



## **GEOCHEMICAL INTERPRETATION OF THERMAL FLUIDS FROM LOW-TEMPERATURE WELLS IN STYKKISHÓLMUR, W-ICELAND AND PYRZYCE, NW-POLAND**

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### **ABSTRACT**

The low-temperature geothermal waters that feed the district heating systems in Stykkishólmur, W-Iceland, and Pyrzyce, NW-Poland, are found in very different geological environments, namely volcanic and sedimentary rocks, respectively. The geothermal water from the production well in Stykkishólmur differs significantly from other low-temperature waters in Iceland. In particular, its Cl/B ratio is very high, 30,000; while this ratio is 4,350 for seawater and about 100 for typical low-temperature waters in Iceland. The Stykkishólmur water has a very high concentration of calcium, almost 1200 mg/l. The isotopic composition is also unusual for geothermal waters in Iceland. The hot water from Pyrzyce is a brine with mineralization above 120 g/l. This is a typical value for waters occurring in the Polish Lowland. The results from geothermometry equations indicate that chalcedony controls the silica concentration in the reservoir in Stykkishólmur, while quartz controls dissolved silica in Pyrzyce, where the reservoir is a long-lived system. Most of the Na-K equations give a calculated temperature significantly different from the measured temperature. Chemical equilibrium calculations for geothermal water from the production well in Stykkishólmur were performed with the speciation programs SOLVEQ, WATCH, and PHREEQCI. They show the distribution of aqueous species in the water, as well as saturation indices for minerals occurring in the reservoir. Graphs of  $\log(Q/K)$  vs. temperature indicate that some alteration minerals found in the well are close to equilibrium with the water at the measured temperature. Chalcedony and anhydrite, in particular, seem to be in full equilibrium. The PHRQPITZ program was used for geothermal water from the production well in Pyrzyce. This software is based on the Pitzer model, which is appropriate for waters with high ionic strength. Parallel chemical equilibrium calculations performed with SOLVEQ, WATCH, PHREEQCI, and PHRQPITZ do not give widely varying results for the saturation indices of selected minerals. Thus, it appears that programs written for dilute solutions may be used, with limitations, for fairly high ionic strength waters.

## 1. INTRODUCTION

The application of geochemistry to the development of geothermal energy is well known and widely described. The interpretation of the chemical composition of geothermal fluids should be introduced at an early stage in any program of geothermal exploration and production. Chemical and isotopic analyses of fluid samples often permit one to estimate the subsurface temperature and determine the origin of the water. These samples can also provide warning of potential problems during production, such as scaling and corrosion. Furthermore, they may yield information about fluid-mixing processes. Regular monitoring of the composition of geothermal fluids constitutes an important tool in the assessment of environmental impact.

This report is divided into two parts. The first part (Section 2) covers the methodology of geochemical techniques used during exploration, exploitation, and utilization of low-temperature geothermal systems. The second part (Sections 3 and 4) describes their practical applications to two district heating systems – in Stykkishólmur, W-Iceland, and Pырzyce, NW-Poland.

## 2. METHODOLOGY

### 2.1 Field sampling and chemical analysis

An important task during geothermal exploration and exploitation is to obtain reliable samples of geothermal fluids for chemical and isotopic analysis. For proper evaluation of low-temperature geothermal water, the following information is needed (Ólafsson, 1988):

1. Total analyses of water and gas;
2. Temperature at the wellhead;
3. Pressure or drawdown at the wellhead;
4. Discharge from the well.

The water temperature, pressure or drawdown, discharge, dissolved oxygen, and hydrogen sulphide should be measured at the wellhead. Hot water should be cooled prior to sampling, to approximately room temperature (20-30°C), with a cooling spiral or with some other kind of cooling device. At Orkustofnun (now ISOR), a cooling spiral made of stainless steel tubing, fitted with a special funnel for measuring dissolved oxygen as well, is used (Ólafsson, 1988). When the sampling apparatus has been set up, rinsed with the water to be sampled for 15-20 minutes, and the water cooled to room temperature, collection can begin. All sample containers have to be rinsed thoroughly with the water to be sampled.

First, a gas-sampling bulb is filled with untreated water for measuring pH, hydrogen sulphide (H<sub>2</sub>S), carbonate (CO<sub>2</sub>(total) or HCO<sub>3</sub><sup>-</sup>), and ammonia (NH<sub>3</sub>). These determinations are done in the laboratory, and the temperature of the pH measurement is recorded. Next, an untreated sample is collected for silica (SiO<sub>2</sub>) analysis. If the SiO<sub>2</sub> content is expected to be more than 100 mg/l, it is necessary to dilute an aliquot of the sample with distilled water. Ideally, the concentration of silica in the diluted sample should be in the range 30-100 mg/l. If dilution is necessary, three such samples are collected into 100 ml polyethylene bottles and the dilution factor is marked on the bottles. The next step is to collect filtered samples into two 500 ml polyethylene bottles. The water is filtered through a 45 µm filter. One bottle is filled with a filtered, untreated sample for TDS, SO<sub>4</sub>, Cl, and F analyses. Another bottle is filled with filtered water and acidified with 2 ml of concentrated HNO<sub>3</sub> (suprapur) for analysing Na, K, Mg, Ca, Al, B, Fe, and other metals. For waters with high sulphide content, it may be necessary to precipitate the sulphide by adding 2 ml of 0.2M Zn(CH<sub>3</sub>COO)<sub>2</sub> solution to 100 ml of a filtered sample. A gas sample is collected into a gas-sampling bulb for the determination of CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and NH<sub>3</sub>. Samples for isotope analyses are collected and prepared according to instructions by the appropriate isotope laboratory.

All data measured during field sampling as well as laboratory chemical and isotopic analyses should be summarized on a uniform “field-record card” and “laboratory-record card” (Appendix I), respectively. The chemical analyses are usually expressed in mg/l or in ppm.

Before any geochemical interpretation based on the analytical results is attempted, the quality of the analyses should be checked. At ISOR, both an ionic balance and a mass balance are calculated (Appendix I). An analysis with a charge balance of  $\pm 10\%$  is usually considered adequate.

## 2.2 Origin of geothermal waters

### 2.2.1 Isotopic composition of geothermal waters

A very important task in geothermal investigations is to determine the recharge to geothermal systems. The isotopic composition of geothermal waters, in particular the concentration of stable isotopes such as those of hydrogen (D or  $^2\text{H}$ ) and oxygen ( $^{18}\text{O}$ ), is used to trace their origin. Geothermal waters are mostly of meteoric origin (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:

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10 \quad (1)$$

$\delta\text{D}$  and  $\delta^{18}\text{O}$  are obtained from the equation

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (2)$$

where  $R$  stands for the isotopic ratio (e.g.  $\text{D}/^1\text{H}$  or  $^{18}\text{O}/^{16}\text{O}$ ) 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  $\delta^{18}\text{O} = 0$  and  $\delta\text{D} = 0$ . The line defined by Equation 1 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 isotopic characteristics ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of precipitation are related to latitude and continental effects. Thus  $\delta^{18}\text{O}$  and  $\delta\text{D}$  decrease from the tropics to the poles and from coastal to inland areas. There are also seasonal fluctuations as well as an altitude effect – a decrease of  $^{18}\text{O}$  and D concentrations with increasing terrain level. The relationship provides a useful reference for geothermal studies in helping to identify recharge areas of geothermal systems. Local meteoric waters in different geothermal areas can, however, have different isotopic compositions. The slope and intercept of any “Local Meteoric Water Line” can be significantly different from the “Global Meteoric Water Line”.

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 decrease in the  $^{18}\text{O}$  content of the rock. This causes the “oxygen isotope shift” in the  $\delta^{18}\text{O}$ - $\delta\text{D}$  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 1). Generally, no corresponding shift is seen in the  $\delta\text{D}$  value, because there is little hydrogen in the rocks relative to that in the water. However, in systems where a large proportion of clay and micaceous minerals occurs 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  $^{18}\text{O}$  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.

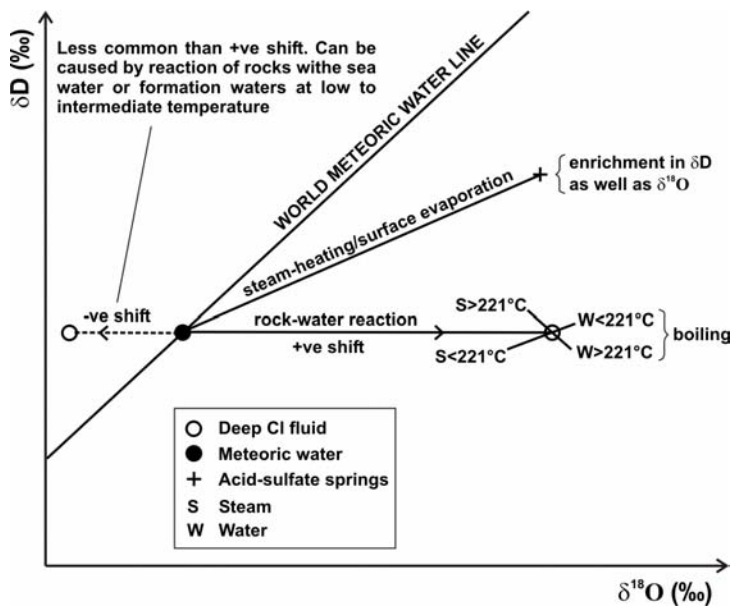


FIGURE 1: Schematic trends in isotopic signatures of meteoric water and geothermal fluids with active processes (from Nicholson, 1993)

## 2.2.2 Cl/B ratio

Chloride and boron are examples of conservative (non-reactive) constituents in geothermal systems (Giggenbach, 1991). Once added to the fluid phase they remain there. Conservative components have not equilibrated in a thermodynamic sense. They are externally fixed, i.e. by their sources of supply to the geothermal fluid. Their contents along the upflow path are changed only by mixing and steam loss. Conservative constituents provide information on the source of the fluid. They have also been termed tracers.

There is a correlation between concentrations of B and Cl in natural waters and associated rocks. The Cl/B molal ratio in natural waters varies from less than 1 to that of seawater

(Arnórsson and Andrésdóttir, 1995). On the whole, it decreases with increasing temperature. The chloride-boron diagram is particularly useful for detecting mixing processes of hot and cold water in the upflow.

## 2.3 Classification of thermal fluids

The Cl-SO<sub>4</sub>-HCO<sub>3</sub> triangular plot is used as an initial classification scheme (anion classification) for geothermal water samples (Giggenbach and Goguel, 1989). In this plot, compositional ranges are indicated for typical groups of thermal waters, such as: “volcanic and steam-heated”, “mature” and “peripheral waters”. It allows one to weed out waters that are not suitable for most ionic solute geothermometers, which “work” only if used with close to neutral waters containing chloride as the major anion (“mature waters”). The compositional area where ionic solute geothermometers may be applied with sufficient confidence is quite small and illustrates the need for this initial classification procedure.

The Cl-SO<sub>4</sub>-HCO<sub>3</sub> diagram allows one to group available samples and evaluate compositional trends.

## 2.4 Geothermometers

### 2.4.1 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):

- Water or solute geothermometers;
- Steam or gas geothermometers;
- Isotope geothermometers.

Water and steam geothermometers are collectively termed chemical geothermometers, and may be either qualitative or quantitative.

The application of quantitative solute geothermometers is based on five basic assumptions (Fournier, 1977):

- Temperature-dependent reactions involving rock and water fix the amount or amounts of dissolved “indicator” constituents in water;
- There is an adequate supply of all reactants;
- There is equilibrium in the reservoir or aquifer with respect to the specific indicator reaction;
- No reequilibration of the “indicator” constituents occurs after the water leaves the reservoir;
- Either no mixing of different waters occurs during movement to the surface or evaluation of the results of such mixing is possible.

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

$$t \text{ } ^\circ\text{C} = \frac{a}{b + \log(K)} - 273 \quad (3)$$

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 ( $K_{\text{SiO}_2}$  for all silica geothermometers,  $K_{\text{Na/K}}$  for all Na-K geothermometers, etc.)

Two methods have been used to calibrate the water geothermometers. One relies on the laboratory measurements of equilibrium constants. The other is based on empirical correlations of measured temperature in drillholes with the concentrations of specific aqueous components in well discharges.

Two main types of water geothermometers are most useful in the exploration of geothermal resources:

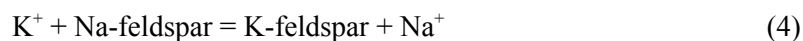
- Silica geothermometers – based on temperature-dependent changes in the solubility of the most common silica minerals;
- Cation geothermometers – based on temperature-dependent exchange reactions, which involve at least two minerals and the aqueous solution, thus fixing the ratios of suitable dissolved constituents.

#### 2.4.2 Silica geothermometers

Solubilities of minerals generally change with temperature and pressure. Pressure and added salt have little effect on the solubilities of quartz and amorphous silica below about 300°C (Fournier, 1989). This allows the dissolved silica concentration in geothermal waters to be used as a chemical geothermometer. Several geothermometry equations have been developed for the different forms of silica, mainly quartz and chalcedony (Appendix II). When calculating temperatures from the silica content of natural water, assuming equilibrium with either quartz or chalcedony, the temperatures are termed quartz equilibrium and chalcedony equilibrium temperatures, respectively. Arnórsson (1983) states that in Iceland, equilibrium with chalcedony seems to be attained up to 180°C, equilibrium with quartz at higher temperatures, but no general rules are specified. In some places (particularly in long-lived geothermal systems), well crystalline quartz may control dissolved silica at temperatures less than 100°C (Fournier, 1989). Which silica mineral constitutes the controlling phase for aqueous silica concentrations depends on the rate of two counteracting processes, dissolution of the primary silicate minerals of the rock, and precipitation of a silica mineral (D'Amore and Arnórsson, 2000). The rate of dissolution of the primary rock minerals is largely controlled by the pH of the water.

### 2.4.3 Cation geothermometers

Cation geothermometers are based on ion exchange reactions that have temperature-dependent equilibrium constants (Appendix II). An exchange reaction between alkali feldspars and  $\text{Na}^+$  and  $\text{K}^+$  in aqueous solution has often been given as an example (Fournier and Truesdell, 1973):



The equilibrium constant for the reaction is:

$$K = \frac{(\text{K-feldspar})(\text{Na}^+)}{(\text{Na-feldspar})(\text{K}^+)} \quad (5)$$

where parentheses denote activities of enclosed species. If pure solid phases are assumed, which by convention have unit activity, and that activity coefficients for Na and K cancel each other, Equation 5 is reduced to:

$$K = \frac{[\text{Na}]}{[\text{K}]} \quad (6)$$

where  $[\text{Na}]$  and  $[\text{K}]$  are the molalities of the respective ions.

There is no universal Na-K geothermometer. Many experimentally derived temperature functions have been presented for the Na-K geothermometers. Most of them work well for the highest temperatures in deeper parts of a system, where waters reside for relatively long periods of time. The Na-K method generally fails to give reliable results for waters from reservoirs with temperatures below 100°C. In particular, low-temperature waters rich in calcium give anomalously high results by this geothermometer (Fournier, 1981). Arnórsson et al. (1983) and Arnórsson (2000) proposed Na-K geothermometers in the range 25–250°C and 0–350°C, respectively.

An equation relating K and Mg concentrations with temperature has only been presented by Giggenbach (1988). Use of the K-Mg method as a geothermometer is limited by its weak temperature dependence and its excessive sensitivity to the addition of non-equilibrated waters, which leads to apparent temperatures of equilibration which are far too low.

Giggenbach (1988) proposed a Na-K-Mg triangular diagram as a graphical technique to evaluate reservoir temperatures, and to assess the degree of attainment of water-rock equilibrium. In this plot, two sets of lines are drawn, one for constant Na/K ratios and another for constant  $\text{K}/\text{Mg}^{0.5}$  ratios. The lines represent these ratios at given temperatures. The ratios are computed from Na-K and K-Mg geothermometers, proposed by Giggenbach (1988). The curve drawn through the points of intersection of equal temperatures for Na/K ratios and  $\text{K}/\text{Mg}^{0.5}$  ratios represents equilibrium for all three ions, Na, K, and Mg. On the basis of the relative abundance of Na, K, and Mg in natural waters, he classified them as “immature”, “partially equilibrated or mixed”, and “fully equilibrated”. The Na-K-Mg diagram allows one to distinguish between waters that are suitable or unsuitable for the application of ionic solute geothermometers. The choice of the Na-K geothermometry equation used for the construction of this diagram considerably affects the estimated subsurface temperature (D’Amore and Arnórsson, 2000).

## 2.5 Mineral-solution equilibria

### 2.5.1 General background

The fundamental criterion for chemical equilibrium in a thermodynamic system is that the total Gibbs free energy be at a minimum. At constant temperature and pressure, the Gibbs free energy change in a chemical reaction is given by:

$$\Delta G = \sum_p \nu_p \mu_p - \sum_r \nu_r \mu_r \quad (7)$$

where  $\mu_p$  and  $\mu_r$  are chemical potentials for the product and reactant species, respectively, and  $\nu_p$  and  $\nu_r$  are the corresponding stoichiometric coefficients. The chemical potentials are given by:

$$\mu_p = \mu_p^o + RT \ln a_p \quad (8)$$

$$\mu_r = \mu_r^o + RT \ln a_r \quad (9)$$

where the superscript  $^o$  indicates the standard state;  
 $R$  = The gas constant;  
 $T$  = The absolute temperature; and  
 $a_p$  and  $a_r$  = The activity of the product and reactant species, respectively.

Substituting, we find that:

$$\Delta G = \sum_p \nu_p [\mu_p^o + RT \ln a_p] - \sum_r \nu_r [\mu_r^o + RT \ln a_r] = \sum_p \nu_p \mu_p^o - \sum_r \nu_r \mu_r^o + RT \sum_p \ln(a_p^{\nu_p}) - RT \sum_r \ln(a_r^{\nu_r}) \quad (10)$$

and

$$\Delta G = \Delta G^o + RT \sum_i \ln(a_i^{\nu_i}) = \Delta G^o + RT \ln \prod_i (a_i^{\nu_i}) \quad (11)$$

where  $\Delta G^o$  is the Standard Gibbs free energy of reaction, and the summation goes over all reactants and products;  $\nu_i$  is positive for products and negative for reactants.

The ion activity product (the reaction quotient) is defined by:

$$Q \equiv \prod_i (a_i^{\nu_i}) = \frac{a_A^{\nu_A} \cdot a_B^{\nu_B} \cdot \dots}{a_M^{\nu_M} \cdot a_N^{\nu_N} \cdot \dots} \quad (12)$$

At equilibrium,  $\Delta G = 0$  and  $Q = K$ , where  $K$  is the equilibrium constant. For a mineral-solute equilibrium, this constant is usually called the solubility product constant. Thus:

$$\Delta G^o = -RT \ln K \quad (13)$$

and

$$\Delta G = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K} \quad (14)$$

For a reaction between an aqueous solution and a mineral, the saturation index is defined as:

$$SI = \log \frac{Q}{K} \quad (15)$$

The saturation index is a measure of departure from equilibrium. It is equal to zero at equilibrium, positive if the solution is supersaturated, and negative if it is undersaturated.

In very dilute solutions, which behave in an almost ideal fashion, the activity of a species is approximately equal to its concentration. In more concentrated solutions, the relationship between activity and concentration is expressed by a proportionality constant, called activity coefficient,  $\gamma$ , thus:

$$\gamma = \frac{a}{m} \quad (16)$$

where  $m$  denotes the molal concentration of a species.

The activity coefficient describes the deviation of an aqueous species concentration from ideality. It can be defined in two ways, either as a mean activity coefficient; or an individual ion activity coefficient. Activity coefficients are currently estimated using either of two types of methods (Bethke, 1996):

- Debye-Hückel equation and variants thereof;
- Virial methods.

The Debye-Hückel equation is given by:

$$\log \gamma_i = -\frac{Az_i^2\sqrt{I}}{1+d_iB\sqrt{I}} \quad (17)$$

where  $A$  and  $B$  = Constants depending on the temperature and the density of the water;  
 $d_i$  = The effective electrostatic radius of ion  $i$  (the effective diameter of the hydrated ion);  
 $z_i$  = Charge of ion  $i$ ; and  
 $I$  = The ionic strength of the solution, which is defined as:

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (18)$$

where  $m_i$  stands for the molal concentration of ion  $i$ .

The Davies equation and the so-called “B-dot” equation are variants of the Debye-Hückel equation. These models are usually limited to an ionic strength of 0.5 molal or less. For solutions with higher ionic strength, virial methods, such as the Pitzer model, are more appropriate. These are based on measured mean activity coefficients.

### 2.5.2 Log (Q/K) diagrams

Using a chemical analysis and a pH measurement made at a known temperature, it is possible to calculate the properties of an aqueous solution, such as speciation and saturation indices, at other temperatures by solving simultaneous mass action and mass balance equations. These calculations provide values of the activities of aqueous ions, which are used to calculate the ion activity product ( $Q$ ) for each mineral from an available database. By computing  $Q$  and the solubility product constant ( $K$ ) over a range of temperatures, log ( $Q/K$ ) diagrams, which show the state of saturation as a function of temperature, are constructed. Reed and Spycher (1984) have proposed that by plotting log ( $Q/K$ ) versus temperature it is possible to determine: 1) whether the water was in equilibrium with a host rock mineral assemblage; 2) probable minerals in the equilibrium assemblage; and 3) the temperature of equilibrium. The numerical value of log ( $Q/K$ ) is greater than zero for supersaturated minerals and less than zero for undersaturated minerals. The equilibrium constants,  $K$ , are both temperature and pressure dependent. However, pressure in the range occurring in geothermal systems (1-200 bars) has a very limited effect compared to temperature. The solubility of minerals is usually strongly dependent on temperature and sometimes varies over a very large range. Therefore, if a group of minerals converges to equilibrium at a particular temperature, this temperature will correspond to the most likely reservoir temperature. Minerals that are taken into account should, of course, occur in the geothermal system under study.



Reed and Spycher (1984) consider their procedure capable of distinguishing between equilibrated geothermal waters and waters that have departed from equilibrium due to boiling or mixing with shallow colder waters.

Aqueous speciation programs, such as WATCH, SOLVEQ, and PHREEQCI, are required to calculate values for the respective mineral saturation indices.

## 2.6 Aqueous speciation calculations

Chemical substances in aqueous solution are found in the form of various atomic and molecular entities known as species. A species may be a simple ion such as  $\text{Na}^+$ , a compound ion, e.g.  $\text{SO}_4^{2-}$ , a complex ion or ion pair such as  $\text{NaSO}_4^-$ , or a neutral molecule, e.g.  $\text{H}_2$ . Species concentrations depend on the chemical component concentrations involved, on temperature, and on the ionic strength of the solution. Chemical analyses of natural waters normally yield only solute component concentrations. Thus, one ordinarily determines only the total concentration of  $\text{SiO}_2$ , Na, Ca, Cl,  $\text{SO}_4$ , and so on. The thermodynamically important quantities, however, are the species concentrations. These are the quantities that enter into calculations of mineral saturation indices, gas partial pressures, redox potentials, and the like. Thus, a central problem in aqueous geochemistry is to compute the concentrations of individual species at some temperature, for given component concentrations. This is normally accomplished by solving a non-linear set of simultaneous equations for species activities and component concentrations. This set of equations consists of a mass balance equation for each chemical component and a mass action equation for each chemical equilibrium. A variety of computer programs have been written for this purpose. Several of these are briefly described below.

The computer program WATCH is mainly intended to serve as a tool for interpreting the chemical composition of geothermal fluids, although it is also useful for non-thermal waters (Arnórsson et al., 1982; Bjarnason, 1994). The program reads chemical analyses of water, gas, and steam condensate samples, collected at the surface, and computes the chemical composition of downhole, or aquifer, fluids. This includes the pH, aqueous speciation, partial pressures of gases, redox potentials, and activity products for mineral dissolution reactions. The mass balance and mass action equations are solved simultaneously by a straightforward iterative procedure. The concentrations of the anions of the weak acids and their complexes are added up, weighted by the number of protons that each can accept, to give the alkalinity sum. This quantity is assumed to be constant for a given sample, independent of temperature. This property is used to compute the pH at the reference temperature. The reference temperature can be chosen in a few ways: as a measured temperature of the well or spring; as chalcedony, quartz, or Na-K chemical geothermometer value; and can also be chosen arbitrarily. The WATCH program can also be used to calculate the composition of the equilibrated sample after cooling or adiabatic boiling from the reference temperature to some lower temperature. This is particularly useful in the study of scaling. The output from the program lists the component and species concentrations, activity coefficients, ionic balance, geothermometer temperatures, partial pressures of gases, as well as redox potentials. Finally, ion activity products and solubility products of selected minerals are also output.

SOLVEQ is a computer program for computing multi-component homogeneous chemical equilibria in aqueous systems (Reed, 1982; Reed and Spycher, 2001). It solves a system of mass balance and mass action equations by the Newton-Raphson numerical technique. For a given temperature and total composition of a homogeneous aqueous solution, SOLVEQ computes the activities of numerous aqueous species, the saturation indices of solids, and gas fugacities. In addition to homogeneous equilibrium (distribution of aqueous species), SOLVEQ also calculates partial heterogeneous equilibrium, wherein equilibration of a given water with specified minerals or gas fugacities can be forced. This capability, combined with SOLVEQ's ability to calculate pH at high temperature from a low-temperature pH measurement (Reed and Spycher, 1984), also makes it useful for processing hydrothermal experimental run products and for geothermometry and other studies of geothermal and oil field waters. SOLVEQ comes with a fairly extensive database of mineral solubilities and aqueous species stability constants. A

companion program to SOLVEQ, called CHILLER, has extensive capabilities for reaction progress calculations, including the titration and precipitation of rock minerals.

PHREEQCI version 2 is a computer program for simulating chemical reactions and transport processes in natural or polluted water (Parkhurst and Appelo, 1999). It is based on the PHREEQE program (Parkhurst et al., 1980), but with additional capabilities. PHREEQCI is designed to perform a wide variety of low-temperature aqueous geochemical calculations. The program is based on an ion-association aqueous model, and has numerous capabilities. First, it handles speciation and saturation-index calculations. Secondly, it can carry out batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, which include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria; and irreversible reactions, which include specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes. Finally, the program allows inverse modelling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits. In PHREEQCI, it is possible to define different temperatures during batch-reaction calculations. The temperature dependence of  $\log K$  is defined either by: 1)  $\Delta H$  and the van't Hoff equation; or 2) by an analytical expression.

All of the three above programs use Debye-Hückel expressions to calculate ion activity coefficients. This type of aqueous model is adequate at low ionic strength but may break down at higher ionic strengths (in the range of seawater and above). The extended Debye-Hückel ("B-dot") equation is considered reasonably accurate in predicting the activities of  $\text{Na}^+$  and  $\text{Cl}^-$  ions to concentrations as large as several molal, and of other species to ionic strengths up to about 0.3 to 1 molal (Bethke, 1996). For high ionic strength waters, the specific interaction approach to thermodynamic properties of aqueous solutions should be used, e.g. the Pitzer equations (Plummer et al., 1988).

The program PHRQPITZ is a computer code, based on the PHREEQE code, capable of making geochemical calculations in brines and other electrolyte solutions to high concentrations using the Pitzer virial-coefficient approach for activity-coefficient corrections (Plummer et al., 1988). Reaction-modeling capabilities include calculations of: 1) aqueous speciation and mineral-saturation indices; 2) mineral solubility; 3) mixing and titration of aqueous solutions; 4) irreversible reactions and mineral-water mass transfer; and 5) reaction path. The computed results for each aqueous solution include the osmotic coefficient, water activity, mineral saturation indices, mean activity coefficients, total activity coefficients, and scale-dependent values of pH, individual-ion activities, and individual-ion activity coefficients. A database of Pitzer interaction parameters is provided at 25°C for the system Na-K-Mg-Ca-H-Cl-SO<sub>4</sub>-OH-HCO<sub>3</sub>-CO<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O, and extended to include largely untested literature data for Fe(II), Mn(II), Sr, Ba, Li, and Br with provision for calculations at temperatures other than 25°C. Geochemical redox reactions may not be attempted in PHRQPITZ. The temperature range for equilibria in the phrqpitz.dat file is variable and is generally from 0 to 60°C; however, the NaCl system is valid to approximately 350°C, and the carbonate system is reliable to about 100°C. The application of this program is somewhat limited, since data for only a few chemical components (those listed above) is available, and most of these data cover only a limited temperature range.

## 2.7 Monitoring of chemical changes during exploitation

The long-term exploitation of geothermal resources causes chemical and physical changes in the reservoir, such as pressure drawdown and cooling. To understand processes occurring in the geothermal system during production, the system must be monitored appropriately. Careful monitoring of the geothermal reservoir is, therefore, a necessary part of any successful management program. The parameters that need to be monitored to quantify the response of a geothermal reservoir to a production load can differ from one geothermal system to another (Kristmannsdóttir et al., 1995), and consequently the methods of monitoring as well as monitoring frequency may differ. The basic aspects that should be included in conventional geothermal monitoring programs are as follows (Axelsson and Gunnlaugsson, 2000):

- Mass discharge history of production wells;
- Enthalpy or temperature of fluid produced;
- Wellhead pressure (water level) of production wells;
- Chemical content of water and steam produced;
- Reservoir pressure (water level) in observation wells;
- Reservoir temperature through temperature logs in observation wells.

Chemical and isotopic monitoring of exploited geothermal reservoirs requires regular sampling of the discharge fluids. More frequent sampling is required for dry and wet steam wells than for hot water wells, and the frequency of sampling is generally highest during the early stages of discharge of each well (Arnórsson and D'Amore, 2000). Changes in the concentrations of selected chemical and isotopic components, both conservative and reactive, may indicate cold water recharge into exploited geothermal reservoirs or recharge of water from a different source. Monitoring of changes in the saturation index with time is important for the evaluation of corrosion and scaling tendencies. Changes in chemistry are often detected before temperature changes are observed. Thus, chemical monitoring may give warning in time for preventive action.

### 3. THE STYKKISHÓLMUR DISTRICT HEATING SYSTEM

#### 3.1 General background

The Stykkishólmur district heating system, or better known in Iceland as the Stykkishólmur hitaveita, is located in the town of Stykkishólmur on the Snaefellsnes peninsula, W-Iceland (Figure 2). The town has a population of approximately 1,500. The Stykkishólmur hitaveita consists of one production well (HO-01), situated some 4.5 km southwest of Stykkishólmur, the main hot-water pipeline, the heat exchangers, and the distribution system within the town. Appendix III shows a schematic layout of the Stykkishólmur hitaveita (Kristmannsdóttir et al., 2002).

Temperature logging in shallow wells showed a geothermal gradient anomaly of up to 400°C/km (Figure 2). Based on this, it was decided to drill a production well. Well HO-01 was drilled from the 7<sup>th</sup> of October to the 29<sup>th</sup> of November 1996. It was drilled with a 12½" drillbit to 157 m, with 9⅞" to 240 m, and with 8½" to 855 m. It is lined with 10" casing to 155 m depth.

The main production aquifers are located at depths of 819 m (90% of the flowrate) and from 171 to 175 m (7% of the flowrate). Minor aquifers are also found, at depths of 262, 451, 778, 785, and 830 m. The aquifer at 171-175 m is a fracture within a basaltic layer, whereas the main aquifer is related to a fracture in a gabbroic intrusion (Figure 3). The temperature log shows the reservoir temperature of 86.4°C (Figure 2).

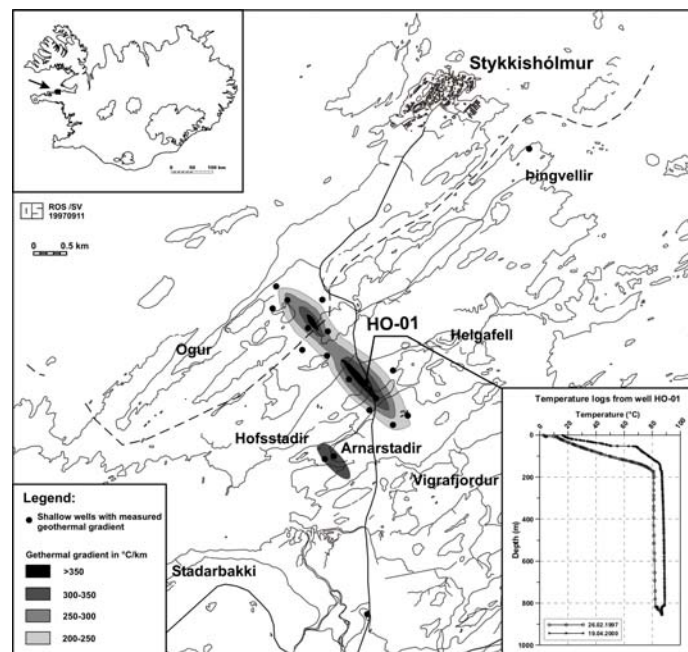


FIGURE 2: Location of Stykkishólmur, W-Iceland; geothermal gradient anomaly according to measurements in shallow drillholes and temperature logs from production well HO-01

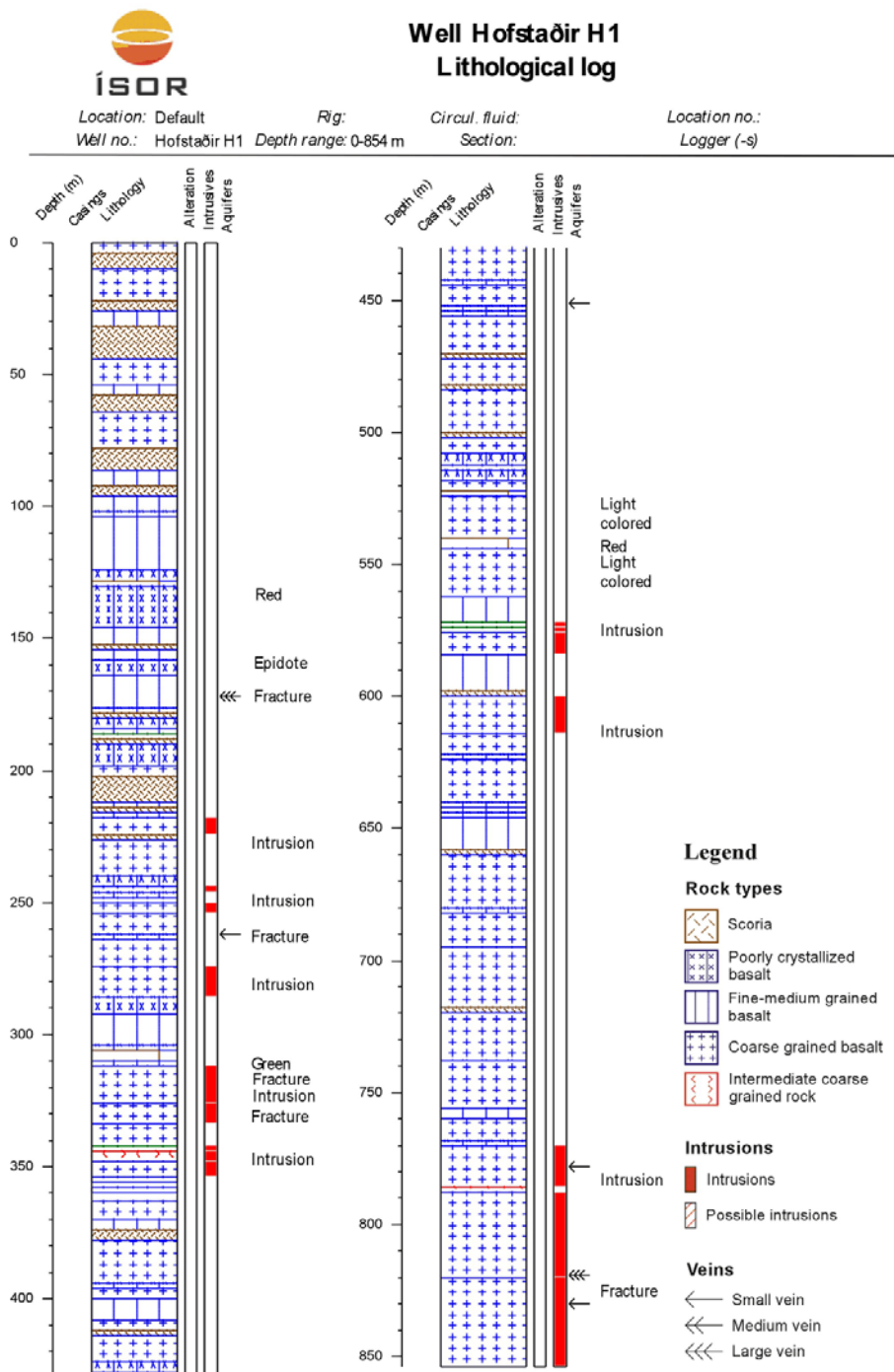


FIGURE 3: Lithological profile of well HO-01 (from Björnsson and Fridleifsson, 1996)

The reservoir rock consists primarily of coarse-grained basaltic units with thin layers of sediments, two of which could be acidic, and a number of mostly basaltic intrusions. From 780 to 855 m depth, i.e. to the bottom of the well, the rock consists of a gabbroic intrusion (Björnsson and Fridleifsson, 1996). Pyrite, mixed layer clays of smectite and chlorite, with chalcedony, quartz, and calcite are found from the surface to 150 m depth. At depths below 150 m, the high-temperature alteration minerals chlorite and epidote are found. Laumontite is found at all depths, and stilbite (with calcite) near the aquifers. The reservoir rock is altered to a high degree with epidote below 150 m depth, indicating an alteration temperature of approximately 250°C, and with amphibole below 300 m depth, which suggests an alteration temperature of ~ 300°C. The high-temperature alteration and intrusions indicate that the well is situated within an extinct central volcano (from

Miocene time, >5 MY). It has been suggested (G.Ó. Fridleifsson, personal communication) that anhydrite might have formed minute grains within the aquifers, but more study of the drill-cuttings is needed to confirm this. This could explain the very high calcium content of the hot water produced from the well. The high degree of alteration of the reservoir rocks indicates much higher temperatures than presently observed. The aquifers in well HO-01 are all associated with fractures, and the last mineral to precipitate in all cases is stilbite.

### 3.2 Chemical and isotope composition of the fluids

Results of the chemical and isotope analyses of hot water samples from the production well in Stykkishólmur are presented in Table 1. These samples were taken in the years 1997–2002 using the standard procedure employed at Orkustofnun or ISOR (Ólafsson, 1988). The chemical and isotopic composition of the hot water from the production well in Stykkishólmur differs from that of other low-temperature areas in Iceland. The low-temperature waters in Iceland, described by Arnórsson (1995), usually are relatively low in dissolved solids (150–500 ppm), and sodium is always the dominant cation. The geothermal water from Stykkishólmur is brackish, with TDS above 5200 ppm, a chloride content of approximately 3000 ppm, and a temperature of 86.4°C. The water is very hard (2942 mg CaCO<sub>3</sub>/l), and weakly alkaline with a pH of 8.34 at 18.6°C. Calcium is the dominant cation (~1200 ppm), and the water type is Cl-Ca-Na.

TABLE 1: Chemical composition of the thermal water from well HO-01 in Stykkishólmur (concentrations in mg/l, except where noted)

Sample no.	1997-0065	1997-0179	1997-0404	1998-0578	1999-0521	2000-0362	2001-0362	2002-0354
Date	97.03.12	97.04.28	97.06.25	98.11.12	99.11.25	00.10.02	01.11.08	02.11.12
Temperature (°C)	86	85.5	87	80.2*	88.2	86.8	86.4	86.2
pH	8.35	8.37	8.45	8.06	8.31	8.4	8.34	8.24
pH temperature (°C)	20.6	21.5	22.7	21.2	23.0	17.0	18.6	22.5
Conductivity (µS/cm)	8990	8960	8940	8860	8640	8750	8770	8230
TDS		5457	4260	5840	6070	5430	5220	5950
CO <sub>2</sub> (total carbonate)	9.42	8.5	9	6.9	3.45	4.43	3.83	3.31
H <sub>2</sub> S (total sulfide)	0.05	0.09	0.07	0.06	0.05	0.7	0.07	0.08
SiO <sub>2</sub>	72.6	71.95	72.9	72.9	72.7	71.7	71.5	71.6
Na	733	733	731	734	716	740	724	717
K	14	14	13.9	14.1	14.1	14.5	13.4	13.6
Ca	1150	1150	1150	1220	1150	1170	1177	1117
Mg	0.45	0.47	0.51	0.51	0.5	0.5	0.51	0.512
Cl	2990	2960	2920	2940	3018	2960	2970	2980
SO <sub>4</sub>	321	318	325	338	327	315	320	326
Sr	6.27	5.92	5.72	5.77				
Mn	0.023	0.022	0.023	0.0164	0.055	0.02	0.0096	
Fe	0.0187	0.0096	0.0099	0.138	0.0076	0.0225	0.0168	
Al	0.0082	0.0072	0.0033	0.006		0.0094	0.014	
Cu	0.0004	0.0003	0.0005					
Zn	0.0031	0.0008	0.0005					
Br	9.87	9.85	9.86	9.61		9.7		10.1
F		1.05	1.07	1.11	1.16	1.23	1.15	1.4
B		0.1	0.11	0.1	0.08	0.11	0.1	0.11
I	0.25	0.25	0.25					
δD (‰SMOW)		-64.8	-65.9	-68.4	-65.5	-68.5	-67.5	-67.1
δ <sup>18</sup> O (‰SMOW)		-11.1	-11.12	-11.08	-11.08	-11.11	-11.06	-11.12
Ionic balance (%)	-1.75	-0.8	0.16	3.3	-3.51	0.66	0	-4.3
Mass balance (%)		-3.52	22.79	-8.62	-12.69	-2.7	1.11	-11.97

\* – very little pumping from well

The δ<sup>18</sup>O-δD relationship in low-temperature geothermal waters in Iceland indicates that they are, for the most part, of meteoric origin (Arnórsson, 1995). Typically, they possess lower δD values (more negative) than the local precipitation. It is also considered that geothermal waters often consist of up to three

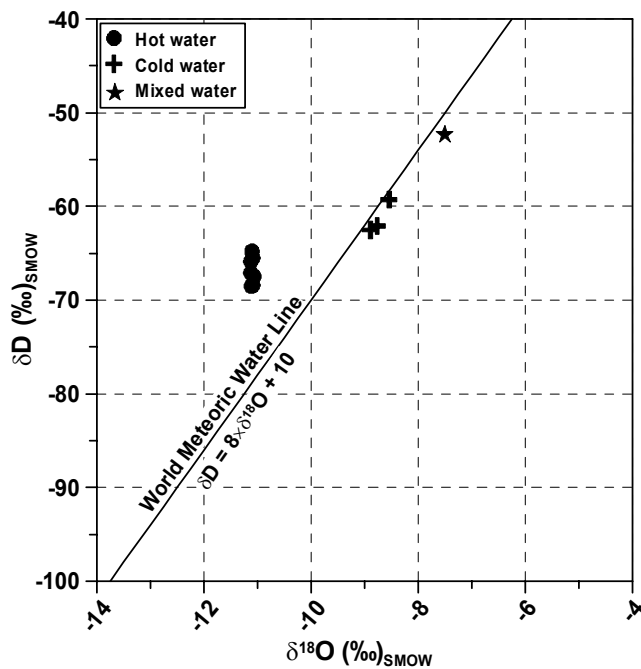


FIGURE 4: The relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in the hot and cold water samples from the study area and in a calculated mixture of seawater and cold water

components, local meteoric water, “ice-age” water, and seawater. Geothermal waters with temperatures of less than  $50^\circ\text{C}$  show very limited oxygen shift, whereas for hotter waters, the shift increases with temperature (Arnórsson et al., 1993).

Figure 4 shows the isotopic composition of hot waters from well HO-01 as well as that of local cold groundwaters. For comparison, the meteoric water line from Craig (1961) is also shown. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for cold waters are close to the World Meteoric Water Line, with a slight shift towards less negative values, while for hot waters the values lie above this line. These values seem to suggest an origin for the hot water different from present-day precipitation.

The Cl concentration of about 3000 ppm suggests that hot water from Stykkishólmur may be a mixture of seawater and freshwater. If it can be assumed that the geothermal water is a mixture of seawater and freshwater, then:

$$[\text{Cl}]_{\text{mixed water}} = X[\text{Cl}]_{\text{seawater}} + (1-X)[\text{Cl}]_{\text{freshwater}} \quad (19)$$

where  $[\text{Cl}]_{\text{mixed water}} = 3000$  ppm (from analysis of the geothermal water);  
 $[\text{Cl}]_{\text{seawater}} = 18,900$  ppm (typical value for waters around Iceland);  
 $[\text{Cl}]_{\text{freshwater}} = 10$  ppm (from analysis of the local cold groundwater).

This gives a seawater fraction,  $X$ , equal to 0.16, and a freshwater fraction,  $1-X$ , equal to 0.84.

In the fresh groundwater, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values are  $-8.9$  and  $-62.5$ , respectively, and in the seawater both are approximately 0. Hence, the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in the geothermal water should be  $-7.5$  and  $-52.5$ , respectively. The observed isotopic composition of the geothermal water is quite different from what was expected (Figure 4). Thus, it appears that the water from the production well in Stykkishólmur cannot be strictly a mixture of present-day freshwater and seawater.

The deuterium excess for the hot waters,  $d$ , defined as  $\delta\text{D} - 8\delta^{18}\text{O}$ , is much higher than expected for present-day precipitation conditions, and amounts to more than 20‰. According to Johnsen et al. (1989), the deuterium excess depends on the moisture at the source of the precipitation. Geothermal water from the production well in Stykkishólmur may be a mixture of seawater and freshwater, both of which entered the bedrock during the deglaciation period, when the climate was colder. The geothermal system in Stykkishólmur lies close to the coast and contains a sizeable seawater component. Arnórsson and Andrésdóttir (1995) consider that low-temperature systems containing water with a significant seawater component could have formed through infiltration of seawater by the end of the deglaciation period, when large parts of the lowlands in Iceland were submerged.

Chloride and boron in Icelandic natural waters act essentially as incompatible (Arnórsson and Andrésdóttir, 1995). Their distribution in low-temperature geothermal systems in Iceland indicates three sources of supply (Arnórsson, 1995): 1) the atmosphere (seawater spray and aerosols); 2) the rock with which the water interacts; and 3) seawater that has infiltrated the bedrock. The Cl/B mass ratios of the cold water are close to that of seawater (4350), or slightly lower. With rising temperature, B and Cl

concentrations increase to 0.05-1 and 10-100 ppm, respectively, and their ratios decrease towards that of the basaltic rock (Figure 5). Arnórsson and Andrésdóttir (1995) explain this relationship by approximately stoichiometric dissolution of Cl and B from the basaltic rock. In case of low-temperature waters containing relatively high concentrations of Cl, they consider mixing of seawater with geothermal meteoric water (Figure 5).

The Cl/B ratio of water from the production well in Stykkishólmur is almost 30,000, so it is about seven times higher than that of seawater. This very high ratio may be caused by boron adsorption onto and incorporation in clay minerals found in the reservoir. This phenomenon was described by Harder (1970) on the basis of experiments.

In the Cl-SO<sub>4</sub>-HCO<sub>3</sub> triangular diagram (Figure 6), data points are located near the Cl corner, close to the area marked “mature waters”.

### 3.3 Estimation of subsurface temperature

Four silica geothermometers, two quartz and two chalcedony, were chosen in this study to estimate subsurface temperatures (Table 2 and Appendix II). The temperatures obtained from chalcedony geothermometers are very close to the measured temperature, 90.8 and 86.4°C, respectively, whereas quartz geothermometers give about 30°C higher temperatures. It appears that the water tends to equilibrate with chalcedony rather than quartz, and that chalcedony controls the silica concentration in the reservoir.

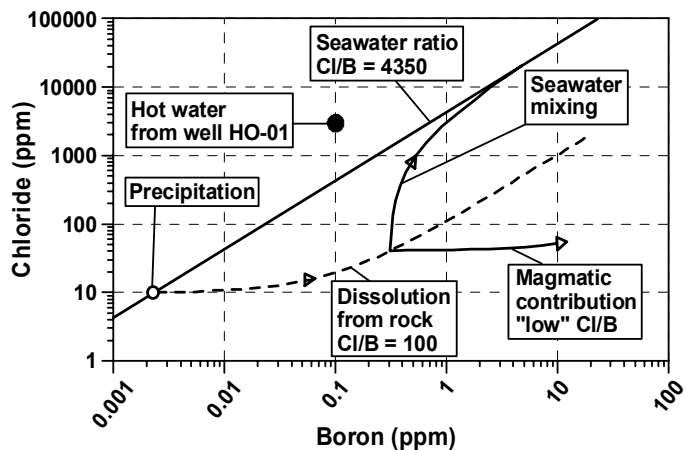


FIGURE 5: Schematic diagram illustrating Cl/B mass ratios and B and Cl concentrations in natural waters in Iceland affected by different processes (from Arnórsson and Andrésdóttir, 1995)

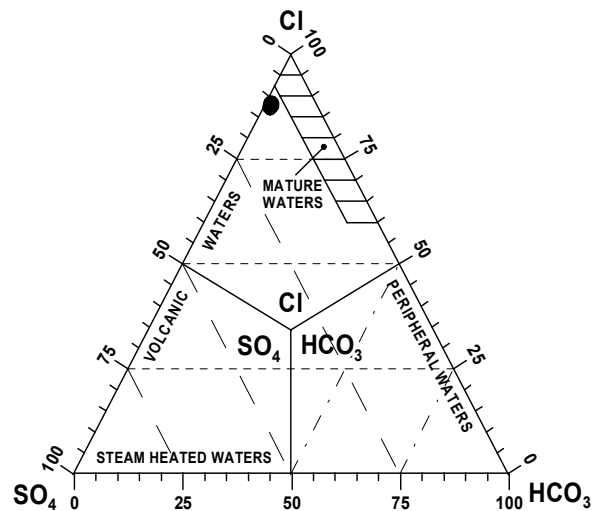


FIGURE 6: The Cl-SO<sub>4</sub>-HCO<sub>3</sub> classification diagram for the hot water from well HO-01 in Stykkishólmur

TABLE 2: Silica geothermometer temperatures for the thermal water from well HO-01 in Stykkishólmur

Geothermometer	T <sub>M</sub>	T <sub>Q1</sub>	T <sub>Q2</sub>	T <sub>Ch1</sub>	T <sub>Ch2</sub>
Range in °C		25-250	25-900	0-250	
T in °C	86.4	119.3	119.5	90.8	90.8

Sources of temperature equations for the silica geothermometers:

- T<sub>M</sub> – measured temperature,
- T<sub>Q1</sub> – Fournier (1977),
- T<sub>Q2</sub> – Fournier and Potter (1982),
- T<sub>Ch1</sub> – Fournier (1977),
- T<sub>Ch2</sub> – Arnórsson et al. (1983)

Na-K geothermometry temperatures range between 69.2 and 126°C, depending on the choice of temperature equation (Table 3 and Appendix II). The value calculated from the equation proposed by Arnórsson (2000), namely 95.7°C, is nearest to the measured temperature. Temperatures calculated using other Na-K equations deviate significantly from the measured temperature, both below as well as above

the expected value. They give unreasonable geothermometry temperatures.

TABLE 3: Cation geothermometer temperatures for the thermal water from well HO-01 in Stykkishólmur

Geothermometer	$T_M$	$T_{Na-K1}$	$T_{Na-K2}$	$T_{Na-K3}$	$T_{Na-K4}$
Range in °C			25-250		0-350
T in °C	86.4	110.7	69.2	126.0	95.7

Sources of temperature equations for the cation geothermometers:

$T_M$  – measured temperature,

$T_{Na-K3}$  – Giggenbach (1988),

$T_{Na-K1}$  – Fournier (1979),

$T_{Na-K4}$  – Arnórsson (2000)

$T_{Na-K2}$  – Arnórsson et al. (1983),

The Na-K-Mg diagram (Figure 7) shows the equilibrium state of the water from the production well. The diagram constructed using Giggenbach's Na-K equation (Figure 7A) shows that water is nearly fully equilibrated, but the temperature is too high. The diagram using Arnórsson's Na-K equation (Figure 7B) is more reliable, as it is constructed on the basis of the Na-K equation giving the temperature closer to the measured value (Table 3). Furthermore, it is derived from interpretation of Icelandic data.

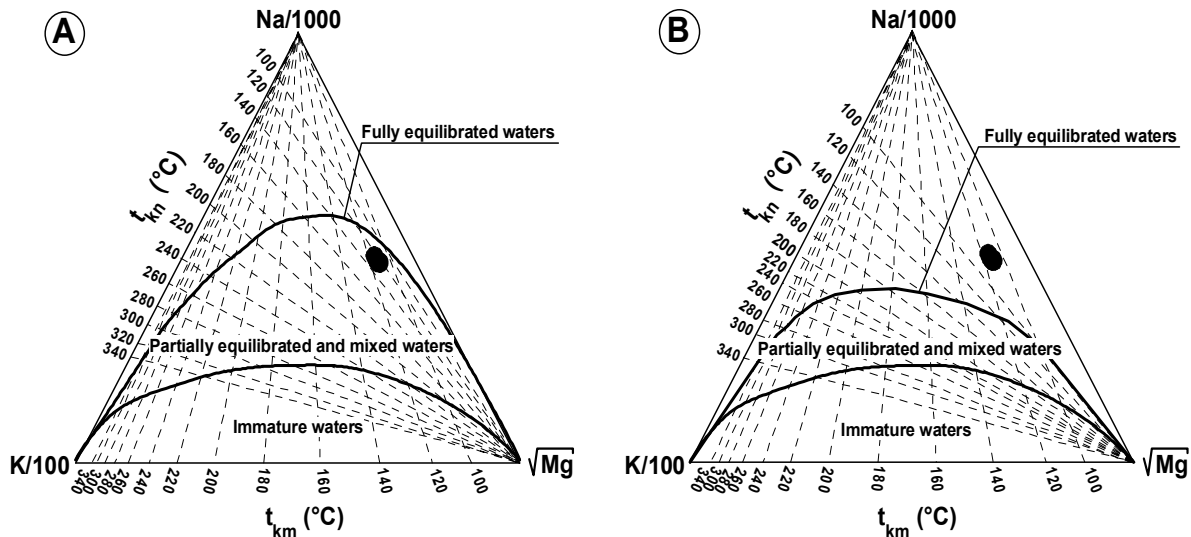


FIGURE 7: The Na-K-Mg diagrams for the hot water from well HO-01 in Stykkishólmur; Na-K geothermometry equations by: A) Giggenbach (1988); and B) Arnórsson (2000)

### 3.4 Geochemical modelling of fluid-mineral equilibrium

Chemical equilibrium calculations for a water sample from the production well in Stykkishólmur were performed using the speciation programs SOLVEQ, WATCH, and PHREEQCI. These programs calculate aqueous speciation distribution in the water and saturation indices for minerals occurring in the reservoir. A water sample collected on November 8, 2001 was chosen for the calculations. The ionic balance and the mass balance are both very small for this sample (Table 1), indicating high quality of the sampling and chemical analysis.

The calculated species (Figure 8) show the possibility of forming more complex entities in the water than simple ions, assumed in traditional analysis. Each analysed component is generally formed in more than one species. Sodium and chloride species exist in the analysed water mainly as simple ions,  $Na^+$  and  $Cl^-$ , respectively, which constitute more than 98% of the component molal concentrations (Figures 8A and 8C). In the case of calcium, a single ion,  $Ca^{+2}$ , constitutes about 93% (Figure 8B). In the case of sulphate, however, a complex ion,  $CaSO_4^0$ , accounts for about 40% of total component concentration (Figure 8D).



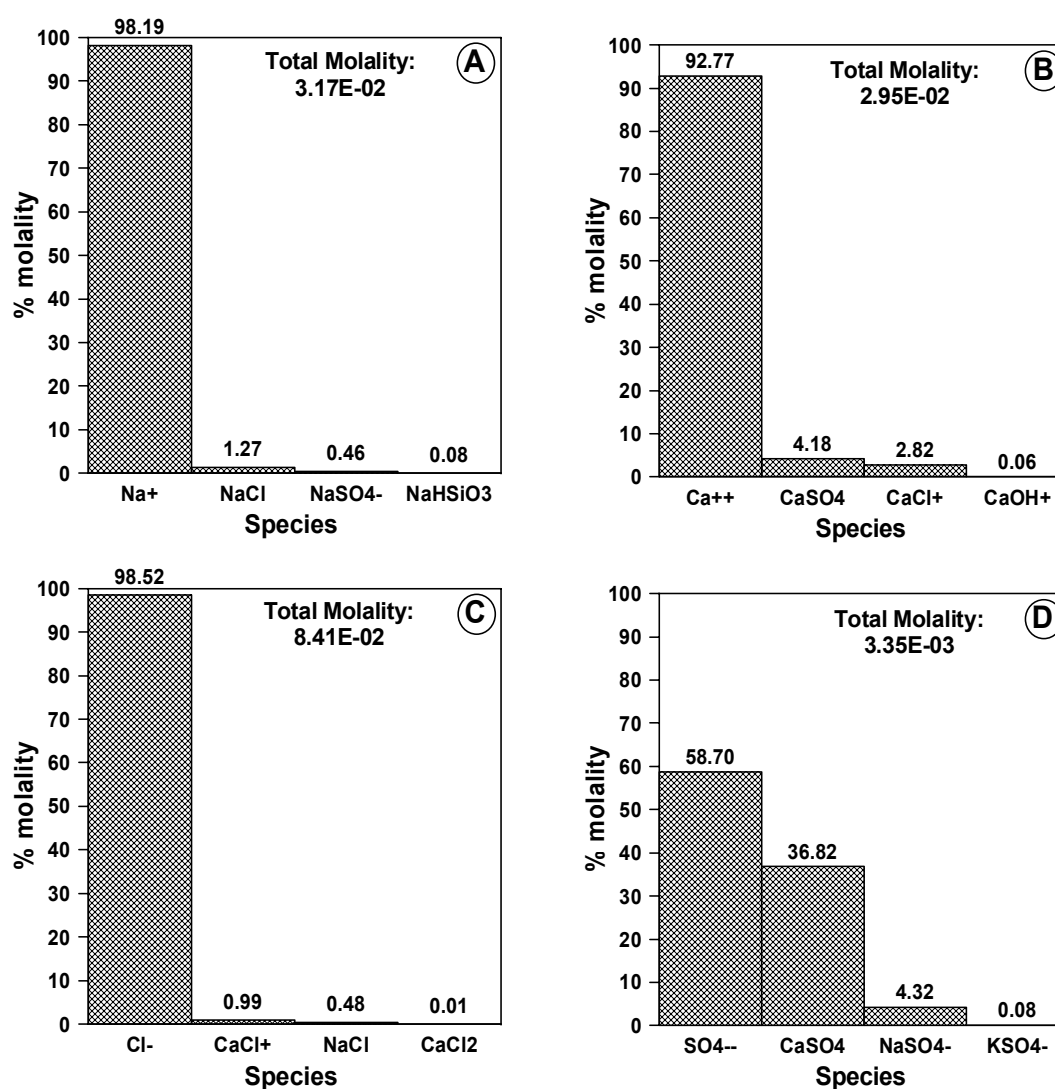


FIGURE 8: Species in the hot water from well HO-01 in Stykkishólmur, A) sodium; B) calcium; C) chloride; and D) sulphate; the distribution of species was calculated with SOLVEQ

The log ( $Q/K$ ) diagrams for the sample from well HO-01 show the state of equilibrium between geothermal water and minerals as a function of temperature (Figure 9). Computations using SOLVEQ, WATCH, and PHREEQCI, indicate that the water attains equilibrium with minerals over a range of temperatures rather than at one specific temperature. The three programs give slightly different results for this sample. This is not surprising, since the three programs use different thermodynamic databases. In Table 4, equations for the solubility product constant (log  $K$ ) for calcite from the three different databases are given. We see how the value of log  $K_{\text{CaCO}_3}$  differs between SOLVEQ, WATCH, and PHREEQCI.

TABLE 4: Equations for the solubility product constants for calcite with results for geothermal water from Stykkishólmur, at a temperature of 86.4 °C

Program	Equation	Result
SOLVEQ	$\log K_{\text{CaCO}_3} = -8.5308 - 0.0006 T - 0.1236229 \text{ E-}03 \times T^2 + 0.43057 \text{ E-}06 \times T^3 - 0.72716 \text{ E-}09 \times T^4$ ; $T$ in °C	-9.2683
WATCH	$\log K_{\text{CaCO}_3} = 10.22 - 0.0349 T - 2476 / T$ ; $T$ in K	-9.2147
PHREEQCI	$\log K_{\text{CaCO}_3} = -171.9065 - 0.077993 T + 2839.319 / T + 71.595 \log(T)$ ; $T$ in K	-9.0724

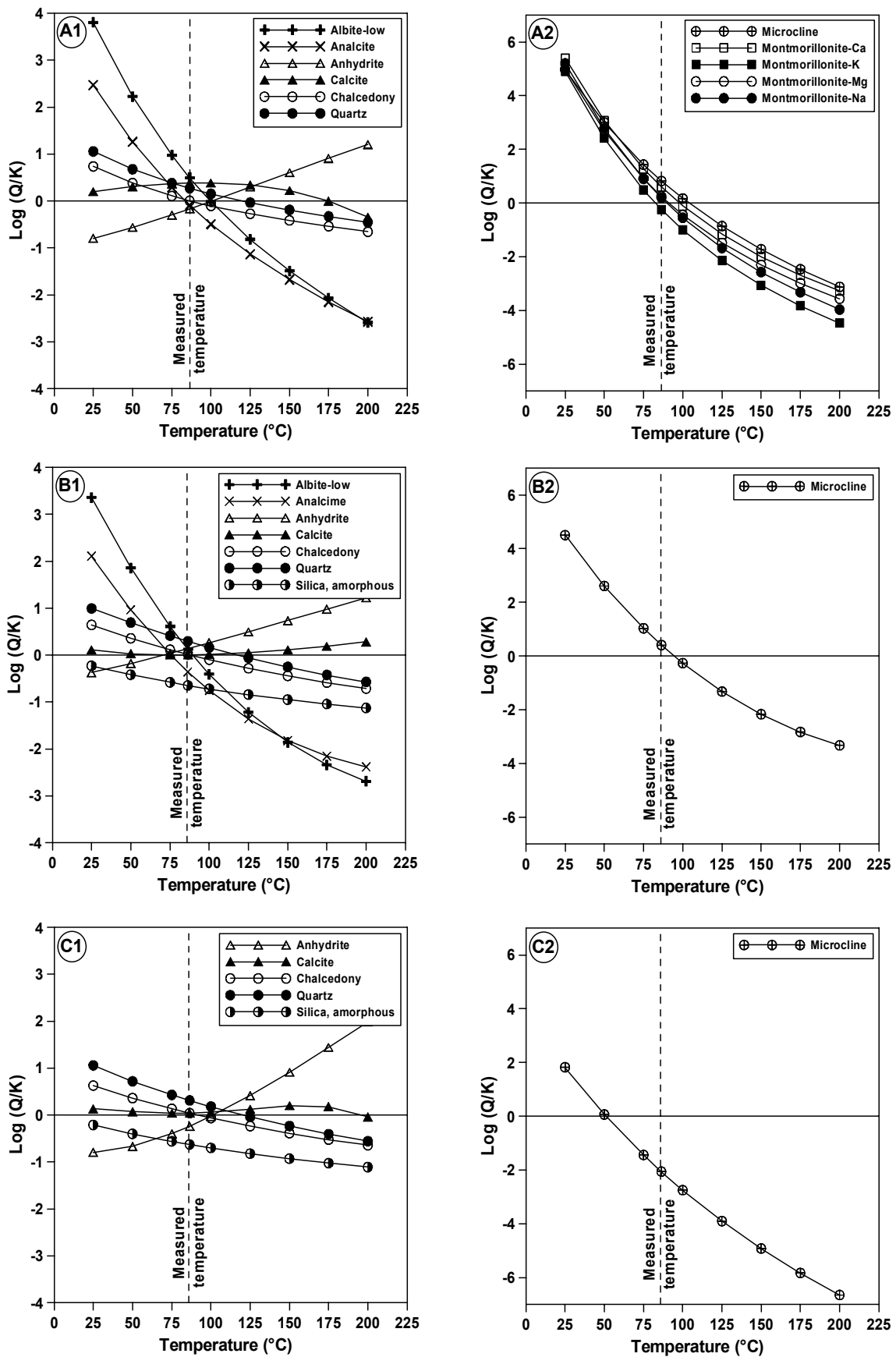


FIGURE 9: Mineral equilibrium diagrams for the hot water from well HO-01 in Stykkishólmur; the saturation index was calculated with: A) SOLVEQ; B) WATCH; and C) PHREEQCI

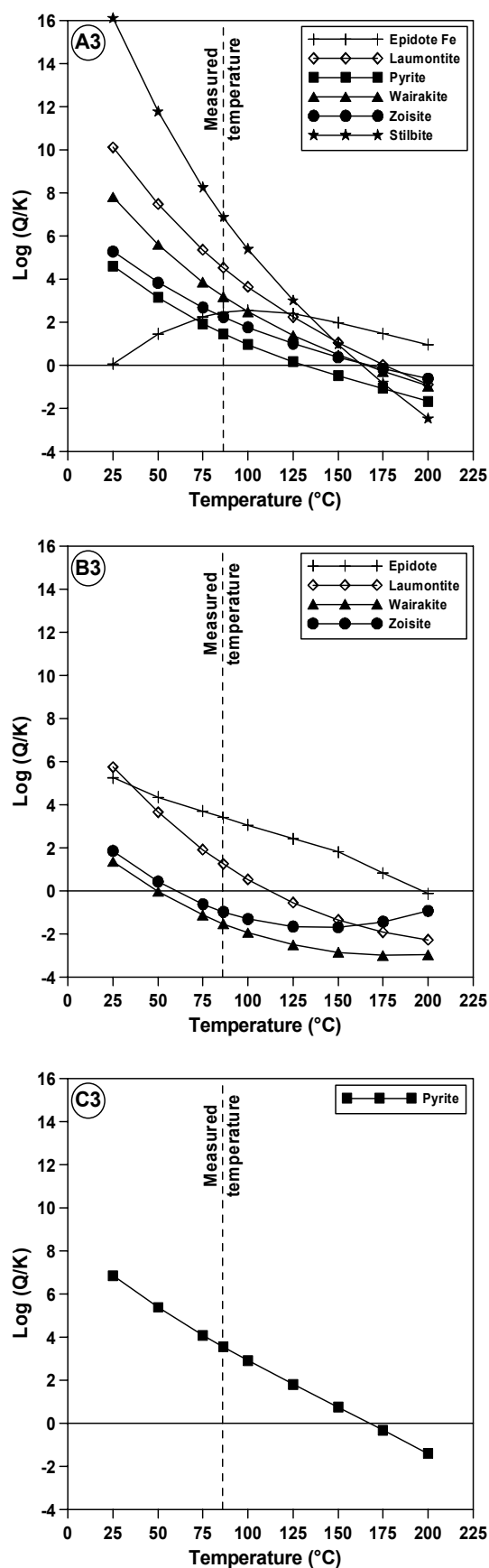


FIGURE 9: Continued

In Figure 9, it can be seen that equilibrium lines for a group of minerals converge in some range close to the measured temperature. Chalcedony and anhydrite intersect the  $SI = 0$  line close to the measured temperature (Figure 9A1, 9B1, and 9C1). The equilibrium temperatures for chalcedony and quartz are almost the same as the estimated temperatures obtained by chalcedony and quartz geothermometers, respectively. Other minerals, found in cuttings, show equilibrium temperatures in the range from 125 to 175°C (Figure 9A3). They are all supersaturated close to the measured temperature.

### 3.5 Chemical monitoring during production

The low-temperature waters utilized in Icelandic hitaveitas are sampled at least once a year for analysis of all main constituents (pH, volatiles, silica, Na, K, Mg, Ca, Al, Fe, Mn, Cl, Br, B,  $SO_4$ , F,  $NO_3$ , TDS, and stable isotopes); and more frequently from fields where the water is slightly mineralized and there is a fear of freshwater inflow (Kristmannsdóttir and Ármannsson, 1996). Occasionally, samples for selected trace elements, such as Li, Sr, Cd, Zn, Hg, Pb, or As, are collected for analysis. For automatic monitoring of the production in low-temperature geothermal fields, Orkustofnun (ISOR) has developed a data logging system (Kristmannsdóttir et al., 1995). Data from hitaveitas are loaded into the logger automatically, and it can measure up to 16 different parameters. Twice a day the main-frame computer at ISOR downloads the collected data. The system is connected to the Internet, and data can be displayed either as values or long-term graphs.

Seven parameters are continuously monitored in the district heating system in Stykkishólmur (Appendix IV). Information about the measured parameters can be found on the following web-site, in Icelandic only: <http://www.isor.is/efirlit/stykkish1.shtml>. Figures 10 and 11 show variations in conductivity, chloride, and silica concentrations with time in the water discharged from production well HO-01. Changes during the first months of operation are due to breaks in discharge. In the years 1996–2002, conductivity decreased slightly from about 9000 to 8700  $\mu S/cm$ . A similar variation is noticed for chloride concentrations, though with larger oscillations. It can be explained by the mixing of waters from the two main aquifers in the well, with probably slightly different compositions. Concentration of silica over the entire observation time is more or less constant, i.e. about 72 ppm.

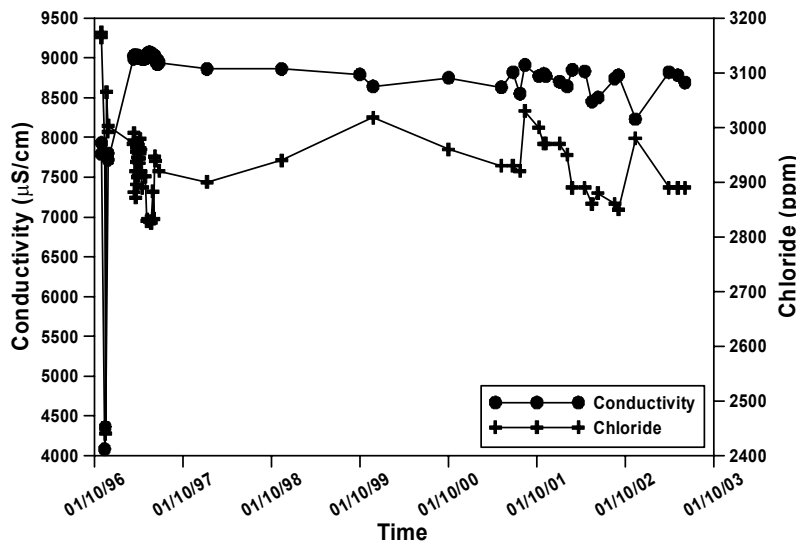


FIGURE 10: Changes in conductivity and chloride concentration with time in the water from well HO-01 in Stykkishólmur

Monitoring of saturation indices of minerals that can precipitate in geothermal systems may provide the opportunity of undertaking preventive actions in time. Geothermal water from Stykkishólmur is in most cases supersaturated at the measured temperature with respect to minerals occurring in the reservoir. However, supersaturation in relation to most important minerals is not significant and does not indicate changes with time (Figure 12).

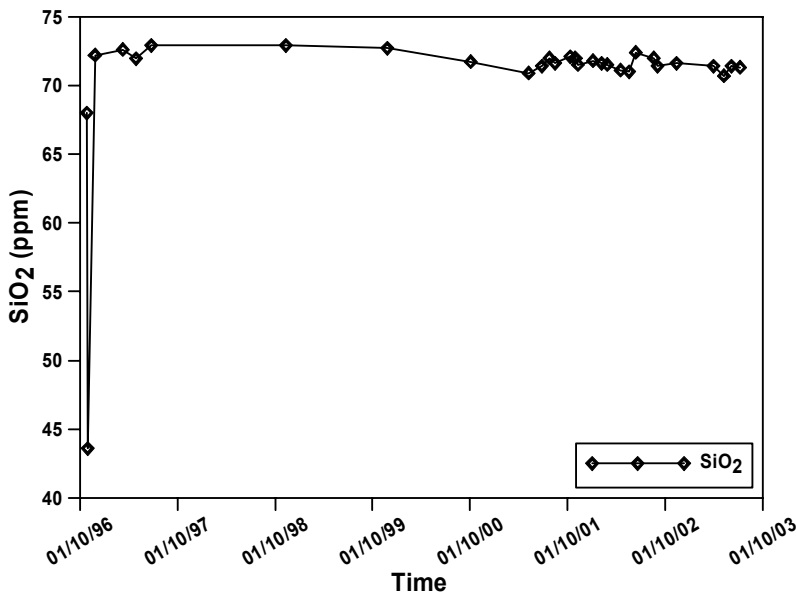


FIGURE 11: Changes in silica concentration with time in the water from well HO-01 in Stykkishólmur

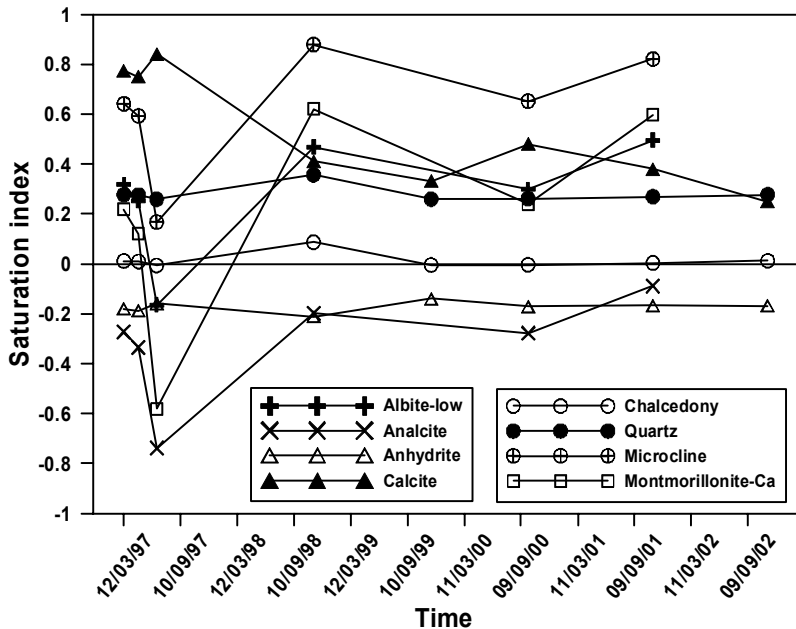


FIGURE 12: Saturation index of selected minerals versus time for the hot water from well HO-01 in Stykkishólmur

## 4. THE PYRZYCE DISTRICT HEATING SYSTEM

### 4.1 General background

The space heating plant in Pyrzyce has been in operation since 1996. This plant is located in NW- Poland (Figure 13) in the Polish Lowland Province, where very good geothermal conditions are found (Sokolowski, 1995). Geothermal aquifers are situated within the Jurassic sandstones (Radowskie and Mechowskie layers) at depths of 1.4 -1.6 km (Figure 14), with very good collector properties, effective porosity from 10 to 30%, and permeability between 900 and 13,000 mD (Biernat, 1993). The total thickness of the aquifer is about 80 m, while the reservoir temperature is 61°C.

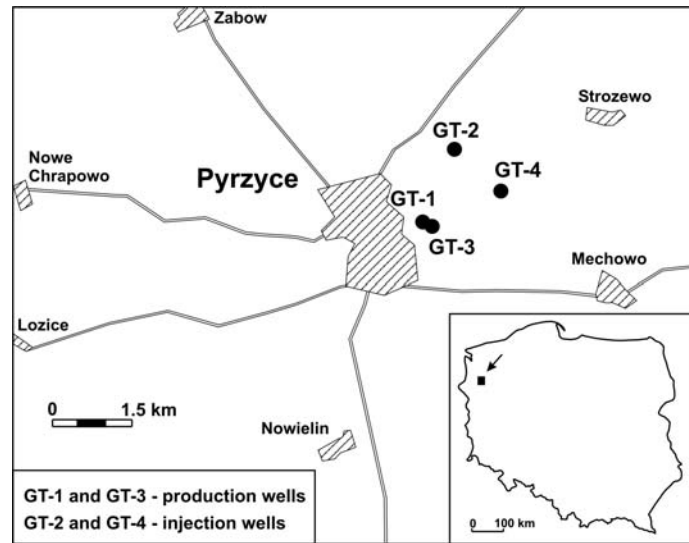


FIGURE 13: Location map of Pyrzyce, NW-Poland

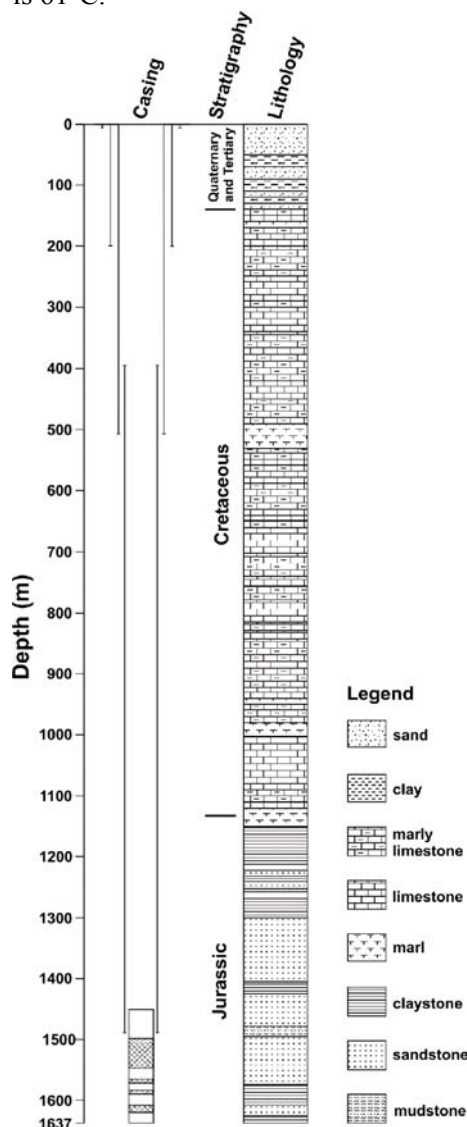


FIGURE 14: Lithological profile and casing of well GT-1

The geothermal system consists of two production wells (GT-1 and GT-3) and two injection wells (GT-2 and GT-4). The location of the injection wells was fixed on the basis of mathematical modelling. The distance between them and the production wells is about 1.5 km (Figure 13). The maximum total yield of both production wells is about 103 l/s (Kepinska, 2003a).

The plant's maximum installed capacity is 48 MWt, including 13 MWt from geothermal water and 35 MWt from heat pumps and gas boilers. However, both the thermal capacity and heating network were oversized while the project was being planned at the beginning of the 1990s. The current maximum capacity is only ca. 27 MWt, because of the closing of several factories, thermomodernization of buildings, installation of thermostatic valves and water-meters by individual heat receivers, and, last but not least, by higher outside temperatures in the last several years (Kepinska, 2003b). The plant replaced 68 low-efficiency coal-based heating plants combusting about 30,000 tonnes of coal annually and generating considerable amounts of emissions. In 2002, geothermal heat production was 95 TJ (Kepinska, 2003a). The share of geothermal energy in total heat generation is about 60%, while the rest comes from gas boilers. The plant supplies district heating and warm water to about 12,000 users out of the town's total population of 13,000. A simplified sketch of the plant is in Appendix III.

Geothermal water exploited in Pyrzyce contains various chemical components such as chloride, sodium, bromide, iodide, iron, and manganese. It has healing properties and can be used for some treatments or bathing. Balneotherapeutic applications are planned as another prospective use, if financial sources to develop this line of activities become available (Kulik and Grabiec, 2003). It should be noted that the Pyrzyce

geothermal project assumed multipurpose uses, i.e. agriculture, bathing, and balneotherapy. Unfortunately, only the heating part has been realized so far.

#### 4.2 Chemical composition of the fluids

Table 5 shows the results of chemical analysis of a hot water sample from the production well GT-1 in Pyrzyce. This sample was taken on March 5, 1997 while the geothermal fluid circulated continuously. The data for a few components, such as free  $\text{CO}_2$ , Al,  $\text{NH}_4$ , and F, were obtained from other samples. Free oxygen, as well as oxygen included in  $\text{NO}_3$  and  $\text{NO}_2$ , probably comes from surface installations, and was eliminated from later calculations for the interpretation of the state of the geothermal water in the reservoir. The hot water pumped from the well has a temperature of  $61^\circ\text{C}$ . It is brine of Cl-Na type with TDS above 120 g/l. This water is weakly acid, very hard (8653 mg  $\text{CaCO}_3/\text{l}$ ), with high concentrations of Fe and Mn. The predominant anion and cation are chloride (>98% meq) and sodium (>90% meq), respectively. Very highly mineralized water is found in the Polish Lowland. This is connected with a normal, vertical hydrochemical zonality, which is manifested by an increasing mineralization of waters with depth, and characterized by a specific sequence of water compositions (Adamczyk, 1995).

The Cl- $\text{SO}_4$ - $\text{HCO}_3$  triangular diagram (Figure 15) for the analyzed sample shows that this geothermal water is a "mature water" containing chloride as the major anion.

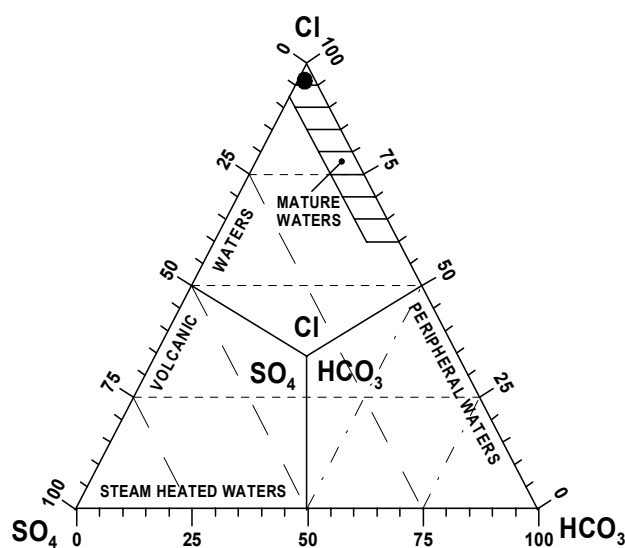


FIGURE 15: The Cl- $\text{SO}_4$ - $\text{HCO}_3$  classification diagram for the hot water from well GT-1 in Pyrzyce

TABLE 5: Chemical composition of the thermal water from well GT-1 in Pyrzyce (concentrations in mg/l, except where noted)

Temperature ( $^\circ\text{C}$ )	61
pH field	5.81
Eh (mV)	-61
Conductivity (mS/cm)	245.6
TDS (g/l)	123.8
Density at $20^\circ\text{C}$ (kg/l)	1.078
Total hardness (meq/l)	173.05
Carbonate hardness (meq/l)	3.73
Alkalinity (meq/l)	3.73
$\text{CO}_2$ free	121
$\text{O}_2$ dissolved	0.23
$\text{SiO}_2$	23.6
Na	39920
K	208.3
Ca	2245.6
Mg	739.3
Cl	65970
$\text{SO}_4$	1115
$\text{HCO}_3$	227.4
Fe	16.4
Mn	1.5
Al	0.15
Li	2
$\text{NH}_4$	16.7
$\text{NO}_3$	16.6
$\text{NO}_2$	0.01
S (total sulfide)	0.035
$\text{PO}_4$	0.16
F	1.2

Note: Most of the above data were obtained by analysis of a sample of thermal water collected on March 5, 1997; the data for a few components were obtained from other samples.

#### 4.3 Estimation of subsurface temperature

The same silica geothermometry equations were used to estimate the reservoir temperature in Pyrzyce as in Stykkishólmur (Table 6 and Appendix II). Temperatures derived from quartz geothermometers,  $66.9$  and  $69.7^\circ\text{C}$ , are a few degrees above the measured temperature ( $61^\circ\text{C}$ ). On the other hand, chalcedony geothermometers give very low temperatures which are not justified by observation. The geothermal reservoir in Pyrzyce is a long-lived

system, and according to Fournier (1989) quartz may control dissolved silica at temperatures less than 100°C.

TABLE 6: Silica geothermometer temperatures for the thermal water from well GT-1 in Pyrzyce

Geothermometer	$T_M$	$T_{Q1}$	$T_{Q2}$	$T_{Ch1}$	$T_{Ch2}$
Range in °C		25-250	25-900	0-250	
T in °C	61.0	66.9	69.7	34.9	38.4

Sources of temperature equations for the silica geothermometers:

$T_M$  – measured temperature,  $T_{Ch1}$  – Fournier (1977),  
 $T_{Q1}$  – Fournier (1977),  $T_{Ch2}$  – Arnórsson et al. (1983)  
 $T_{Q2}$  – Fournier and Potter (1982),

Of the Na-K geothermometers, only the one proposed by Giggenbach (1988) shows a temperature similar to that obtained from quartz geothermometry equations, and it is about 10°C above the measured temperature (Table 7). Other Na-K equations give very scattered results for the reservoir temperature, ranging from 11.7 to 54.0°C, and in all cases lower than expected.

TABLE 7: Cation geothermometer temperatures for the thermal water from well GT-1 in Pyrzyce

Geothermometer	$T_M$	$T_{Na-K1}$	$T_{Na-K2}$	$T_{Na-K3}$	$T_{Na-K4}$	$T_{K-Mg}$
Range in °C			25-250		0-350	
T in °C	61.0	54.0	11.7	71.5	46.5	86.4

Sources of temperature equations for the cation geothermometers:

$T_M$  – measured temperature,  $T_{Na-K3}$  – Giggenbach (1988),  
 $T_{Na-K1}$  – Fournier (1979),  $T_{Na-K4}$  – Arnórsson (2000),  
 $T_{Na-K2}$  – Arnórsson et al. (1983),  $T_{K-Mg}$  – Giggenbach (1988)

The point representing the analysis of hot water on the Na-K-Mg diagrams (Figure 16) is located in the area above the line of fully equilibrated waters, both on the diagrams constructed using Giggenbach’s Na-K equation (Figure 16A) as well as Arnórsson’s Na-K equation (Figure 16B).

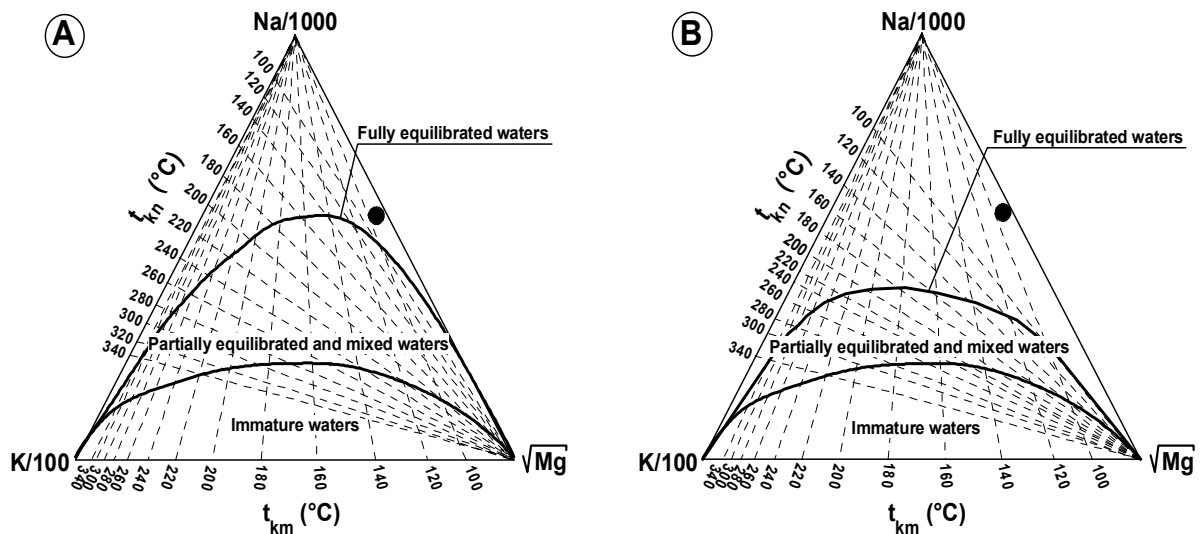


FIGURE 16: The Na-K-Mg diagrams for the hot water from well GT-1 in Pyrzyce; Na-K geothermometry equations by A) Giggenbach (1988); and B) Arnórsson (2000)

#### 4.4 Geochemical modelling of fluid-mineral equilibrium

Geothermal water from the production well in Pyrzyce is a brine with a very high ionic strength of 4 molal. For this water, the software that includes the ion interaction model developed by Pitzer should be used, because the Debye-Hückel theory cannot yield sufficiently accurate results. One such program is PHRQPITZ. The application of PHRQPITZ, however, is limited to only a few chemical components (Plummer et al., 1988). Parallel calculations of chemical equilibrium at measured temperatures were carried out with the computer codes SOLVEQ, WATCH, PHREEQCI, and PHRQPITZ. Figure 17 shows the difference in saturation indices for four selected minerals, namely anhydrite, gypsum, calcite, and dolomite. The differences in SI obtained from these programs are not significant, and the best convergence in relation to results received from PHRQPITZ occurs in the case of PHREEQCI. Thus, PHREEQCI was chosen for water-mineral equilibrium calculations for the full analysis of hot water from the production well in Pyrzyce.

No mineralogical studies have been carried out for the geothermal reservoir. Therefore, minerals for the  $\log(Q/K)$  diagrams were chosen arbitrarily. The  $\log(Q/K)$  diagrams for the sample from well GT-1 show that most of the selected minerals do not attain equilibrium with water at the measured temperature (Figure 18), with the exception of goethite and chalcedony.

A better interpretation of the chemical composition of the geothermal water from the production well in Pyrzyce can be made after more information about mineralogy of the reservoir becomes available and properly collected water samples are obtained.

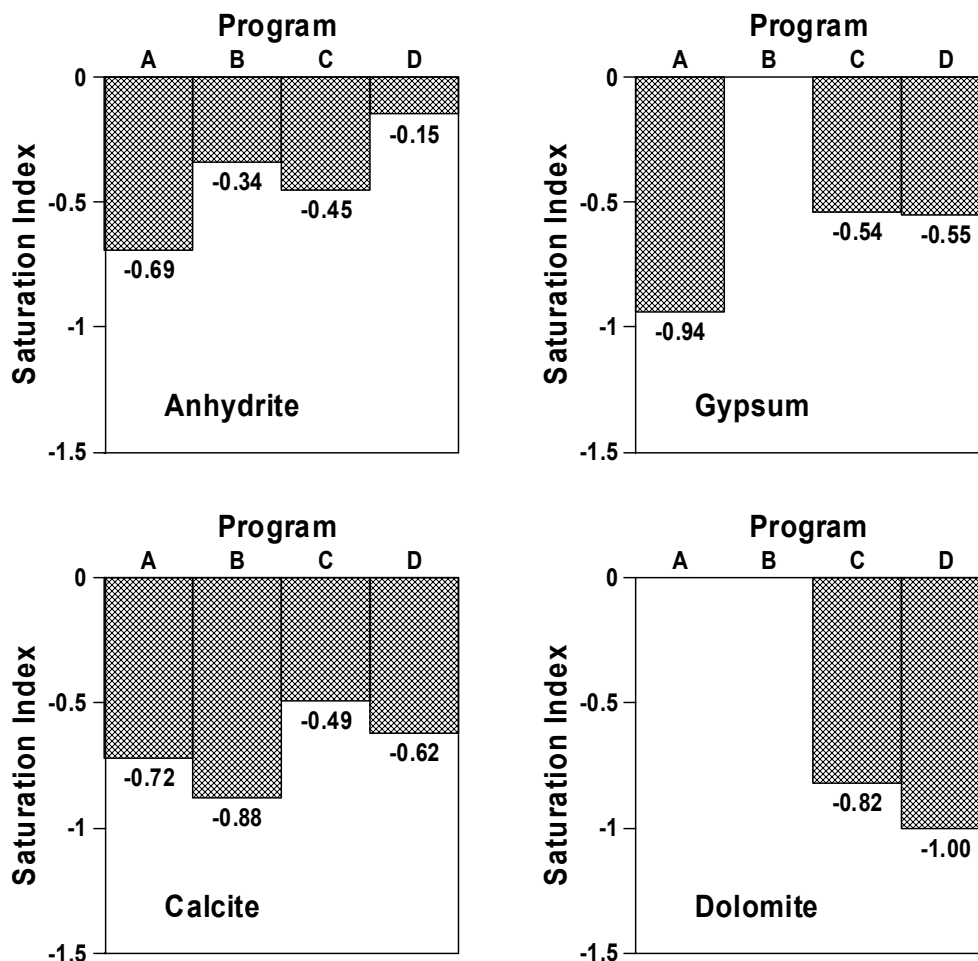


FIGURE 17: Comparison between saturation indices calculated with: A) SOLVEQ; B) WATCH; C) PHREEQCI; and D) PHRQPITZ for selected minerals in well GT-1 in Pyrzyce



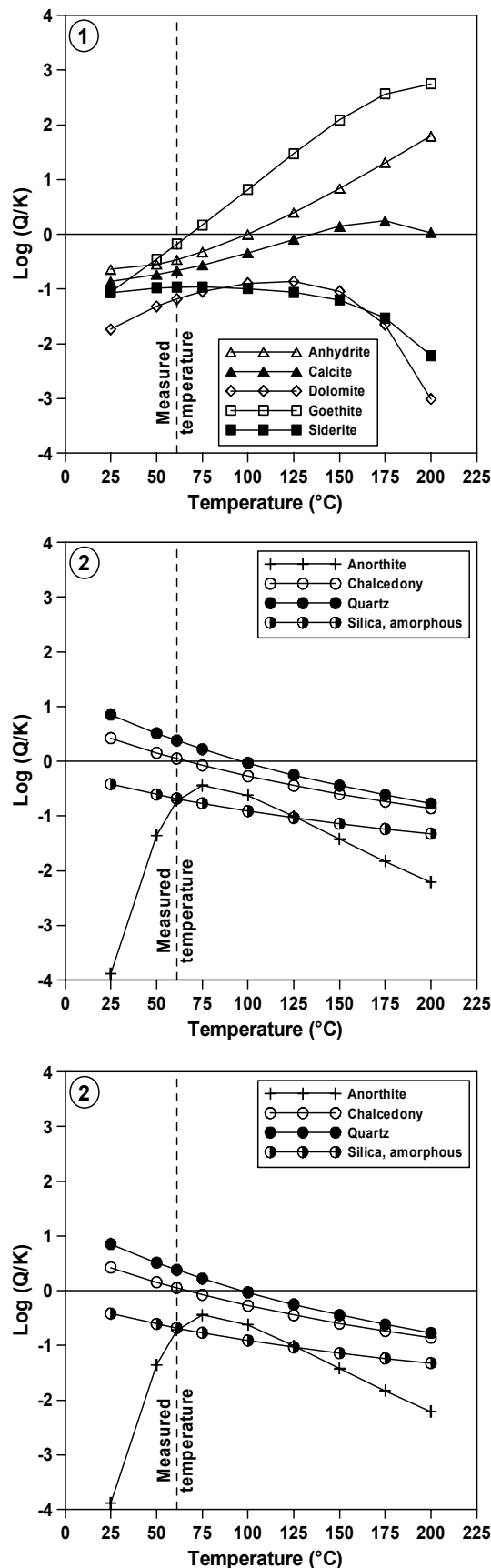


FIGURE 18: Mineral equilibrium diagrams for the hot water from well GT-1 in Pyrzyce; the saturation index was calculated with PREEQCI

### 5. CONCLUSIONS

The main conclusions of this report are the following:

- Geothermal water from the Stykkishólmur district heating system differs significantly from other low-temperature waters in Iceland. This water contains a high concentration of Cl, which suggests mixing of seawater with geothermal water of meteoric origin. The isotopic composition of the hot water from the production well indicates that this water is not strictly a mixture of seawater and present-day freshwater. The deuterium excess of geothermal water is much higher than expected for present-day precipitation conditions, and amounts to more than 20 ‰. The Cl/B mass ratio of the hot water is almost 30,000, so it is about seven times higher than that of seawater and a few hundred times higher than that of typical low-temperature waters in Iceland. It may be caused by the uptake of boron by clay minerals which are found in the reservoir.
- The results from silica geothermometers for water from Stykkishólmur indicate that chalcedony controls the silica concentration in the reservoir. The temperatures obtained from chalcedony geothermometers are very close to the measured temperatures, 90.8 and 86.4°C, respectively. Temperatures calculated using Na-K equations deviate significantly from the measured temperature, only in one case giving a temperature close to that observed.
- Chemical equilibrium calculations for geothermal water from the production well in Stykkishólmur, performed with the speciation programs SOLVEQ, WATCH, and PHREEQCI, give the aqueous speciation distribution in the water, as well as saturation indices for minerals occurring in the reservoir. There are some differences in results of  $\log(Q/K)$  diagrams depending on which thermodynamic database was used. Some alteration minerals found in the well converge in a range of about 30°C around the measured temperature. In any case, the  $\log(Q/K)$  diagram for chalcedony intersects the  $SI = 0$  line at the measured temperature.
- The geothermal reservoir in Pyrzyce is a long-lived system, and chemical geothermometers indicate that quartz may control dissolved silica in the water. Temperatures derived from quartz geothermometers, 66.9 and 69.7°C, are a few degrees above the measured temperature (61°C), while chalcedony geothermometers give temperatures that are too low.

- The geothermal water from the production well in Pyrzyce is a brine with mineralization above 120 g/l. For this water, with its high ionic strength, the specific interaction approach to the thermodynamic properties of aqueous solutions should be used, i.e. the Pitzer model. Parallel chemical equilibrium calculations for hot water from Pyrzyce, performed with four different programs, SOLVEQ, WATCH, PHREEQCI, and PHRQPITZ, do not give very different results for the saturation indices of selected minerals. This allows programs written for dilute solutions to be used for fairly high ionic strength waters, with some limitations.

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#### APPENDIX I: Laboratory analysis of geothermal waters

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pH	8.34	Li		Al	.014	EFNASAMSETNING			
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SiO2	71.5	Br		Cd		NH3		B	
Uppl	5220	I		Sb		Ar		Na	
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Rn		NO3		Pb		EFNASAMSETNING			
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FIGURE 1: A laboratory-record card used at ISOR

**The Ionic Balance equation:**

$$\text{Ionic Balance} = \frac{\text{Cations} - \text{Anions}}{(\text{Cations} + \text{Anions})/2} \times 100, \text{ in } \%$$

where Cations and Anions represent the sums of all cation and anion concentrations, respectively, expressed in milli-equivalents.

**The Mass Balance equation:**

$$\text{Mass Balance} = \frac{\text{Mineralization} - \text{TDS}}{\text{TDS}} \times 100, \text{ in } \%$$

where Mineralization is the sum of all constituents determined in the analysis, and TDS (total dissolved solids) is the mass of residue after evaporation and drying at 105°C; both in ppm or mg/l.

**APPENDIX II: Temperature equations for the silica and cation geothermometers**  
Concentrations are in ppm unless otherwise specified

Geothermometer	Equation	Range (°C)	Source
Quartz	$t \text{ } ^\circ\text{C} = \frac{1309}{5.19 - \log(\text{SiO}_2)} - 273.15$	25–250	Fournier (1977)
Quartz	$t \text{ } ^\circ\text{C} = -42.2 + 0.28831 \text{ SiO}_2 - 3.6686 \times 10^{-4} \times (\text{SiO}_2)^2 + 3.1665 \times 10^{-7} \times (\text{SiO}_2)^3 + 77.0341 \log(\text{SiO}_2)$	25-900	Fournier and Potter (1982)
Chalcedony	$t \text{ } ^\circ\text{C} = \frac{1032}{4.69 - \log(\text{SiO}_2)} - 273.15$	0-250	Fournier (1977)
Chalcedony	$t \text{ } ^\circ\text{C} = \frac{1112}{4.91 - \log(\text{SiO}_2)} - 273.15$	25-180	Arnórsson et al. (1983)
Na-K	$t \text{ } ^\circ\text{C} = \frac{1217}{1.438 + \log(\text{Na} / \text{K})} - 273.15$		Fournier (1979)
Na-K	$t \text{ } ^\circ\text{C} = \frac{933}{0.993 + \log(\text{Na} / \text{K})} - 273.15$	25-250	Arnórsson et al. (1983)
Na-K	$t \text{ } ^\circ\text{C} = \frac{1390}{1.750 + \log(\text{Na} / \text{K})} - 273.15$		Giggenbach (1988)
Na-K <sup>a</sup>	$t \text{ } ^\circ\text{C} = 733.6 - 770.551Y + 378.189Y^2 - 95.753Y^3 + 9.544Y^4$	0-350	Arnórsson (2000)
K-Mg	$t \text{ } ^\circ\text{C} = \frac{4410}{14 - \log(\text{K}^2 / \text{Mg})} - 273.15$		Giggenbach (1988)

<sup>a</sup> – Y designates the logarithm of the molal ratio of Na/K

**APPENDIX III: Schematic diagrams of the heating systems in Stykkishólmur and Pырzyce**

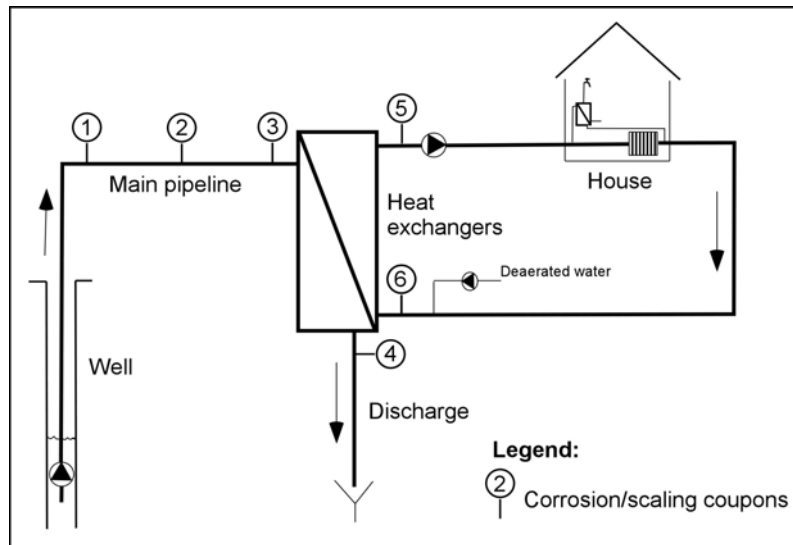


FIGURE 1: Scheme of water distribution in the Stykkishólmur hitaveita (from Kristmannsdóttir et al., 2002)

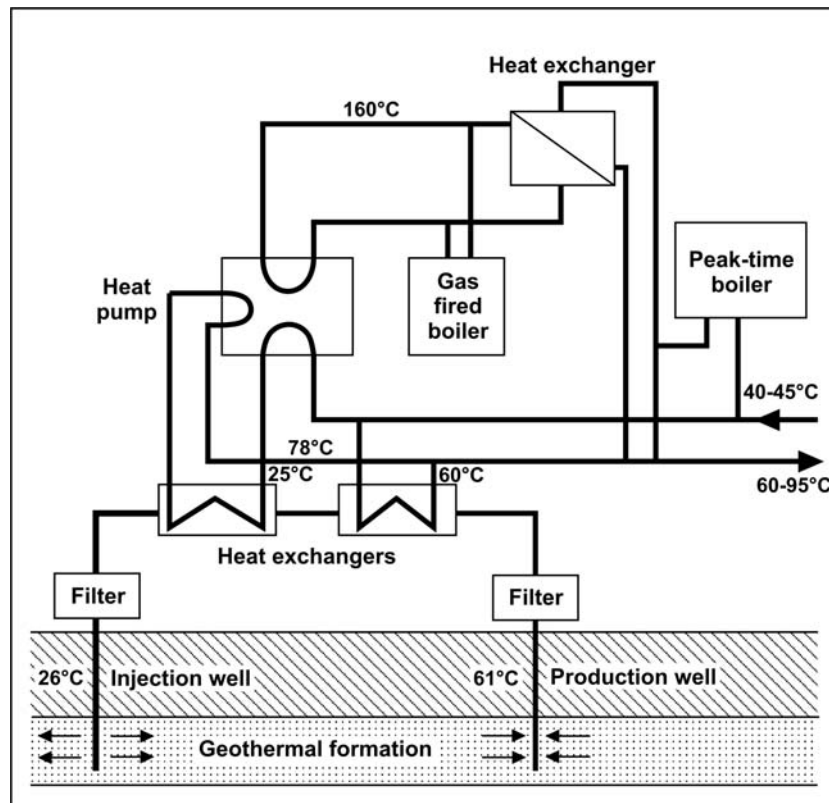


FIGURE 2: Scheme of the geothermal heating plant in Pырzyce (from Sobański et al., 2000)

### APPENDIX IV: Monitoring of the Stykkishólmur district heating system

TABLE 1: List of parameters recorded every hour in the Stykkishólmur hitaveita

Column	Parameter	Unit	Operating range	Complementary note
1	Date			Date in "ISO" form
2	Id for data			
3	Discharge	l/sek	0-30 l/sek	Discharge from well
4	Pressure	bar	0-10 bar	Water table in well
5	Temperature	°C	0-100 °C	Temperature of water in well
6	Pressure	bar	0-10 bar	Pressure on main pipeline at wellhead
7	Current	A	0-255 A	Current used by downhole pump
8	Voltage	V	12 V	Status of battery in datalogger
9	Temperature	°C		Temperature within datalogger

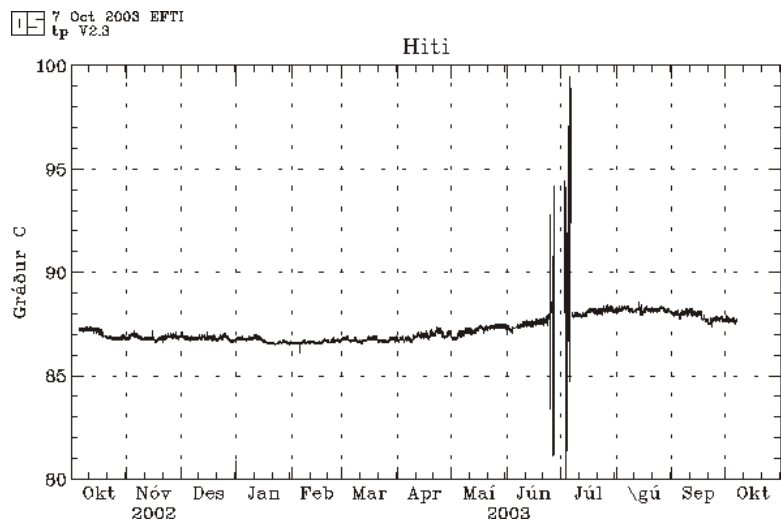


FIGURE 1: Changes in temperature over the last year in the water from well HO-01 in Stykkishólmur; the diagram, which presents raw data, is taken from the website <http://www.isor.is/efirlit/stykkish1.shtml>

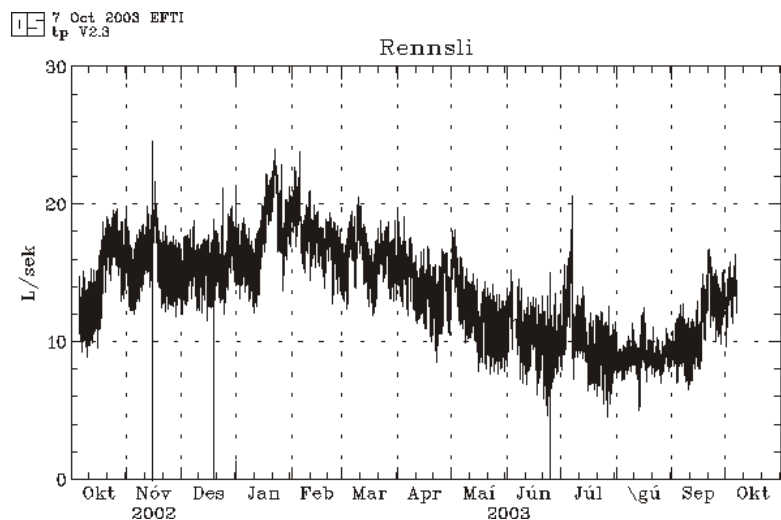


FIGURE 2: Changes in discharge over the last year from well HO-01 in Stykkishólmur; the diagram which presents raw data is taken from the website <http://www.isor.is/efirlit/stykkish1.shtml>