Jökull*, 32, 83-90.

Neuhoff, P.S., Fridriksson, Th., Arnórsson, S., and Bird, D.K., 1999: Porosity, evolution and mineral paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, eastern Iceland. *Am. J. Sci.*, 299, 467-501.

Nicholson, K., 1993: *Geothermal fluids: chemistry and exploration techniques*. Springer-Verlag, Berlin, 268 pp.

Reed, M.H., and Spycher, N.F., 1984: Calculation of pH and mineral equilibria in hydrothermal water with application to geothermometry and studies of boiling and dilution. *Geochim. Cosmochim. Acta*, 48, 1479-1490.

Saemundsson, K., 1980: Application of geology in geothermal research in Iceland (in Icelandic with English summary). *Náttúrufræðingurinn*, 50/3-4, 157-188.

Saemundsson, K., and Fridleifsson, I. B., 1980: Geothermal energy and geothermal investigations (in Icelandic with an English summary). *Náttúrufræðingurinn* 50, 157-188.

Saemundsson K., Kristjánsson L., McDougall L., and Walkins N.D., 1980: K-Ar dating, geological and paleomagnetic study of a 5 km lava succession in Northern Iceland. *J. Geophys. Res.*, 85, 3628-3646.

Siegenthaler, U., 1979: In: Jager, and Hunziker, J.C. (editors), *Lectures in isotope geology*. Springer-Verlag, 264-273.

Sveinbjörnsdóttir, Á.E., Arnórsson, S., and Heinemeier, J., 2001: Isotopic and chemical characteristics of old "ice age" groundwater in North Iceland. *Proceedings of the 10<sup>th</sup> International Symposium on Water-Rock Interaction, Balkema*, 205-208.

Sveinbjörnsdóttir, Á.E., Johnsen, S.J., 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*, 1043-1048.

Truesdell, A.H., 1991: Effects of physical processes on geothermal fluids. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 71-92.

Walker, G.P.L., 1960: Zeolite zones and dyke distribution in relation to the structure of the basalts of eastern Iceland. *J. Geol.*, 68, 515-528.

**APPENDIX I:  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  concentrations of samples from Tröllaskagi**

Date	Sample no.	Temperature (°C)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
09-Sep-87	246		-10.853	
09-Sep-87	247		-11.359	
09-Sep-87	248		-11.33	-71.73
09-Sep-87	249		-10.767	
09-Sep-87	250		-10.599	
09-Sep-87	251		-11.215	
09-Sep-87	252		-10.621	
09-Sep-87	253		-10.499	
09-Sep-87	255		-9.905	
09-Sep-87	256		-10.552	
09-Sep-87	257		-10.565	
09-Sep-87	258		-10.56	
09-Sep-87	259	2.7	-10.595	
09-Sep-87	260	2.1	-9.918	
09-Sep-87	261		-9.846	
09-Sep-87	262		-9.752	
09-Sep-87	263	4.8	-9.723	
09-Sep-87	264		-9.874	
09-Sep-87	265	3.8	-10.017	
10-Sep-87	266		-8.06	-56.14
10-Sep-87	267	2.9	-10.06	-69.02
10-Sep-87	268	3.5	-9.124	-63.01
10-Sep-87	269	3.5	-9.359	-62.94
10-Sep-87	270	4	-9.075	-62.69
10-Sep-87	271		-8.918	-60.83
10-Sep-87	272		-9.284	-63.3
10-Sep-87	273	4.5	-9.058	-62.18
10-Sep-87	274		-4.101	-32.75
10-Sep-87	275	5	-7.779	-57.93
10-Sep-87	276		-7.809	-54.91
10-Sep-87	277		-8.014	-55.81
10-Sep-87	278	5.5	-8.622	-61.67
10-Sep-87	279	3.6	-9.362	-63.78
10-Sep-87	280	6.5	-8.287	-58.93
11-Sep-87	281		-9.92	-66.08
11-Sep-87	282		-11.445	-76.16
11-Sep-87	283	65	-12.755	-89.91
11-Sep-87	284	56	-12.518	-85.39
11-Sep-87	285		-9.48	-59.76
11-Sep-87	286		-8.887	-59.97
11-Sep-87	287	60	-13.025	-89.34
11-Sep-87	288	38	-12.826	-88.2
11-Sep-87	289	48	-13.025	-90.01
11-Sep-87	290	26	-12.702	-87.6
11-Sep-87	291	58	-12.991	-88.61
11-Sep-87	292	61	-12.888	-90.59
11-Sep-87	293		-11.185	-77.52
11-Sep-87	294		-11.548	-79.44
11-Sep-87	295		-10.672	-74.02
11-Sep-87	296	2	-10.926	-74.55
11-Sep-87	297	5.1	-10.714	-74.12
11-Sep-87	298		-11.36	-76.82
11-Sep-87	299	5.2	-11.214	-76.44
11-Sep-87	300		-10.766	-75.43
11-Sep-87	301	31	-12.88	-89.35
11-Sep-87	302	7.5	-10.856	-75.44
11-Sep-87	303	6.2	-11.167	-76.63
11-Sep-87	304	45	-12.54	-85.98

Date	Sample no.	Temperature (°C)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
11-Sep-87	305	6.2	-11.02	-76.9
11-Sep-87	306	3.5	-11.193	-76.23
11-Sep-87	307	15	-11.597	-78.05
11-Sep-87	308	17	-11.992	-81.53
11-Sep-87	309	18.7	-11.941	-81.75
11-Sep-87	310	5.7	-10.742	-74.29
11-Sep-87	311	8	-11.104	-74.51
12-Sep-87	87-312	32	-10.785	-72.02
12-Sep-87	313	5.5	-10.323	-70.39
12-Sep-87	314		-10.202	-69.79
12-Sep-87	315	3.5	-10.397	-69.66
12-Sep-87	316	4.2	-10.325	-70.61
12-Sep-87	317	66	-11.956	-80.53
12-Sep-87	318	57	-8.37	-56.79
12-Sep-87	319	4	-10.557	-72.05
12-Sep-87	320	3.9	-10.82	-71.8
24-Aug-93	01	9.3	-12.76	-92.6
24-Aug-93	02	7.4	-12.66	-92.7
24-Aug-93	03	8.8	-12.45	-91.8
24-Aug-93	04	8.2	-12.7	-91.7
24-Aug-93	05	7.7	-13	-92.3
24-Aug-93	06	7.7	-13.14	-94.8
24-Aug-93	07	8.5	-12.56	-88.6
24-Aug-93	08	8.8	-12.88	-91.5
24-Aug-93	09	5.4	-12.93	-93.6
24-Aug-93	10	5.7	-13.1	-92.9
25-Aug-93	11	6.4	-12.62	-89.5
25-Aug-93	12	10.3	-12.41	-86.5
25-Aug-93	13	12	-12.26	-88.1
25-Aug-93	14	6.4	-12.64	-89.4
25-Aug-93	15	5.4	-12.48	-87.9
25-Aug-93	16	5.5	-12.31	-86.1
25-Aug-93	17	5.2	-12.62	-88.4
25-Aug-93	18	4.6	-12.98	-92.2
25-Aug-93	19	12.8	-11.7	-83.2
25-Aug-93	20	5.7	-12.02	-83.8
25-Aug-93	21	11.2	-11.91	-85.5
25-Aug-93	22	7.2	-11.16	-77.7
25-Aug-93	23	1.8	-12.31	-87.1
25-Aug-93	24	11.2	-12.34	-91.2
25-Aug-93	25	4.2	-12.07	-91.4
25-Aug-93	26	5.5	-12.86	-92.4
25-Aug-93	27	6.7	-12.68	-90.9
25-Aug-93	28	7.9	-12.63	-89.8
25-Aug-93	29	6.7	-12.89	-93.6
25-Aug-93	30	13.1	-12.09	-87.9
25-Aug-93	31	7.6	-11.52	-81
25-Aug-93	32	9.2	-11.44	-78.7
25-Aug-93	33	7	-11.27	-78.9
25-Aug-93	34	7.6	-11.34	-78.9
25-Aug-93	35	6	-11.76	-81
25-Aug-93	36	7.8	-12.56	-87.2
25-Aug-93	37	6.3	-11.88	-83.3
25-Aug-93	38	13.6	-12.52	-88.6
25-Aug-93	39	7.5	-13.19	-93.1
25-Aug-93	40	8.2	-13.44	-95.7
25-Aug-93	41	11	-13.34	-97.1
25-Aug-93	42	6.8	-13.17	-93.7
25-Aug-93	43	5.8	-13.15	-94.3
25-Aug-93	44	7.4	-13.38	-97.4

Date	Sample no.	Temperature (°C)	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)
25-Aug-93	45	8.9	-13.39	-95.1
25-Aug-93	46	10.1	-13.39	-97.1
25-Aug-93	47	6.4	-13.38	-98.8
25-Aug-93	48	10.6	-11.86	-88.9
25-Aug-93	49	7.4	-13.6	-95.8
25-Aug-93	50	5.7	-13.21	-92
25-Aug-93	51	8.2	-12.91	-90.8
26-Aug-93	52	7.3	-10.6	-72.9
26-Aug-93	53	4.3	-10.93	-77.4
26-Aug-93	54	4.7	-10.52	-73.1
26-Aug-93	55	4.6	-11.08	-76.3
26-Aug-93	56	5.6	-10.91	-78.2
26-Aug-93	57	4.5	-11.03	-76.6
26-Aug-93	58	7.2	-10.85	-74
26-Aug-93	59	4.9	-11.62	-82.8
26-Aug-93	60	4.9	-12.17	-85.2
26-Aug-93	61	4.5	-13	-92.6
26-Aug-93	62	5.6	-13.1	-94.7
26-Aug-93	63	5.8	-12.5	-89.5
26-Aug-93	64	5.9	-12.8	-90.8
26-Aug-93	65	4.3	-12.97	-92.7
26-Aug-93	66	3.4	-12.48	-91.5
26-Aug-93	67	4.2	-13.05	-91.7
26-Aug-93	68	5.5	-13.33	-95.5
26-Aug-93	69	9	-12.37	-88.6
26-Aug-93	70	5.6	-13.16	-93.1
26-Aug-93	71	5.9	-13.3	-94.5
26-Aug-93	72	7.1	-12.23	-86.8
26-Aug-93	73	8.2	-12.5	-89.8
26-Aug-93	74	10.3	-12.21	-87.7
03-Dec-98	02-033	60.5	-13.87	-100.0
14-Nov-98	02-083	71.6	-11.34	-76.1
14-Nov-98	02-084	67.0	-11.94	-81.4
14-Nov-98	02-085	56.3	-11.53	-78.0
15-Nov-98	02-086	64.5	-14.76	-104.0
15-Nov-98	02-087	73.4	-14.95	-109.0
15-Nov-98	02-088	76.7	-14.85	-109.2
12-Mar-98	02-030	104.1	-13.99	-101.1
12-Mar-98	02-031	4.0	-12.62	-90.9
12-Mar-98	02-032	85.7	-14.17	-101
12-Apr-98	02-034	75.7	-14.07	-100.8
12-Apr-98	02-035	83.4	-13.5	-95.8
12-Apr-98	02-036	92.1	-13.81	-98.8
12-May-98	02-037	94.4	-13.33	-96.6
12-May-98	02-038	81.4	-13.95	-101.6
12-Jun-98	02-039	3.1	-12.39	-88.6
12-Jun-98	02-040	2.9	-12.53	-89.4
05-May-99	03-042	18.8	-13.6	-98.4
23-Jun-99	03-043	2.8	-12.25	-86.2
23-Jun-99	03-044	4.0	-11.37	-81.1
23-Jun-99	03-045	5.4	-11.37	-80.8
10-Nov-99	03-096	91.0	-13.81	-106.4
10-Nov-99	03-097	70.6	-13.46	-98.5
10-Nov-99	03-098	68.8	-13.23	-95.9
23-Sep-04	04-025	5.2	-9.41	-64.6
01-Mar-05	05-004	61	-13.85	-100.4
02-Mar-05	05-005	1.1	-12.60	-89.1