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WATER-ROCK INTERACTION IN THE BAKKI LOW-TEMPERATURE GEOTHERMAL FIELD, SW-ICELAND

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ABSTRACT

Water-rock interaction is a fundamental process in natural geothermal systems, both in high-temperature and low-temperature ones. The Bakki geothermal field which is utilized for a district heating system, is a low-temperature geothermal system with the maximum measured temperatures varying from 120 to 137°C in the wells. A relict high temperature alteration is evidenced by the occurrence of the mineral epidote. Reservoir rocks are alternatively basalt lavas and basaltic hyaloclastites. A silica-enthalpy mixing model indicates that the reservoir temperature may exceed 150°C. Use of CHILLER, a program for computing water-rock reactions, for mixing model suggests that the change in chemical composition in well HJ-01 revealed by chemical monitoring may be interpreted by dilution of the geothermal water with fresh local groundwater in a ratio of about 0.5-0.6. Based on the thermal fluid chemistry as well as the secondary minerals occurring, a modelling study was performed by using CHILLER. Due to the complicated alteration history of the area, two water-rock interaction models, one at present temperatures and one at high temperature, were applied. Most of the important alteration minerals such as calcite, laumontite, stilbite, clinochlore, epidote-ord, clinozoisite, wairakite and muscovite were both identified in the actual field and by geochemical modelling. The evolution of the fluid may suggest that most of the major components found in the geothermal system such as Na^+, Al^{3+}, K^+, Fe^{2+} and SiO_2 come from the dissolution of the reservoir rocks. Cl^- is very stable due to its chemically conservative character and the low concentration in added rocks, so the high concentration of Cl^- and Na^+ in the two studied wells is due to the dissolution of salts left in the sediments formed by the repeated transgression of the sea over the land.

1. INTRODUCTION

Geothermal energy is an important energy resource and its utilization has a relatively insignificant environmental impact. Geochemical research plays an important role during every stage of geothermal exploration and utilization. The principal purpose of a geochemical survey is to predict subsurface temperatures, to obtain information on the origin of the geothermal fluid and to reveal subsurface flow directions. During geothermal exploration, drilling and later assessment of the reservoir, geochemical research produces data on the chemical properties of the discharged fluid, and steam to water ratio in the reservoir. In this way, it contributes to the overall understanding of production characteristics of geothermal reservoirs. It also quantifies scaling and corrosion tendencies. After production has been initiated, geochemical monitoring is one of the most useful tools in recording the response of the reservoir to the production load, including recharge, pressure drawdown and possible enhanced boiling. It is common to establish geochemical laboratory facilities at geothermal power plants to strengthen monitoring studies that contribute data pertinent to optimising the economy of exploitation.

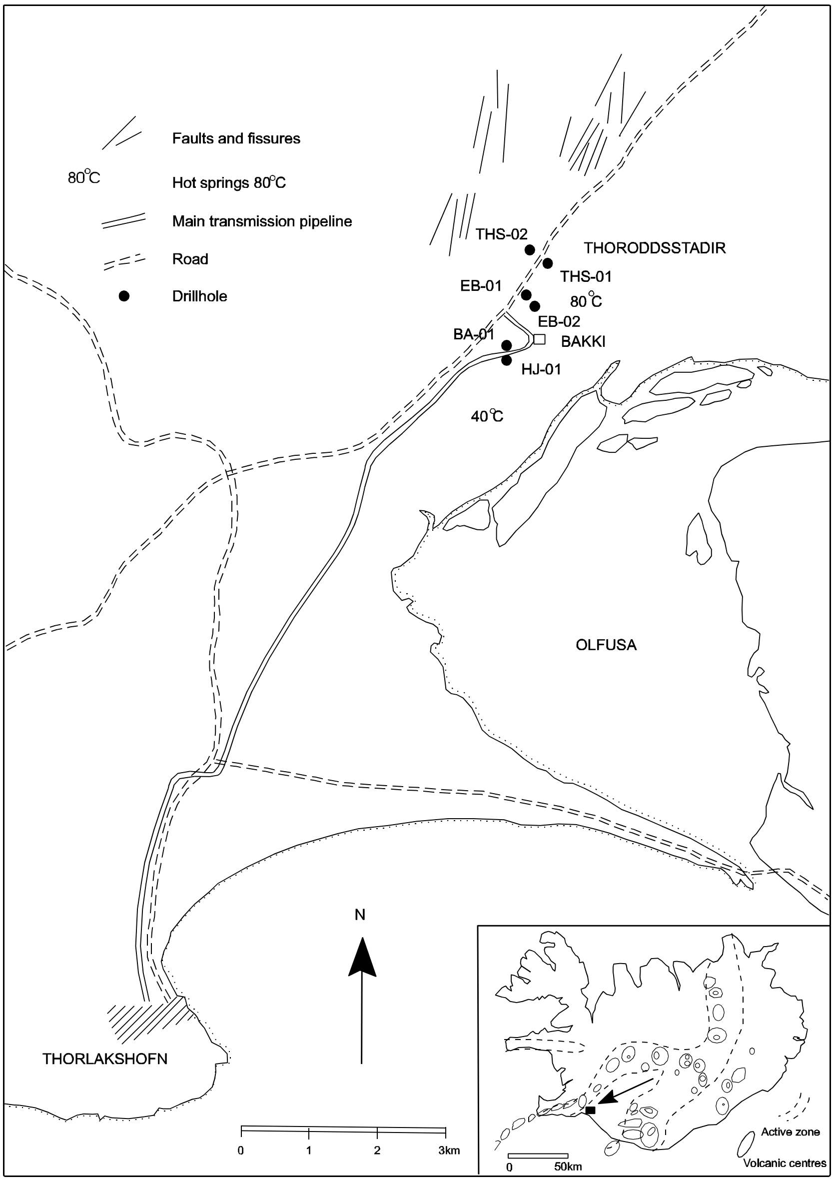

FIGURE 1: The location of the Bakki geothermal field

The Bakki geothermal field, which is located on the flank of the western active volcanic zone in southern Iceland (Figure 1), is at present a low-temperature geothermal system but it can be considered as a border-case between low- and high-temperature geothermal systems. It has been a production field for a district heating system for the small town, Thorlákshöfn. During 22 years of exploitation the first production well BA-01, in the Bakki-Thóroddsstadir geothermal field has not shown noticeable changes. But for well HJ-01 chemical changes indicating inflow of colder water were noticed only a few months after connection to the distribution system in 1987. The cooling started from the bottom aquifer, which is unique in the exploitation of Icelandic geothermal fields. It is explained by an inflow through a fracture or fracture system directly connected to the reservoir feeding the bottom aquifer (Kristmannsdóttir and Sveinbjörnsdóttir, 1992). So, in late 1990, the bottom aquifer in well HJ-01 was sealed off by cementing. The production water appeared to be slowly regaining its original chemical composition during the first two years after the bottom aquifer was sealed off (Kristmannsdóttir and Sveinbjörnsdóttir, 1992), but further regular monitoring showed that it did not.

The aims of this study were to compile all existing geochemical data from this area in order to detect and explain possible changes in chemical composition and properties of the thermal fluids with time. Also to evaluate reservoir temperatures and equilibrium conditions by the use of chemical geothermometers and equilibrium calculations. Further, to evaluate the effects of mixing processes on the HJ-01 well fluids and water-rock interaction in both of the two utilized wells by using CHILLER, a program for computing water-rock reactions, boiling, mixing and other reaction processes in aqueous-mineral-gas systems.

2. THE BAKKI GEOTHERMAL FIELD

2.1 Geological setting

Low-temperature geothermal fields in Iceland are mainly found in Quaternary rocks which border the active volcanic zones, but also in Tertiary rock formations, mainly in the northern and western parts of Iceland. In the Ölfus region the reservoir rocks are Quaternary rock formation similar to the low-temperature geothermal fields within and in the neighbourhood of the capital Reykjavík. The rock formations are alternatively hyaloclastites and basalt lavas.

The Hengill and Ölfus areas are at a triple junction in SW-Iceland, where the South Iceland seismic zone meets the western rift zone and the Reykjanes peninsula oblique rift zone. It is, therefore, a zone of intense crustal deformation due to volcanic activity and earthquakes associated with the spreading plate boundary. The Bakki geothermal field in Ölfus, SW-Iceland, is located along a northeast elongated strip, with the same trend as the main fault swarms in the region. The field is about 15 km south of the borders of the Hengill central volcano which comprises major high-temperature geothermal areas. The Ölfus region is on the eastern flank of the western active volcanic zone with high heat flow and many low-temperature geothermal fields (Saemundsson, 1979). Natural hot springs occurred both northeast and southwest of the production field at Bakki (Figure 1). Those northeast of the field had temperatures up to 80˚C, but they dried up soon after well BA-01 was drilled in 1977. Those southwest of the field had temperatures of 20-45˚C, and were still active in 1990 (Kristmannsdóttir et al., 1990a). The tectonic and volcanic activity strongly affects the geothermal activity in this area. For example, HJ-01, one of the geothermal wells in Bakki, stopped flowing in November 1998, mainly due to an earthquake sequence in the Ölfus region. The largest event was a M=5.0 earthquake, located west of Hjalli in Ölfus striking on November 13, at 10:38 am (GMT); the second largest event was a M=4.7 striking on November 14, at 14:24 (GMT), close to Thurá in Ölfus. Aftershock activity continued for a few days, but by November 16 the seismicity had decreased considerably. The zone activated in the November 1998 earthquake sequence was about 14 km long (E-W) and 2-3 km wide (N-S) (Rögnvaldsson et al., 1998).

About 130 boreholes have been drilled in the Ölfus region, excluding the boreholes at the Nesjavellir field and other high-temperature fields of the Hengill area. Generally, the rock cuttings are obtained every 2 m in each borehole during drilling and studied in order to develop the stratigraphic section of rocks and to study the degree and kind of hydrothermal alteration. It is possible to make a geological cross-section by combining the analysis of the rock cuttings and the available logging data. One such geological cross-section, made through the western part of the Ölfus region is shown in Figure 2 (Saemundsson and Fridleifsson, 1992). It has a direction of N40˚E, going from northeast and a well in Hveragerdi (H-6), through Kröggólfsstadir, Núpar, Thurá, Thóroddsstadir, Riftún, Bakki 3 (EB-01), Bakki 1 (BA-01), Bakki 2 (HJ-01) and Hjallakrókur, Laekur, Hlídardalsskóli and Litlaland, just north of Thorlákshöfn town. There is a some gap in the section due to lack of wells between Thurá and Núpar.

The cross-section shows various features. Five groups of geological formations can be recognized, including the different tuffs of the Hálsa-, Ölfus- and Hreppa formation, basaltic lava and surface alluvium or sediment. As shown in the cross-section (upper part of Figure 2), all the formations are nearly horizontal; most of them have an inclination of 2-4˚. The location of each well and their depths are shown in the cross-section. The temperature distribution, based on the information from temperature logging, is also shown in the section. The highest temperature is 190˚C close to the bottom of the deepest well, Litlaland (which is 2200 m deep). The temperature of the other wells is lower than 150˚C so they are classified as low-temperature wells, according to the Icelandic definition. The secondary minerals are shown in the lower part of Figure 2, based on studies of the of cuttings. Three alteration zones can be distinguished in this section, a laumontite zone, chlorite and wairakite zone and epidote zone.

Normally in Icelandic low-temperature geothermal areas (temperature <150˚C in the uppermost 1 km), four distinct zeolite zones are found, corresponding to distinct formation-temperature intervals (Kristmannsdóttir and Tómasson, 1978). In the order of increased formation temperatures these zones are; the uppermost chabazite zone, the mesolite /scolecite zone, the stilbite zone and the lowermost

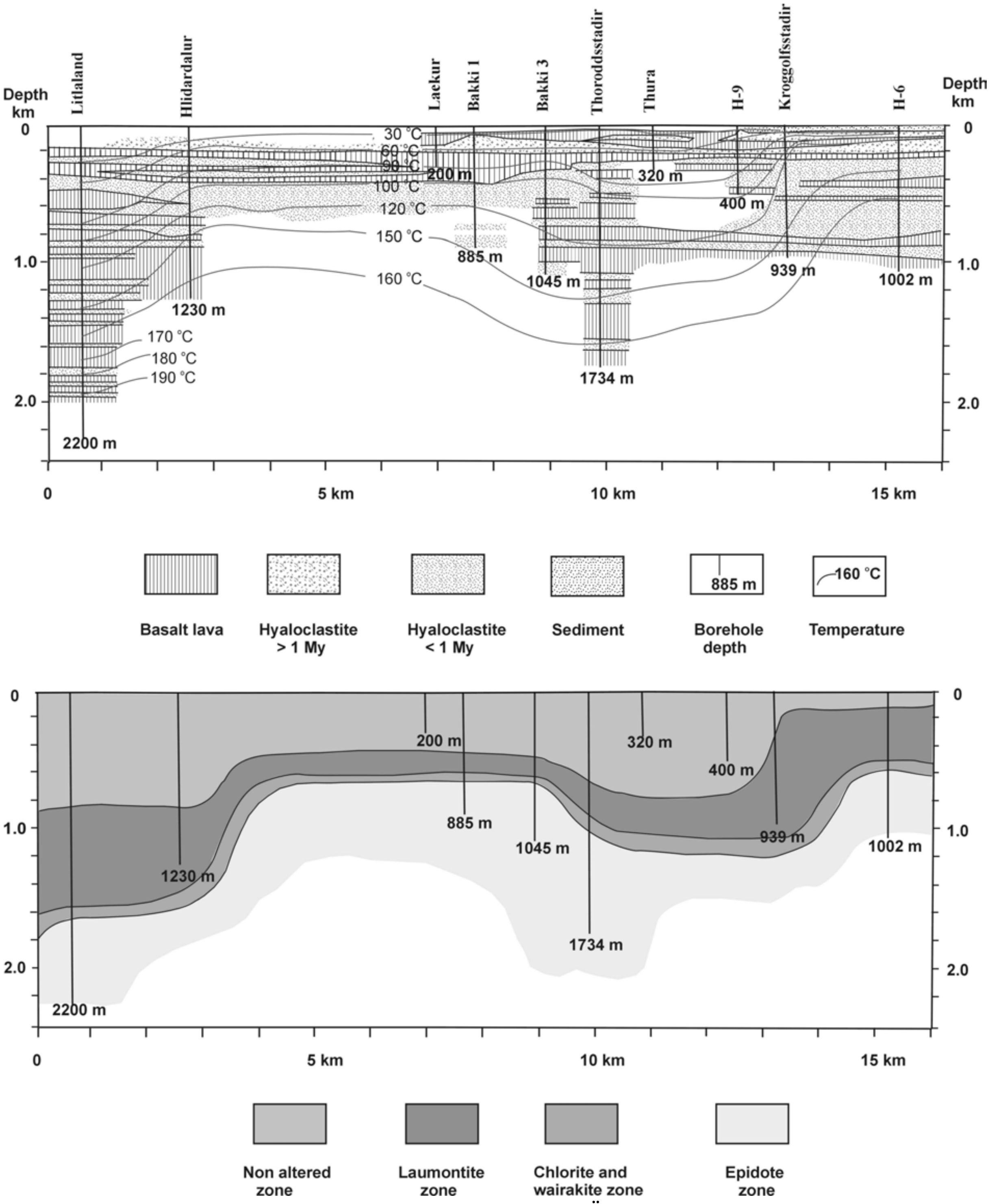

FIGURE 2: Cross-section through wells in the Ölfus region striking N40˚E;
a) Geological section; b) Alteration zones (Saemundsson and Fridleifsson, 1992)

laumontite zone. Relict alteration is found in an area surrounding two nearby Quaternary volcanic centers. Epidote is always relict, and its retrograde transformation to prehnite has been observed. The clay minerals are partly relict and partly formed by the most recent low-temperature geothermal activity. Therefore, the occurrence of the epidote zone in this area suggests former high-temperature activity which is now extinct. The area has since drifted out of the active volcanic zone.

Some geophysical studies, mainly Schlumberger resistivity soundings, were carried out in the Bakki area prior to drilling. The results from Schlumberger and later TEM soundings indicate that there is an extensive area of low resistivity, 4-8 Ωm at 800 m b.s.l. The 5 Ωm contour line encloses the area of main activity and, hence, can be said to define the boundaries of the main field (Georgsson, 1989). The TEM method has given good resolution of the resistivity structure in the uppermost kilometre at Bakki. The low-resistivity layer at a depth of 200-850 m is the main feed zone for geothermal water at a temperature of 100-150˚C. Deeper low-resistivity structures at Bakki may be related to the upflow zone. The results of the combined interpretation of TEM and MT soundings show a deep (> 5 km) low resistivity layer at Bakki that may be related to the heat source (Onacha, 1990).

2.2 Reservoir rocks and alteration

Basalt lavas are the most common volcanic rocks in Iceland. The primary mineral composition of basaltic rocks in Iceland is relatively uniform, comprising calcium rich plagioclase, clinopyroxene, olivine and magnetite-ilmenite ore minerals. If the basaltic magma cools rapidly, quenched volcanic glass results. Hyaloclastite tuff may be composed of volcanic glass only, while the breccias and the lavas range in glass content from a lot to little or none. Under the influence of hydrothermal fluids, primary minerals alter to similar and/or different alteration minerals as follows:

Glass alters mostly to clays, sphene (titanite), epidote, calcite, zeolite and quartz. Olivine alters to iddingsite or clays, sphene, calcite or sulphides. Pyroxene is relatively resistant to hydrothermal alteration but alters mainly to clays. Plagioclase is also relatively resistant to alteration but it starts to alter to clay minerals and in accordance with increasing temperature it alters to albite, calcite, sphene, chlorite, epidote and adularia. Wairakite is a common replacement mineral of plagioclase phenocrysts. Iron ore minerals alter to sphene and sulfides, usually pyrite and pyrrhotite. In general, the order of decreasing susceptibility to alteration is glass, olivine, pyroxene and plagioclase. Due to more extensive alteration in deeper parts of the well, deeper cuttings are light coloured while shallower cuttings are darker and the quantity of the alteration minerals is in direct proportion of the water/rock ratio (Nouraliee, 2000).

The lithology in wells BA-01 and HJ-01 is shown in Figure 3. There are mainly basalt lavas, basaltic hyaloclastites and clastic sediments of young Quaternary age; the surface is covered by alluvium. The

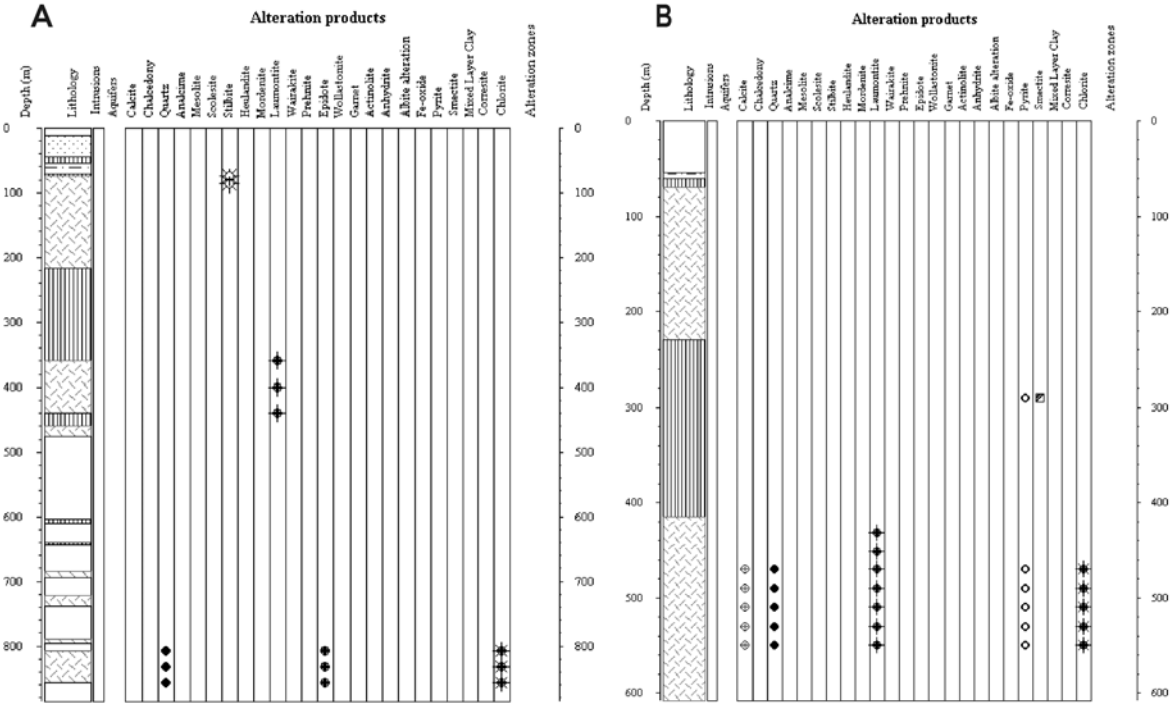

FIGURE 3: Lithology and distribution of hydrothermal alteration minerals, a) BA-01; and b) HJ-01

basalt lavas are olivine-tholeiite or tholeiite; some of the fresh hyaloclastites breccia is fresh looking glass. In well HJ-01, the basalt lavas are pillow lavas. Most of the rocks are altered due to the water-rock interaction. The most abundant alteration minerals in these two wells are stilbite, laumontite, quartz, chlorite, pyrite, smectite and epidote. In well BA-01, stilbite is found at 74-86 m depth. Laumontite is found at 360-460 m depth, while epidote, quartz and chlorite are found at 808-856 m depth. In well HJ-01, smectite and pyrite are found at 290-296 m depth. Laumontite is found at 432-470 m depth, while at 470-540 m depth a very clear alteration zone is found with the minerals quartz, chlorite, pyrite and laumontite.

The minerals found in the two studied wells include epidote whose formation temperature requires at least 230°C as well as chlorite, which also needs at least 200°C formation temperature (Kristmannsdóttir, 1979). It is, thus, clear that this low-temperature geothermal field was formerly a high temperature field, now extinct, and has since drifted out of the active volcanic zone by the spreading of the mid ocean ridge.

Another characteristic feature of the reservoir rock is quite high content of salt due to the repeated transgression of the sea over the land during the build-up of the rock formations. This has resulted in slightly saline groundwater in the region. The permeability of the rock formations is generally high and the field is fractured with northeast trending faults and fissures, resulting in high transmissivity and fairly well-yielding geothermal wells.

2.3 Utilization istory

The water from wells BA-01 and HJ-01 is utilized for a district heating system, hitaveita, in the town of Thorlákshöfn with about 1200 inhabitants, and also for nearby fish farms. The water is piped to the town in an insulated steel pipeline and distributed to the houses in steel pipes. In each house a heat-exchanger has been installed, as there is a potential risk of calcium carbonate scaling. There is also a risk of steel corrosion in this hitaveita, due to the salinity of the water. The water is not directly corrosive as it leaves the separator at wellhead, but there is a risk of oxygen uptake due to the drop in pressure in house installations. There were no major problems in the operation of the system during the 11 years of exploitation from 1979 to 1990 (Kristmannsdóttir et al., 1990b). Minor scaling has occurred in heat-exchangers and separators, but it has been manageable by simple cleaning with a product of acid solution.

When the hitaveita started operation in 1979 only well BA-01 was used. In May 1987 well HJ-01 was connected to the distribution system. The pressure and temperature at wellhead and the discharge have been monitored regularly. The geothermal water was analysed just after drilling, and during utilization the chemical composition of the geothermal water was monitored regularly. Minor changes of temperature or pressure at wellhead have been observed. The chemistry of water from well BA-01shows almost no change since the start of utilization. But for well HJ-01, remarkable changes in the chemistry of the water were noticed in late 1987, only a few months after connection to the distribution net. As the main change appeared to be the dilution of the geothermal water with fresh water, it was suspected that an inflow of colder groundwater through damaged casing was causing the chemical changes. The inflow was found to be from the bottom aquifer in well HJ-01 which was subsequently sealed by cementing in late 1990. After the bottom aquifer was sealed off, the water seemed to be slowly regaining its original chemical composition (Kristmannsdóttir and Sveinbjörnsdóttir, 1992). But so far, the original chemical composition and isotopic value have not been reached.

3. METHODOLOGY

3.1 Calculation of chemical equilibrium

Thermodynamic geochemical approaches based on theoretical calculations and modelling have become increasingly useful as tools for understanding the various processes occurring in hydrothermal systems.

Calculations of chemical equilibrium have been applied in 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 mineral *k* in terms of log $(Q/K)_k$:

$$\log(Q/K)_k = \log\prod^{i} a_{i,k}^{v_{i,k}} - \log K_k \tag{1}$$

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

The numerical value of log $(Q/K)_k$ is greater than zero for supersaturated minerals and less than zero for undersaturated minerals. By plotting log *Q/K* vs. temperature for geothermal water, it is possible to determine

a) Whether the water was in equilibrium with a host rock mineral assemblage;
b) Probable minerals in the equilibrium assemblage; and
c) The equilibrium temperature.

The speciation program WATCH (Arnórsson et al., 1983; Bjarnason, 1994) has been used to do the equilibrium calculations. Due to the fact that the different minerals have different accuracy for both equilibrium constant and reaction quotient, this program gives no simple answer for how much difference would be significant for non-equilibrium. For example, simple minerals such as calcite, quartz, chalcedony, fluorite and anhydrite, solubility is accurately known, within 0.1-0.2 log *K* units. Thus, if no other errors are involved, the conclusion of an existing equilibrium is only safe if the differences between log *Q* and log *K* is within 0.1-0.2 log units. But for complex Al silicates, the uncertainties in calculated log *K* values are frequently of the order 0.5 log units and even higher (Arnórsson, 2000a).

3.2 Geothermometry

Using geothermometers to predict subsurface temperatures and the response of geothermal reservoirs to the production load is one of the most important applications of geochemistry for both exploration and monitoring of geothermal resources. Geothermometers have been classified into three groups, water or solution geothermometers, steam or gas geothermometers and isotope geothermometers. Water and steam geothermometers are collectively termed chemical geothermometers. When geothermometers are applied to estimate surface or aquifer temperature, there is a basic assumption that a temperature-dependent chemical or isotope equilibria prevails in the source aquifer. Further, that the chemical and isotopic reactions do not significantly modify the composition of the fluid as it ascends from the source aquifer to the point of sampling, whether it is a thermal spring, fumarole or wellhead.

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 temperature due to lack of equilibrium between the solution and 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. The water geothermometers used in the WATCH program and this report are listed here below.

Chalcedony geothermometer, 0-250˚C (Fournier, 1977):

$$t(°C) = \frac{1032}{4.69 - \log SiO_2} - 273.15 \tag{2}$$

Quartz geothermometer, 20-330˚C (Fournier and Potter, 1982):

$$t(°C) = -42.2 + 0.28831\, SiO_2 - 3.6686\times10^{-4}\,(SiO_2)^2 + 3.1665\times10^{-7}\,(SiO_2)^3 + 77.034 \log SiO_2 \tag{3}$$

Na/K geothermometer, 0-250˚C (Arnórsson et al., 1983):

$$t(°C) = \frac{933}{0.993 - \log(Na/K)} - 273.15 \tag{4}$$

Na-K-Mg-geothermometer. Giggenbach (1988) suggested that a triangular diagram with Na/1000, K/100 and √Mg at the apices can be used to classify water as being in full equilibrium, partial equilibrium or immature (dissolution of rock with little or no chemical equilibrium). The triangular diagram is employed to determine whether the fluid has equilibrated with hydrothermal minerals as well as to predict the equilibration temperatures. It is based on the temperature dependence of the three following reactions:

$$K\text{-}feldspar + Na^+ = Na\text{-}feldspar + K^+ \tag{5}$$

$$2albite + 0.8K\text{-}feldspar + 1.6water + Mg^{2+} = 0.8muscovite + 0.2clinochlore + 5.4silica + 2Na^+ \tag{6}$$

$$2.8\ K\text{-}feldspar + 1.6\ water + Mg^{2+} = 0.8\ muscovite + 0.2\ clinochlore + 5.4\ silica + 2\ K^+ \tag{7}$$

All involve minerals of the full equilibrium assemblage that are expected to form after isochemical recrystallization of average crustal rock under geothermal conditions. Na, K and Mg contents of water in equilibrium with this assemblage are accessible to rigorous evolution (Giggenbach, 1991). The theoretical temperature dependence of the corresponding concentration quotients may then be used to derive the two geothermometers:

$$t_{kn} = 1390 / (1.75 - L_{kn}) - 273 \tag{8}$$

and

$$t_{km} = 1390 / (1.75 - L_{km}) - 273 \tag{9}$$

where L_{kn} = $\log(C_K/C_{Na})$;
L_{km} = $\log(C_K^2/C_{Mg})$, C_i in mg/kg.

Individual application of Equations 8 and 9 frequently leads to significantly different apparent temperatures of equilibration. This observation is readily explained in terms of differing rates of re-adjustment of the two reactions to changes in the physical environment encountered by the rising water. Reaction 9 is found to respond much faster and, therefore, gives usually lower temperature estimates. The values of L_{km} are also very sensitive to the admixture of non-equilibrium and acid water, while L_{kn} is much less affected by such shallow processes. By combining the two sub-systems, a method allowing an assessment of the degree of water-rock equilibrium and eliminating unsuitable samples is obtained.

3.3 Modelling studies

The program CHILLER, a program for computing water-rock reactions, boiling, mixing and other reaction processes in aqueous-mineral-gas systems, has been executed for both a mixing model of geothermal fluids with cold groundwater, and water-rock interaction inverse modelling study.

CHILLER, which composes the two parts, SOLVEQ and CHILLER, is a FORTRAN computer program for computing multicomponent heterogenous chemical equilibria among solids, gases and an aqueous phase, which applies a numerical method to solve a system of mass-balance and mass-action equations, together with a heat balance equation if needed (Reed, 1982). SOLVEQ is used primarily for processing water analyses of all types, but is also useful for certain types of modelling of geochemical processes. For a given temperature and total composition of a homogeneous aqueous solution, SOLVEQ computes the activities of all aqueous species and the saturation indices of solids and the fugacities of gases. SOLVEQ also calculates partial heterogeneous equilibrium, wherein equilibration of given water with specified minerals or gas fugacities can be forced. The forced equilibria fix the total concentrations of specified component species. SOLVEQ's forced mineral equilibrium capability, combined with its ability to calculate pH at high temperature from a pH measurement at low temperature, make it useful for processing hydrothermal experimental run products and for geothermometry and other studies of geothermal and oil field water (Spycher and Reed, 1998).

CHILLER was originally a program for modelling mineral precipitation during cooling of hydrothermal solutions or the reaction of solutions with rock. CHILLER then absorbed the rock titration capability of MINSOLV and has been further improved to include fluid-fluid mixing, gas or rock titrations, boiling, condensation, and evaporation. Because the equilibria between the different phases are computed with respect to an aqueous phase, CHILLER is not suitable for modelling processes that do not include an aqueous phase. For a given temperature, pressure, and total composition of a chemical system, CHILLER computes the compositions of the aqueous, solid, and gas phases at equilibrium. For a chemical system including a gas phase, enthalpy, instead of pressure, can be specified. The saturation pressure is then computed using a heat balance equation that takes into account the temperature, enthalpy, and composition (Spycher and Reed, 1988; Reed and Spycher, 1998). To model geochemical processes, CHILLER provides for stepwise incremental changes in T, P, enthalpy or composition with re-calculation of the equilibrium phase assemblage, mineral compositions and aqueous composition after each step. CHILLER is a sophisticated program for computing complex chemical processes. It is most successful in the hands of those who have a good working knowledge of the chemistry of aqueous systems and those who carefully set up runs to evaluate well-formulated chemical hypotheses. Often it is necessary to make six or ten runs to evaluate an idea, changing the input between runs on the basis of the previous results (Reed and Spycher, 1998).

One special use of CHILLER for treatment of oxidation-reduction processes is to allow the use of negative amounts of H^+, SO_4^{2-} and HS^- and to include a mass balance on water. The increasingly negative value of M_H^+ with rock titration can be understood in terms of the dissolution of oxide rock components according to reactions such as the following:

$$CaO_{(rock)} + 2\,H^+_{(aq)} = Ca^{2+} + H_2O \tag{10}$$

From Equation 10, it is apparent that one mole of CaO contains two negative moles of H^+. The dissolution of CaO in the aqueous phase consumes H^+ from the system, which causes pH to increase. The precipitation of most minerals involves the reverse of the above-mentioned reactions. Such hydrolysis adds H^+ to the aqueous phase through the effect of H^+ mass balance by adding negative H^+ to the produced solids.

4. GEOCHEMISTRY OF FLUIDS

For the present study only two wells, BA-01 and HJ-01, used for the same district heating system, were selected. All available geochemical data, including the chemical monitoring data were compiled. Both wells have been free flowing for most of the production time. The temperature at the wellhead is about

116-120˚C for well BA-01 and 107-110˚C for well HJ-01. The water is flashed in a wellhead separator to atmospheric pressure. A downhole pump was bought after the earthquake in November 1998 and installed in well HJ-01. In July 2000 the maximum downhole temperature in well BA-01 was 137˚C and originally it was 119˚C in well HJ-01. The water is slightly saline and in the beginning water in both wells contained approximately 650-700 mg/l of chloride. Table 1 shows the water composition of well BA-01 during the years 1979 to 2000, Table 2 shows similar data from well HJ-01.

TABLE 1: Chemical composition of water from well BA-01 (mg/l)

Data no.	**197907 0018**	**198501 0006**	**198701 0009**	**198801 0008**	**198901 0023**	**199001 0004**	**199101 0007**	**199201 0022**	**199301 0002**	**199401 0002**	**199501 0006**	**199601 0037**	**199701 0004**	**199801 0073**	**199901 0048**	**200001 0025**
MWT (ºC)	126?	116	111	117	117.5	118	119	121	116	118	120	118	117	118	118	-
pH/T (ºC)	8.8/20	8.71/22	8.89/23	8.91/22	8.87/24	8.88/24	8.69/24	8.68/22	8.9/22	8.78/24	8.9/23	8.9/22	8.9/21	8.8/22	8.8/22	8.92/24
CO_2	6.7	7.7	6.8	10.2	6.4	6	7.8	10	3.6	6.2	5.3	6	9.5	6.4	5.1	2.9
H_2S	0.5	0.29	0.36	0.47	0.37	0.27	0.61	0.64	0.48	0.46	0.49	0.66	0.65	0.64	0.61	0.62
B	0.33	-	-	-	0.27	0.27	0.26	0.27	0.28	0.25	-	0.27	0.27	0.26	0.26	0.26
SiO_2	134	133	130	131	131	131	129	129	131	131	130	130.1	129.5	132	130	127
Na	388	386	407	395	396	397	389	399	397	389	390	387	397	396	397	393
K	19.6	19.2	17.9	18.2	19.0	19.3	19.5	17.5	17.8	17.1	19.2	17.2	17.2	18.8	17.5	17.3
Mg	0.02	0.015	0.023	0.03	0.02	0.016	0.01	0.009	0.1	0.008	0.004	0.012	0.009	0.011	0.014	0.012
Ca	67.1	74.37	73.86	72.9	70.9	69.9	76.1	71.5	78.4	71.4	72	68	71.5	72	71.9	68.3
F	0.55	0.50	0.5	0.52	0.54	0.49	0.50	0.49	0.52	0.51	0.52	0.5	0.49	0.47	0.5	0.36
Cl	659	634	658	654	649	637	650	655	676	658	626	655	634	628	647	650
SO_4	123	121	125	121	123	120	115	118	122	119	116	118	111	119	118	115
Al	0.07	0.08	-	-	0.068	0.069	0.078	0.078	0.07	0.064	-	0.065	0.062	0.06	0.06	-
Fe	0.021	-	0.07	0	0.05	-	-	0.031	0.007	0.016	-	0.007	0.015	0.007	0.011	-
TDS	1513	1470	1505	1423	1468	1470	1474	1444	1432	1412	1310	1415	1476	1380	1390	1398
δ^2H	-	-	-71.8	-71.3	-72.3	-70.1	-72.6	-	-	-	-	-74.9	-69.6	-70.4	-71.5	-73.2
$\delta^{18}O$	-	-9.35	-9.22	-9.21	-9.25	-9.23	-9.26	-9.26	-9.23	-9.19	-9.21	-9.13	-9.14	-9.21	-9.15	-9.15
Qu	150	150	147	148	147	148	148	149	148	149	147	147	147	149	148	145
Ch	125	125	121	122	122	122	123	123	122	123	122	122	121	124	123	119
Na/K	135	134	123	127	131	132	134	123	125	123	133	124	122	130	124	123

MWT: Measured wellhead temperature; δ^2H in ‰$_{SMOW}$, $\delta^{18}O$ in ‰$_{SMOW}$
Chemical geothermometers: Qu - Quartz (Fournier & Potter, 1982); Ch - Chalcedony (Fournier, 1977); Na/K (Arnórsson et al., 1983)

TABLE 2: Chemical composition of water from well HJ-01 (mg/l)

Data no	**198501 0007**	**198701 0010**	**198801 0097**	**198901 0022**	**199001 0003**	**199101 0003**	**199201 0021**	**199301 0025**	**199401 0001**	**199501 0007**	**199601 0038**	**199701 0003**	**199801 0074**	**199901 0045**	**200001 0024**
MST (˚C)	108	102	99	99	100	100	99	99	98	98	99	99	100	100	100
pH/ T(˚C)	8.72/22	8.82/23	8.94/23	9/24	9.02/24	9.05/24	9.04/22	8.98/24	8.93/23	9.1/23	9.8/22	9.1/21	9/22	9/21	9.2/22
CO_2	8.7	8.8	9.8	6.4	7.7	8.6	8.1	6.3	6.8	6.8	8.5	10.3	8.1	6.9	4.3
H_2S	0.3	0.26	0	0.1	0.13	0.12	0.1	0.15	0.14	0.16	0.21	0.2	0.2	0.19	0.18
B	-	-	-	0.2	-	0.19	-	-	-	-	0.19	0.18	0.19	0.16	0.18
SiO_2	118	118	114	109	109	110	111	113	110	110	108	105	104	105	101
Na	402	427	322	300	282	260	293	281	276	279	268	279	282	294	281
K	17.3	15.8	14.0	11.6	11.1	11.2	10.8	10.3	10	11	9.8	9.9	11	10.3	10.8
Mg	0.024	0.021	0.06	0.021	0.007	0.0006	0.003	0.011	0.008	0.008	0.009	0.009	0.001	0.016	0.014
Ca	86.8	78.56	55.79	44.1	36.4	35.1	39.4	42.3	38.9	40.4	34.6	39.8	40.5	43.4	47.6
F	0.47	0.48	0.53	0.5	0.54	0.56	0.53	0.53	0.53	0.53	0.54	0.5	0.47	0.5	0.4
Cl	682	674	525	463	415	396	435	452	441	419	424	453	429	442	477
SO_4	127	128	100	94	83	75	84	83	82	79	79	75	83	84	85
Al	0.06	0.06	0.07	0.073	0.084	0.1	0.093	0.093	0.095	-	0.085	-	0.079	0.08	-
Fe	-	0.06	0	0	0	-	0.006	0.030	0.006	-	0.002	0.003	0.002	0.004	-
TDS	1546	1555	1160	1076	989	939	1005	926	980	950	952	984	1100	940	998
δ^2H	-	-71.0	-65.4	-64.2	-65.6	-64.6	-	-	-	-	-66.8	-62.1	-64.9	-63.8	-64
$\delta^{18}O$	-9.39	-9.21	-8.86	-8.8	-8.79	-8.67	-8.71	-8.7	-8.68	-8.67	-8.71	-8.04	-8.7	-8.74	-8.68
Qu	143	142	139	137	135	136	137	138	137	137	135	134	134	135	132
Ch	117	116	113	110	108	109	110	111	111	110	108	107	106	107	105
Na/K	122	110	123	114	115	122	110	110	109	115	110	108	114	107	113

MST: Measured separator temperature in degree; Others are the same as in Table 1.

4.1 Classification of fluids

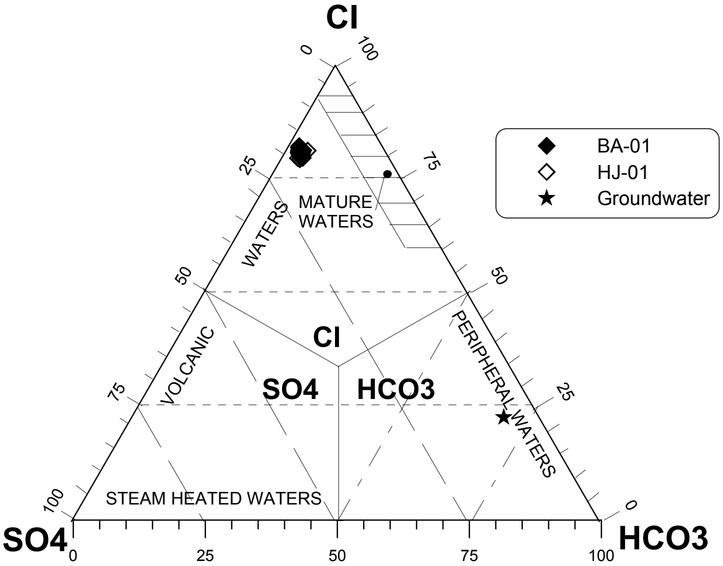

FIGURE 4: Cl-SO_4-HCO_3 triangular diagram for the fluids from wells BA-01, HJ-01 in Bakki geothermal field and local groundwater

The Cl-SO_4-HCO_3 triangular diagram (Giggenbach, 1991) classifies geothermal water on the basis of major anions, i.e. Cl, SO_4 and HCO_3. The source of Cl is seawater and rock dissolution, while for SO_4, a small amount comes from seawater; a large amount is usually derived from the oxidation of sulphide in volcanic steam. Carbonates are present at the periphery of high-temperature systems. CO_2 is obtained by the degassing of volcanic formations like deep-seated intrusions. In cold water, carbonates originate from biological sources. High concentrations of sulphate and carbonates, thus obtained, give erroneous geothermometer results. In some old magmatic systems, equilibrium with alteration minerals is established in the presence of excess sulphate in the water and water acidity is not increased.

The chemical compositions of the fluids from both the studied wells of Bakki geothermal area (Figure 4) belong to Cl-rich geothermal water which may suggest that the geothermal water is of seawater origin or that the Na and Cl could be obtained by transgressions of the sea over the rock formations, resulting in reservoir rocks containing quite a high content of salt.

4.2 Changes during utilization

4.2.1 Chemical changes

As mentioned before well, BA-01 has been utilized for the heating system from 1979 and has not exhibited noticeable changes. But chemical changes indicating inflow of colder water were noticed only a few months after well HJ-01 was connected to the heating system. The chemical monitoring is mainly from 1985, but the chemical composition is available for well BA-01 from 1979 (Table 1). Figure 5 shows the changes in silica, sulphate, sodium and chloride over time. It shows some minor changes in the chemical composition in well BA-01 with a tendency for a slight decrease in silica. But for the well HJ-01, there is a noticeable decrease of chemical concentration over time, during the 15 years of utilization. Silica has dropped from 118.3 to 101.2 mg/l, sodium changes from 402.1 to 281 mg/l, sulphate changes from 127.3 to 85.3 mg/l and chloride from 682.4 to 477 mg/l. The biggest change happened between 1987 and 1991. Five downhole samples were taken from different aquifers in this well in the early 1990, and results of chemical analyses clearly show the inflow of colder water at the bottom (Table 3 and Figure 6) (Kristmannsdóttir and Sveinbjörnsdóttir, 1992). In late 1990, the bottom aquifer in well HJ-01 was sealed off by cementing and the water chemistry recovered somewhat, but chemical monitoring shows that it has not fully recovered.

As shown in Figure 7 there is also a notable change in stable isotopic composition in HJ-01, both in oxygen 18 and deuterium, while well BA-01 is more stable, especially in oxygen 18.

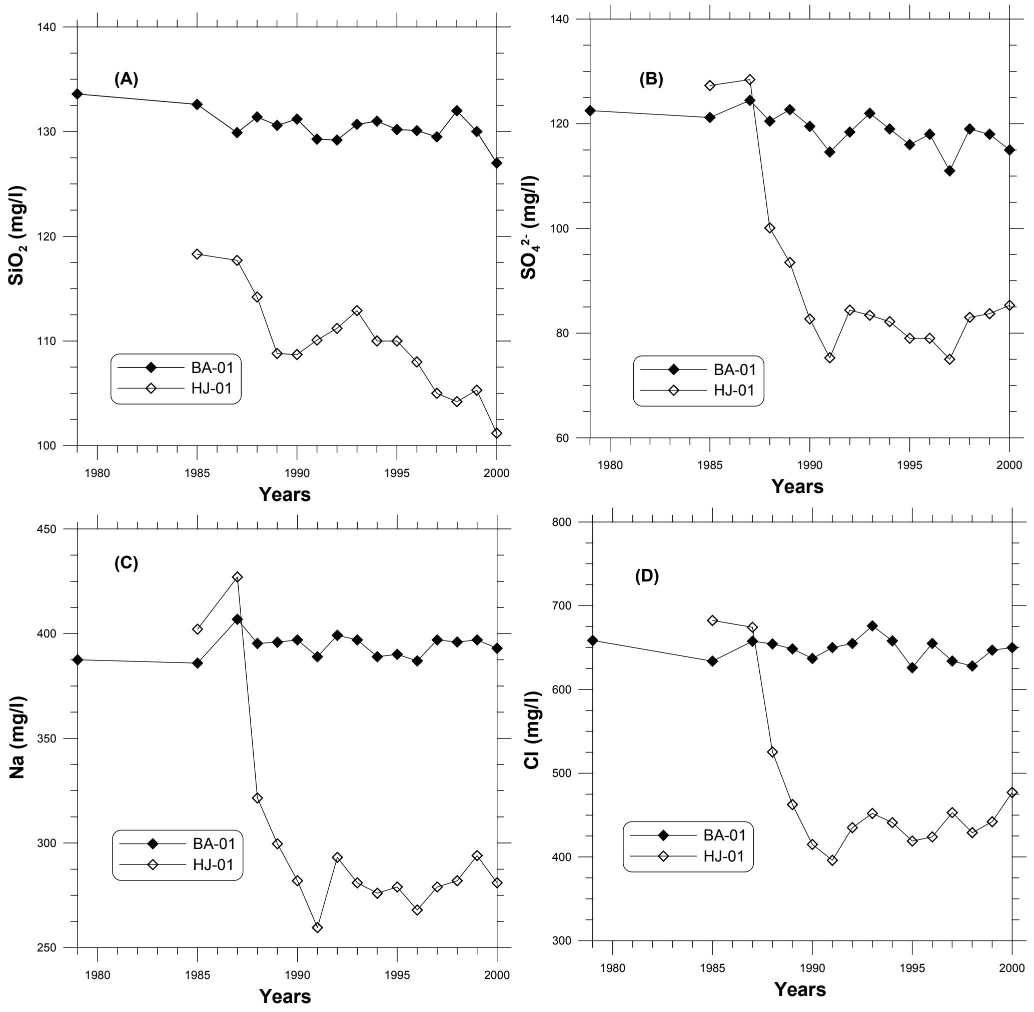

FIGURE 5: Changes in chemical composition for wells BA-01 and HJ-01 over time

TABLE 3: Chemical composition of water from well HJ-01 at different depths (mg/l) in 1990

Data no.	**19900216 0017**	**19900216 0016**	**19900216 0012**	**19900216 0013**	**19900216 0014**	**19900216 0015**
Depth (m)	0	410	70	425	480	583
Flowrates (l/s)	5	5	15	15	15	15
Mea. temp (˚C)	116.8	118.5	114.5	115.4	106.5	104
pH/T (˚C)	9.03/23	8.87/24	8.89/23	8.78/22	8.94/23	8.98/23
CO_2	6	9	12	12	11	11
H_2S	0.2	<0.003	0.10	<0.003	<0.003	<0.003
Br	1.58	1.53	1.42	1.42	1.23	1.09
SiO_2	114	110	105	105	95	91
Na	290	287	258	263	232	208
K	12.0	11.9	10.6	10.7	8.4	7.2
Mg	0.008	0.009	0.017	0.035	0.011	0.009
Ca	43	41	37	37	32	26
F	0.56	0.52	0.52	0.51	0.50	0.50
Cl	442	431	398	398	344	303
SO_4	88	87	81		70	64
TDS	1046	1027		936	832	750
$\delta^{18}O$	-8.8	-8.9	-8.2	-9.0	-8.7	-8.5
Qu	138	138	135	136	129	127
Ch	111	111	108	109	102	99
Na/K	119	119	118	118	109	106

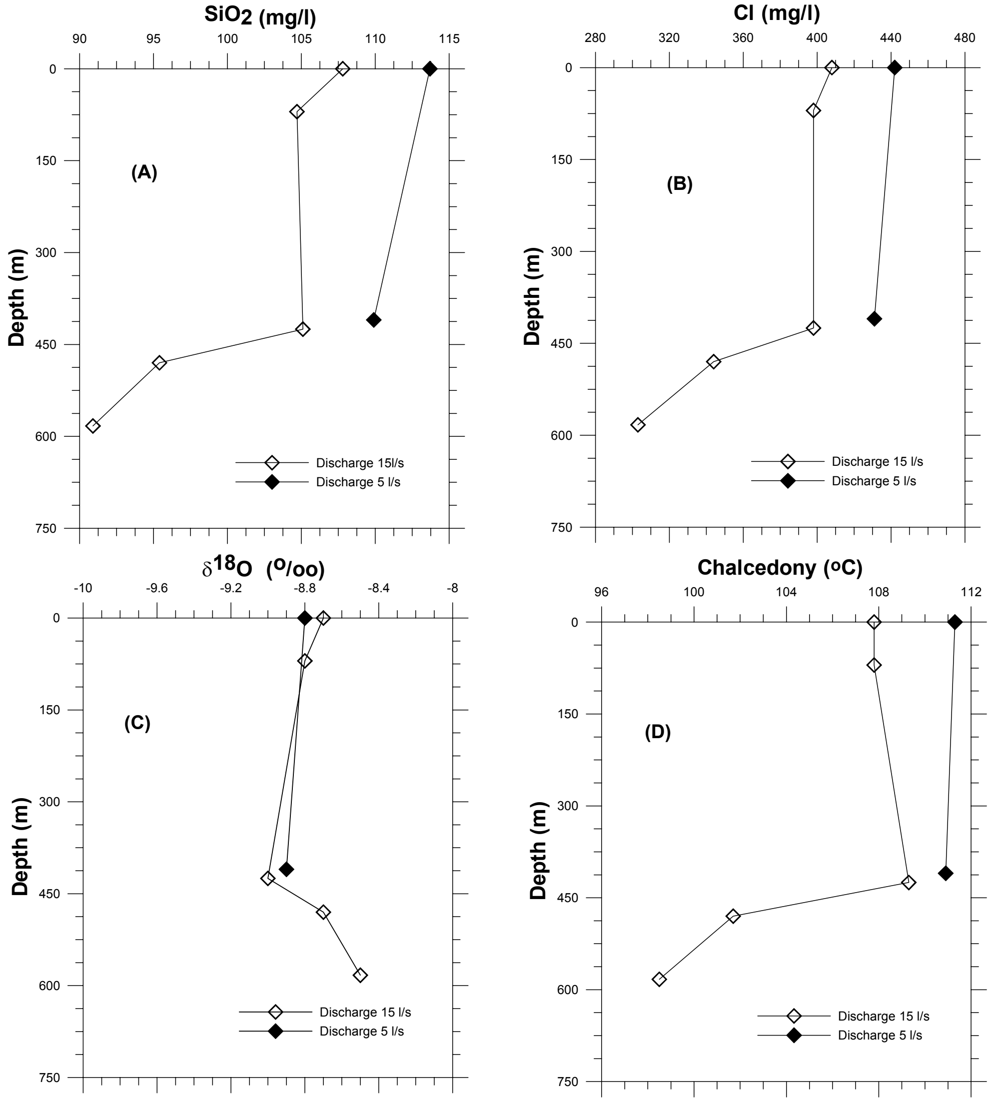

FIGURE 6: Concentration of silica, chloride, δ^{18}O and calculated chalcedony temperature vs. depth in well HJ-01at different flowrates

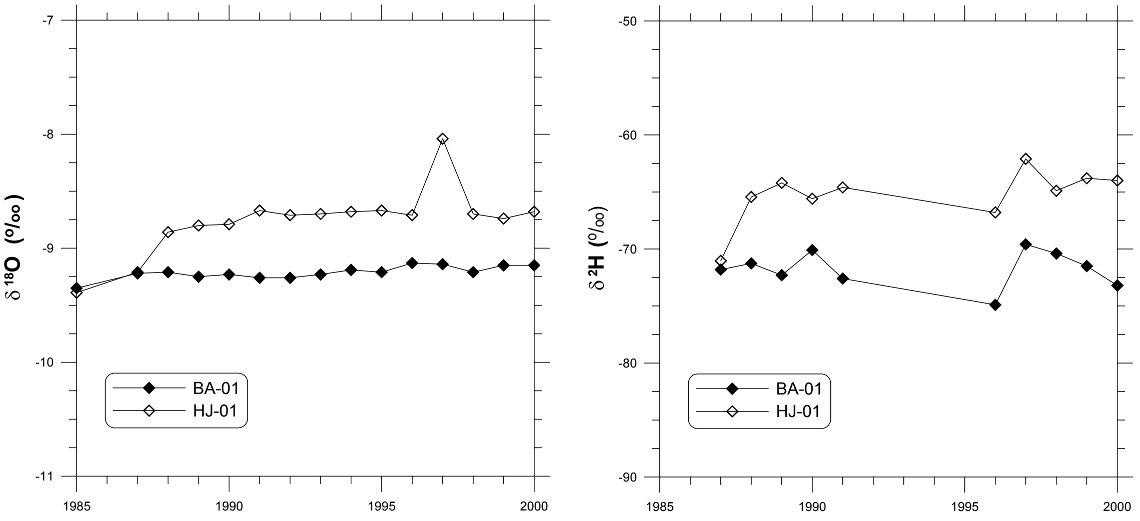

FIGURE 7: Changes over time of stable isotopic ratios, δ^{18}O and δ^{2}H, for water in wells BA-01 and HJ-01

4.2.2 Temperature changes

For well BA-01, measured wellhead temperature does not appear to have changed significantly over time (Table 1), most years being around 119˚C with a difference of less than 2˚C, except in 1979 and 1987, when the measured wellhead temperature was 126˚C and 111˚C, respectively. The reason is not exactly known, but most likely it is a measurement error.

For well HJ-01, measurements are only available as the separator temperature, so geothermometry methods must be used to estimate the temperature changes. In this report, three kinds of geothermometry calculations have been used to uncover the subsurface temperature and the temperature changes occurring during utilization. Firstly quartz, chalcedony and Na-K geothermometry temperatures were calculated by the WATCH program; secondly, the Na-K-Mg triangular diagram was used, and thirdly the log *Q/K* vs. temperature diagram was utilized.

Quartz, chalcedony and Na-K temperature change: The WATCH program calculates three kinds of geothermometers, giving quartz, chalcedony and Na-K temperature. The calculated temperatures are shown in Figure 8.

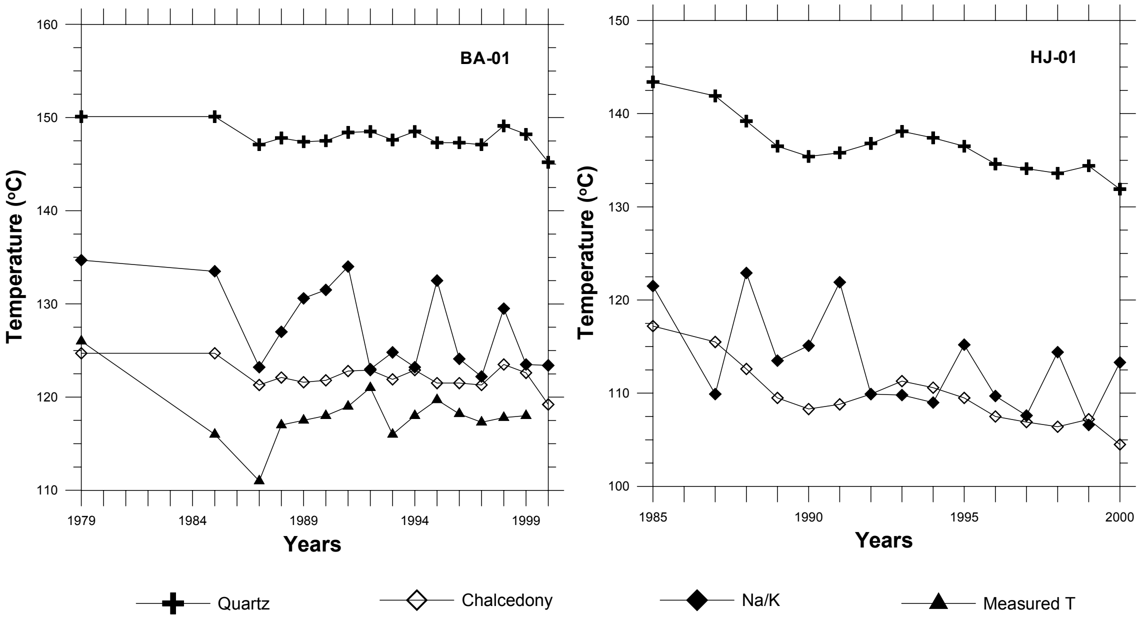

FIGURE 8: Changes over time of measured temperature at wellhead and geothermometer temperatures for quartz, chalcedony and Na/K, calculated by the WATCH program for the production wells at Bakki geothermal field

In low-temperature geothermal systems, chalcedony rather than quartz, predominately controls the silica-fluid equilibrium, so the calculated chalcedony temperatures are always closer to the real temperature. Corresponding to the chemical changes, there is nearly a 9˚C drop in calculated chalcedony temperature in well HJ-01during the years 1985-1990.

The Na-K-Mg triangular diagram (Arnórsson et al., 1983; Giggenbach, 1988) has been proven to be a powerful tool for the evaluation of conditions deep within geothermal systems. Figure 9 shows that most of the fluids in wells BA-01 and HJ-01 are fully equilibrated or nearly fully equilibrated at reservoir temperature. The t_{kn} temperature varies within the range of 160-180˚C. The t_{km} temperature shows, however, more scatter, from 240 to 140˚C, but most fall between 200 and 160˚C. The main reason is that the K-Mg geothermometer adjusts faster to a change in temperature than the K-Na system.

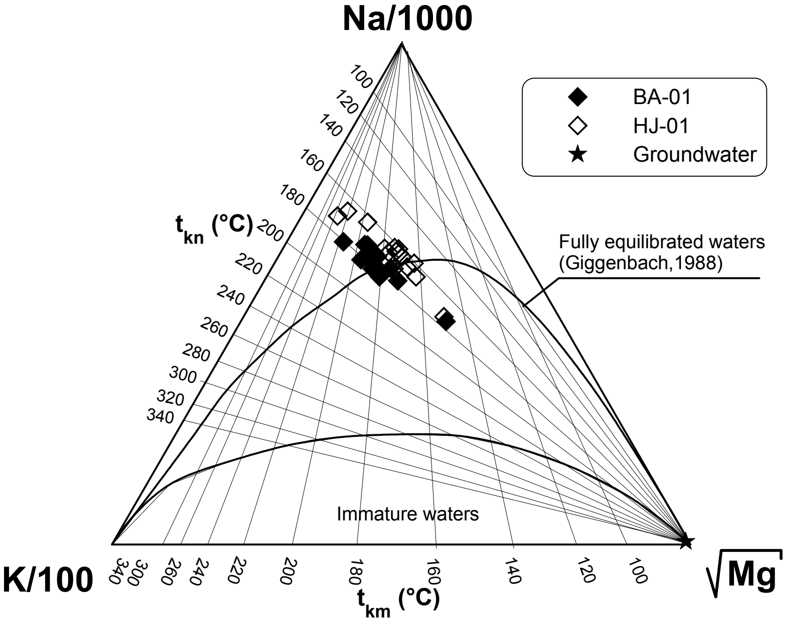

FIGURE 9: Na-K-Mg triangular diagram for the fluids of wells BA-01 and HJ-01 in Bakki geothermal field

Log Q/K diagram: The WATCH program has been used to make the log *Q/K* diagram. Generally it contains the following steps: firstly, the ionic balance for all data considered in the area was evaluated, and data with less than 10% difference between cation and anion concentration were selected for the study. Secondly, saturation indices, with respect to a number of hydrothermal minerals potentially present in the geothermal system, were calculated at varying temperatures by means of WATCH (may be calculated by other programs like SOLVEQ). The plausible alteration minerals in the system were selected with reference to some available records of alteration minerals in the feed zones of the wells. The log *Q/K* vs. temperature diagrams for the wells BA-01 and HJ-01 at different times are shown in Figures 10-11. The calculated saturation index (*SI* = log *Q*/log *K*) vs. temperature for water from well BA-01 is shown in Figure 10, and for well HJ-01 in Figure 11. 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. In this respect it is, of course, important to select the appropriate minerals to represent the likely secondary minerals formed by hydrothermal activity in the system in question. In the case of well BA-01, the curves do not intersect the zero line at a fixed point, but most of them intersect in the temperature interval 100-160˚C. Part of them intersect below the line at still higher temperatures, indicating mixing with water at higher reservoir temperatures. For well HJ-01 the curves similarly cross the zero line within a temperature range, in this case in the interval 100-140˚C. There is also indicated mixing with water of still higher reservoir temperatures.

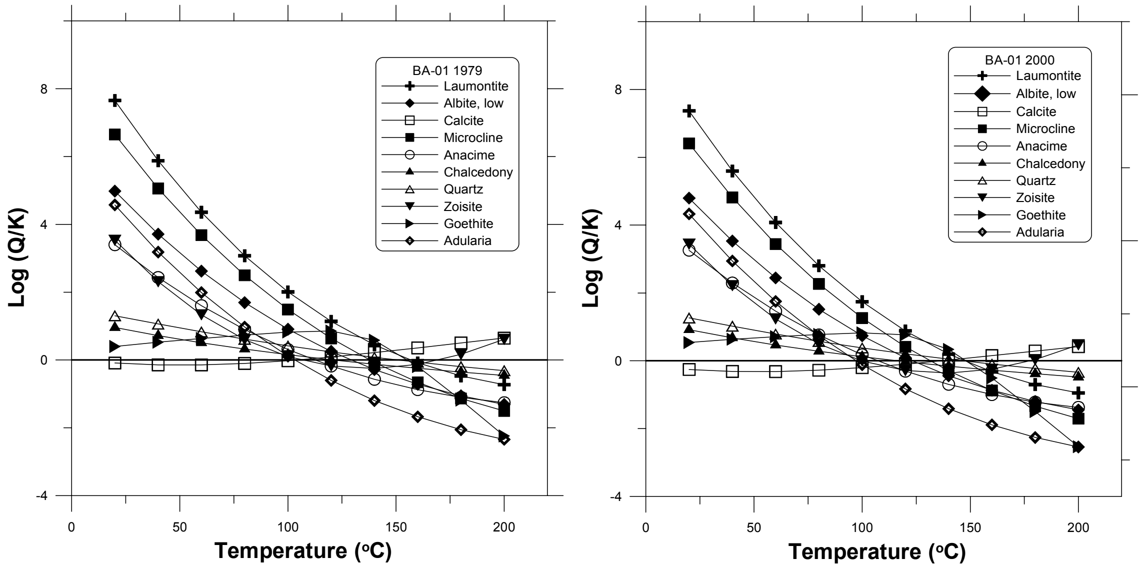

FIGURE 10: The log *Q/K* vs. temperature diagram for fluid from well BA-01

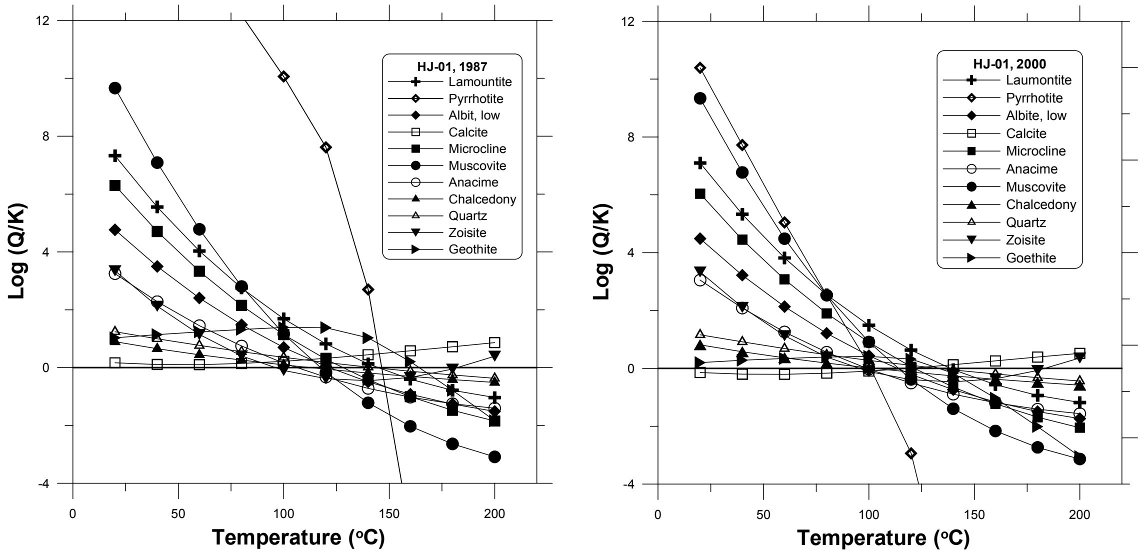

FIGURE 11: The log *Q/K* vs temperature diagram for fluid from well HJ-01

4.3 Stable isotopes

Figure 12 shows the isotopic composition of the Bakki geothermal fields. In this area the original geothermal water has the isotopic composition $\delta^{18}O$ = -9.3‰ and δ^2H= -71‰; and the local precipitation have the isotopic compositions of $\delta^{18}O$ = -8.3‰ and δ^2H= -56‰, (Kristmannsdóttir and Sveinbjörnsdóttir, 1992). Figure 12 shows us two things:

1. That low δ^2H value of the original thermal water suggests a distant origin of the water; most likely it originates from the Langjökull ice cap, some 70 km north of the area (Kristmannsdóttir and Sveinbjörns-dóttir, 1992). Due to the inflow of local groundwater, the δ^2H value changes from -71.0‰ to around -65‰ in well HJ-01.

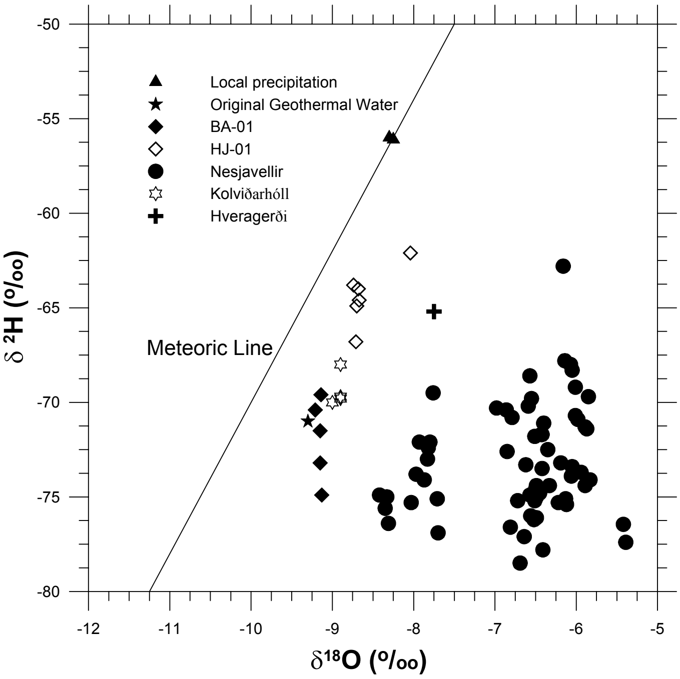

FIGURE 12: The stable isotopic composition of the Bakki geothermal field

2. There is a distinct oxygen shift of about 1‰, the first such reported for water from low-temperature geothermal fields in Iceland (Kristmannsdóttir and Sveinbjörnsdóttir, 1992). The reason for the oxygen shift in the Bakki field is not exactly known, there are several possibilities. One is that the underground rocks are very young and contain much fresh and reactive glass that might allow an effective oxygen isotope exchange even at those low temperatures. The oxygen isotopic exchange between palagonite and progressively hotter fluid, which has a maximum calculated fluid temperature range of 150-183˚C in the core through Surtsey island, records the cumulate effective of 12 years of low-temperature alteration of basaltic tephra (Karlsson et al., 1992). The author believes that there is oxygen exchange between water rock interactions even at these moderate temperatures. The salinity of the water may also increase its reactivity and, therefore, enhance isotopic exchange. Thirdly, the recharge to the Ölfus low-temperature fields could partly be runoff from the high-temperature fields

within the Hengill volcanic area, which is situated only 15 km to the north of Bakki geothermal field. As shown in the same diagram (Figure 12) the water from the Kolvidarhóll high-temperature geothermal field (one of the high-temperature geothermal fields in the Hengill area) has stable isotopic ratios almost identical to those of Bakki low-temperature field.

4.4 Mixing

Hot water ascending from a geothermal reservoir may cool by mixing in the upflow with shallow, relatively cold water. Mixing is most prone to occur where there is a change in permeability. And since cold water is most often lower in dissolved solids than geothermal water, mixing is often referred to as dilution. Recognition of mixed water on the basis of the chemical composition of a single sample is generally not convincing. In this report, different mixing models were used to demonstrate the mixing processes, mainly in well HJ-01.

4.4.1 Evidence of mixing

Large variations in the temperature and flow rates of thermal springs in a particular field that can be linked with parallel variations in the concentrations of non-reactive components in the water, such as Cl, usually constitute the best evidence that mixing has occurred. Mixing of geothermal water with local cold water may manifest itself in a linear relationship between the δ values for H and O or between these values and the aqueous concentrations of conservation elements such as Cl (Arnórsson, 2000b).

The geochemical study of this area strongly suggests that mixing happened in well HJ-01, evidenced by the following:

1. The downhole log shows a direct proof of mixing, and that the mixing comes from the bottom aquifer at 583 m depth (Figure 6).
2. The wellhead temperature has dropped from 108 to 104°C, or nearly 5°C (Kristmannsdóttir et al., 1990b).
3. The chemical composition has changed drastically during 1988-1990, and the initial chemical composition and isotopic values have not been recovered so far (Figures 5 and 7).
4. The diagrams showing log *Q/K* vs. temperature diagrams (Figure10-11) also strongly suggest dilution, not only by the different equilibrium temperatures displayed by the different minerals assemblages, but by a notable drop of the best cluster points at temperatures of 160 and 140°C in well BA-01 and of 140 and 118°C in well HJ-01; also, by comparison of the log *Q/K* vs. temperature diagram for the year 2000 with the original fluid of each well.
5. There are nearly linear relationships between SiO_2, B, δ^2H, $\delta^{18}O$ and the conservative element Cl as shown in Figure 13 that constitute the best evidence that mixing has occurred.

4.4.2 The silica-enthalpy mixing model

The silica-enthalpy mixing model is one of the commonly applied mixing models used to estimate subsurface temperature. When applying mixing models to estimate subsurface temperature, several simplifying assumptions are made. Conservation of mass and heat is always assumed, both during and after mixing. Thus, it is assumed that chemical reactions occurring after mixing are insignificant and do not modify water composition.

As shown in Figure 14, the best-fit line between the cold groundwater and the mixed geothermal water intersects the chalcedony solubility curve at a point of enthalpy equal to 650 kJ/kg, which indicates that a temperature of 150°C would be expected in the reservoir.

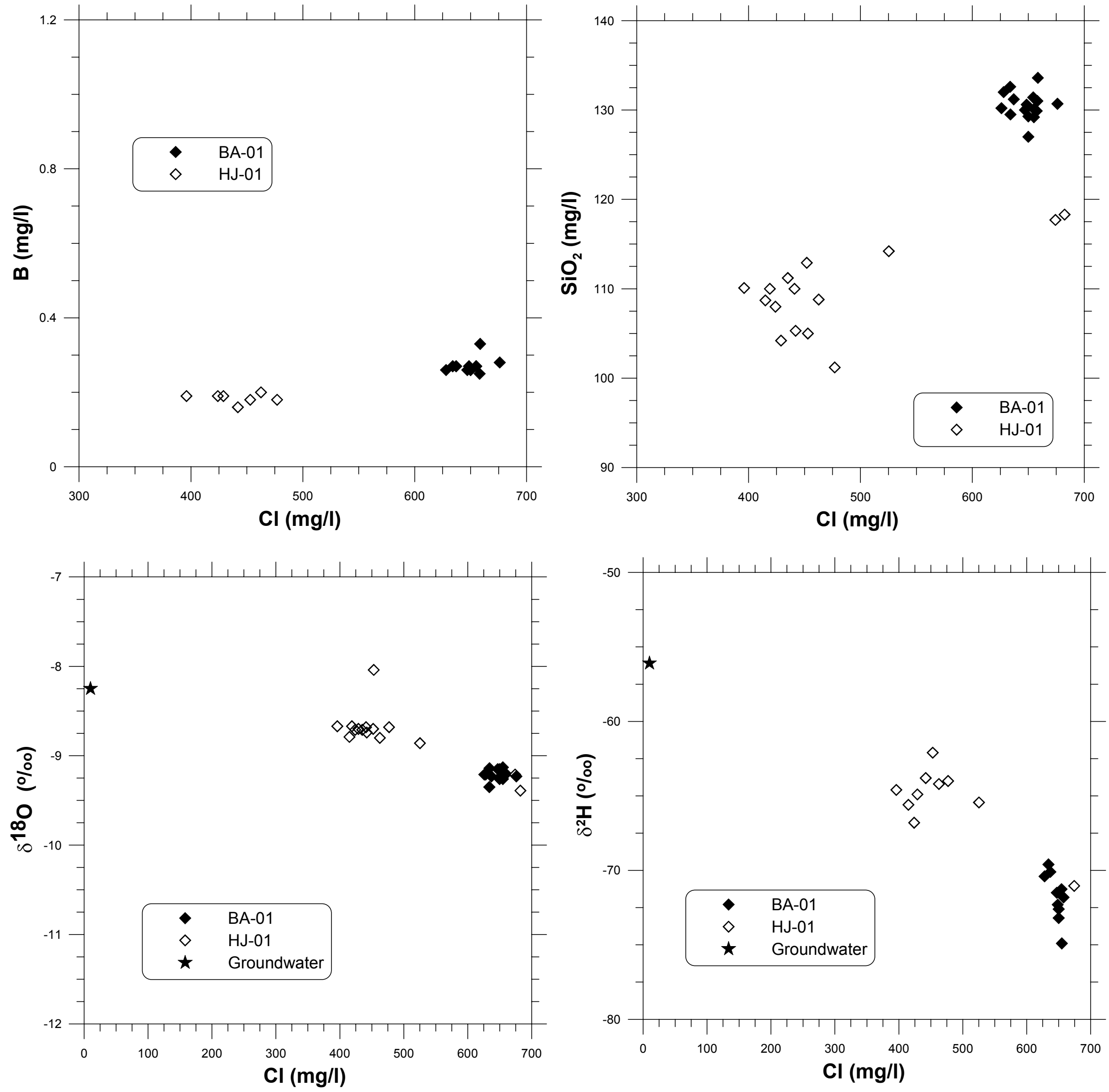

FIGURE 13: Boron, silica, $\delta^{18}O$ and δ^2H vs. chloride for water from the Bakki geothermal field

4.4.3 Fluid-fluid mixing model of CHILLER

As mentioned before, the Bakki geothermal field is a very complicated system. Well HJ-01 is probably on the edge of the system and may easily be affected by the fault swarms and tectonic movements such as earthquakes. Therefore, it is very difficult to try to find a simple mixing model to fit the whole system. The mixing calculation presented here is designed to investigate the chemical characteristics of the mixing with two-end members, i.e. the surface groundwater (Table 4) and the cooler water at 583 m depth in HJ-01 (Table 3).

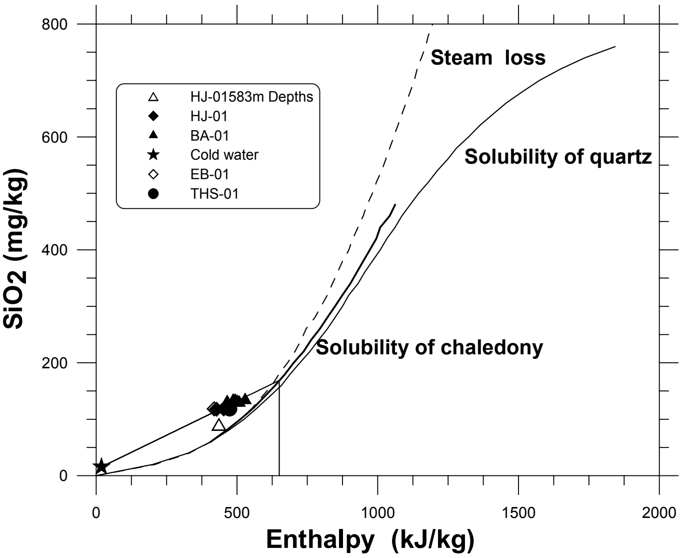

FIGURE 14: The silica-enthalpy mixing model for the Bakki geothermal field

TABLE 4: Groundwater composition in the Bakki area (mg/l)

Date	No.	T. (˚C)	pH/ T(˚C)	CO_2	H_2S	B	SiO_2	Na	K	Mg	Ca	F	Cl	SO_4	Al	Fe	δ^2H	$\delta^{18}O$
9207	929018	4.4	8.56/25.5	16.6	0.02	<0.01	16.4	11.6	0.61	1.86	5.1	0.05	15.9	3.06	0.01	0.0011	-56.1	-8.25

Figure 15A shows the temperature decrease calculated for different mixing models. When hot water is mixed in the ratio of 1:1 (hot: cold) with the cool water at 583 m depth, the temperature drop would be expected to be 5˚C which matches with the measured temperature change at wellhead (Kristmannsdóttir and Ármannsson, 1996).

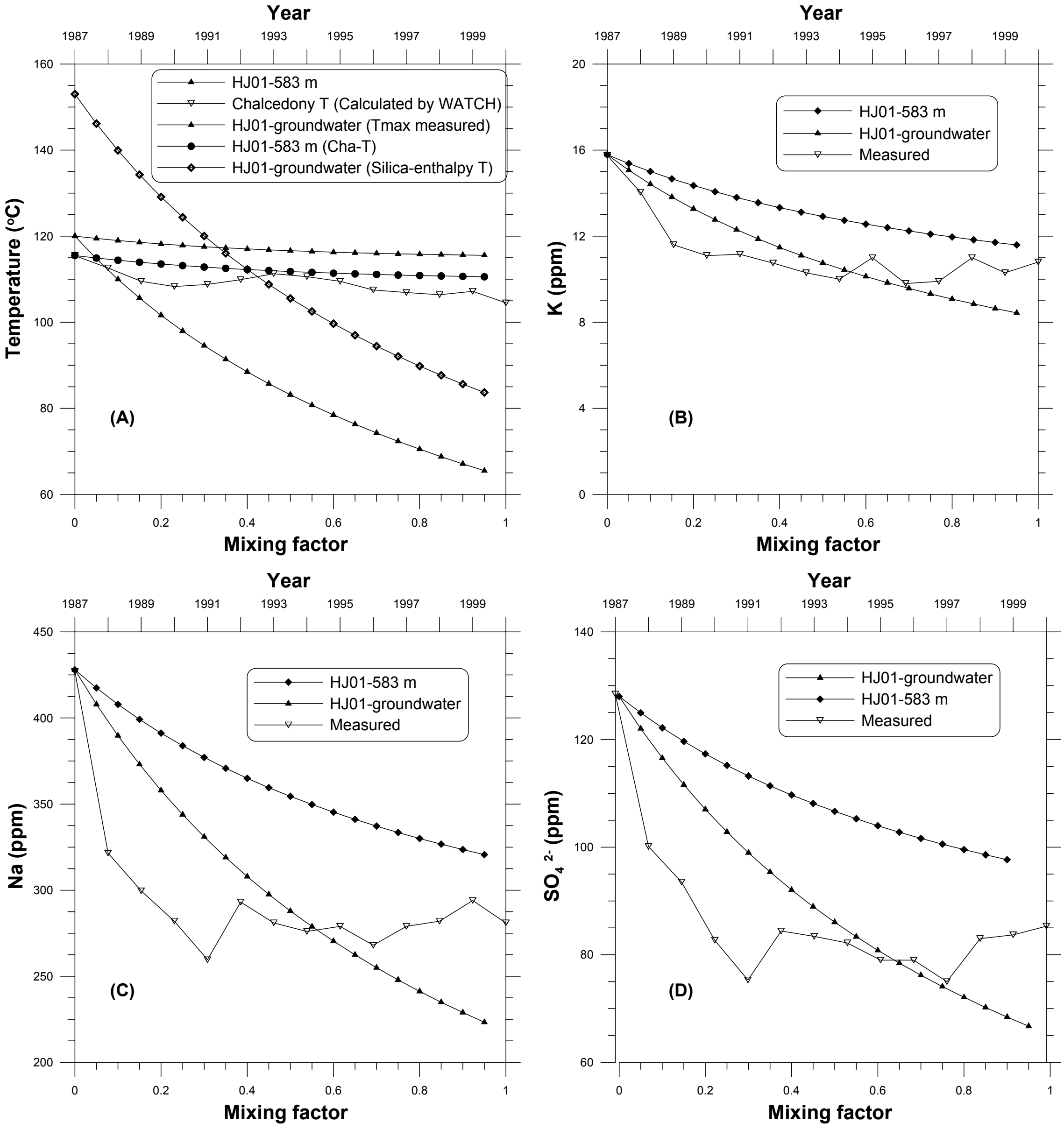

FIGURE 15: Fluid-fluid mixing between HJ-01 hot geothermal fluid and groundwater and cooler water at 583 m depth of HJ-01, respectively; a) Change in temperature; b) Change in concentration of K; c) Change in Na; d) Change in SO_4; *HJ01-583 m* denotes the hot water of well HJ-01 mixed with the cool water at 583 m depth; *Chalcedony T* denotes calculated chalcedony temperature by the WATCH program; *HJ01-Groundwater* denotes the hot water of well HJ-01 mixed with local groundwater ; *Measured* denotes the concentration as measured in the fluid phase through the years

On the other hand, when mixing with groundwater of 4.4˚C, the temperature would be expected to decrease to 81.8˚C (by using the temperature indicated by the silica-enthalpy model) when the mixing ratio reaches 1:1. When the mixing factor is between 0.5 to 0.6, the temperature varies between 105.5 and 100˚C. Figures 15B, 15C and 15D, show the concentration changes of the individual elements by changing the mixing factor. It is very clear that the concentration of this element and temperature have a value close to the measured values in well HJ-01 at a mixing factor of 0.5-0.6. So it can be concluded that a likely rate of groundwater mixed with the reservoir water is a ratio of 0.5-0.6.

4.5 Discussion and summary

In chemical composition the fluids are classified as Cl-rich geothermal water. Minor changes in the chemistry of the water were observed during the first 10 years of exploitation, but when HJ-01 was put into operation, chemical changes were detected very soon by chemical monitoring. The changes appeared to be dilution of the geothermal water with fresh local groundwater. Continuous changes took place from 1988 to 1990, the salinity decreased steadily, the oxygen isotope value changed suddenly and the calculated chalcedony temperature dropped suddenly but then appeared to reach a relatively stable stage. For well HJ-01, the chalcedony temperature has dropped 13˚C during the 15 years of utilization.

The log *Q/K* vs. temperature diagrams (Figures 10-11) for well BA-01 show that the curves do not intersect the zero line at a fixed point. Most of them intersect in the temperature interval 100-160˚C, but some intersect below the line at still higher temperatures, indicating mixing with water of higher reservoir temperatures. For well HJ-01, the curves similarly cross the zero line at a temperature range, in this case about 100-140˚C. There is also indicated mixing with water of higher reservoir temperatures.

The silica-enthalpy mixing model shows that the reservoir temperature may exceed 150˚C. The CHILLER mixing model suggests that the change in chemical composition in well HJ-01 revealed by chemical monitoring may be interpreted by dilution of the geothermal water with fresh local groundwater at a ratio of around 0.5 to 0.6.

5. WATER-ROCK INTERACTION

Water-rock interaction (WRI) is among the important processes occurring in a hydrothermal system. An active hydrothermal system is an open or half-open geochemical system where various kinds of water-rock interactions are taking place. Isotopic exchange, chemical evolution of geothermal fluids and alteration of rocks are closely related to water-rock interaction. Therefore, a study of the interaction between geothermal fluids and reservoir rocks will be helpful

- to determine the origin of geothermal fluids;
- to explore the mechanism of many complicated geochemical reactions in a geothermal system;
- and to provide useful information on the exploitation and utilization of geothermal resources.

There are many methods for dealing with water-rock interaction, a detailed study of fluids and the alteration of minerals is always a prerequisite, while experimental study is also a common method. Modelling studies have proved helpful as the natural systems involve complex, interactive chemical reactions that involve hundreds of chemical species in simultaneous, non-linear, partial equilibria. These processes take counter-intuitive twists that can best be understood by computer modelling of the simultaneous equilibria in the complete chemical system. The aim of geochemical modelling is to interpret and/or predict chemical reactions of minerals, gases and even organic matter with aqueous solutions in real or hypothetical water-rock systems. Geochemical modelling is founded on chemical and thermodynamic principles that are independent of the geologic environment. Therefore, the principles are equally applicable to water-rock interaction in different systems such as the formation of metallic ore deposits, the metamorphism of crystalline rocks and a geothermal system. The field of geochemical modelling has advanced simultaneously along two fronts: 1) measurement, evaluation, and generalization of thermodynamic data for a large number of minerals and aqueous solutions and 2) the incorporation of these data into sophisticated, computerized mathematical descriptions of complex water-rock systems. Two general approaches to modelling water-rock interactions exist: 1) "forward modelling", which predicts water compositions and mass transfer that can result from hypothesized reactions, and 2) "inverse modelling", which defines mass transfer from observed chemical and isotopic data. Forward modelling begins with a defined initial water composition and simulates the chemical evolution of water and rock for a set of specified reactions. Inverse modelling produces mineral mass transfers that can account for compositional variations observed in the aqueous system. Both models are capable of describing the thermodynamic properties of aqueous solutions (Plummer, 1992).

A series of reaction programs, which can be used to model natural water-rock interactions, have been developed such as PHREEQC, EQ3/6 and CHILLER. In this report, all the calculations were performed by the computer program CHILLER that operates for geothermal systems. However, it must be realized that many reactions that take place in the model may not occur in the natural systems. An essential component of the effective use of the computer models is to compare model results with their natural counterparts to identify similarities and differences. This type of analysis and comparison greatly enhances understanding of the natural processes (Reed, 1982).

As mentioned before, the Bakki geothermal field, which is located on the east flank of the western active volcanic zone in South Iceland, is now a low-temperature geothermal system. An earlier high temperature alteration is detected by the occurrence of the mineral epidote. It can, therefore, be considered a borderline case between low- and high-temperature geothermal areas. Two water-rock interaction modelling runs have been made. One is at present temperatures which corresponds to 140˚C for BA-01 and 120˚C for HJ-01, respectively; the other is at a higher temperature of 250˚C, which is suggested by the occurrence of epidote.

5.1 Modelling at present temperature

The main aim of the modelling study is to imitate the interaction between the reservoir rocks, basalt glass and groundwater that can be inferred by chemical and isotopic data. The composition of the basalt glass (Trønnes, 1990) and the groundwater are listed in Tables 5 and 4, respectively. During the modelling processes, 0.01 or 0.1grams of rocks were titrated into 1 kg groundwater until the limit given, making it convenient to control the water/rock ratio. For the present study, the main emphasize is on comparison of the secondary minerals occurring and the evolution of the fluid, and to try to identify the main mineral controlling reactions.

TABLE 5: Chemical composition of basalt glass used for water-rock interaction (%)

SiO_2	**Al_2O_3**	**FeO**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**
48.1	13.9	8.1	4.8	0.24	6.58	12.0	2.52	0.29

Figure16A shows the evolution of the fluid during water-rock interaction at 120˚C. The elements behave differently during water-rock interaction. The major cations such as Na^+, Al^{3+}, K^+, Fe^{2+} increase in concentration with a decrease in the water/rock ratio, which means they are dissolved from the rock during the reaction. However, other cations like Ca^{2+} and Mg^{2+} will be included into the crystal structure of the secondary minerals such as calcite, laumontite and clinochlore during the reaction, so their concentrations decreased when the water/rock ratio (W/R) decreased. SiO_2, the main component of the rocks, dissolves during reaction, so its concentration in the aqueous phase increases when W/R decreases. Of the anions (Table 6), Cl is very stable due to its chemically conservative nature and the low concentration in added rocks. HCO_3^- shows a little change due to the formation of calcite. The change of HS^- and SO_4^{2-} are due to the formation of andradite and hematite, partly due to the calculations necessary for the oxidation-reduction reaction, (see Equations 12 and 22 in Table 7 below). The negative moles of HS^- and SO_4^{2-} just correspond to the moles going into the solid phase, necessary for the oxidation-reduction calculation as mentioned above.

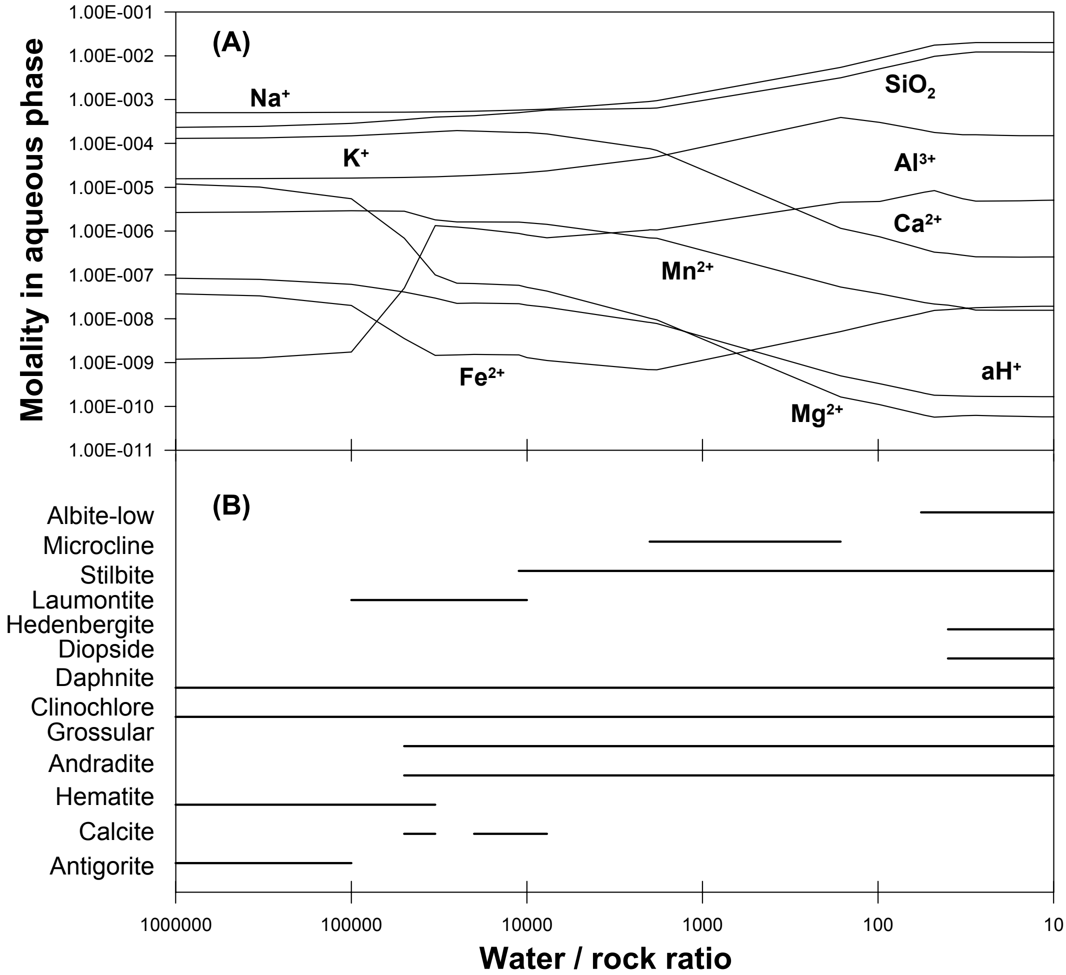

FIGURE 16: Water-rock interaction at the temperature 120˚C, a) Evolution of cations in the fluid; b) Deposition of secondary minerals

TABLE 6: The evolution of total molality of anions in aqueous phase during water-rock interaction (mole/l)

Rock added (g)	Temperature 120˚C				Temperature 140˚C			
	Cl^-	SO_4^{2-}	HCO_3^-	HS^-	Cl^-	SO_4^{2-}	HCO_3^-	HS^-
0	2.97E-04	3.19E-05	5.32E-04	6.05E-07	2.97E-04	3.19E-05	5.32E-04	6.05E-07
0.001	2.97E-04	3.19E-05	5.32E-04	5.46E-07	2.97E-04	3.19E-05	5.32E-04	5.57E-07
0.003	2.97E-04	3.21E-05	5.32E-04	4.35E-07	2.97E-04	3.20E-05	5.32E-04	4.59E-07
0.01	2.97E-04	3.24E-05	5.32E-04	1.38E-07	2.97E-04	3.24E-05	5.32E-04	1.38E-07
0.02	2.97E-04	3.25E-05	5.32E-04	1.45E-10	2.97E-04	3.25E-05	5.32E-04	1.31E-08
0.03	2.97E-04	3.25E-05	5.32E-04	-7.82E-11	2.97E-04	3.25E-05	5.32E-04	-6.34E-11
0.04	2.97E-04	3.25E-05	5.31E-04	-7.29E-11	2.97E-04	3.25E-05	5.32E-04	-3.91E-11
0.05	2.97E-04	3.25E-05	5.32E-04	-6.63E-11	2.97E-04	3.25E-05	5.32E-04	5.56E-11
0.1	2.97E-04	3.25E-05	5.31E-04	1.22E-10	2.97E-04	3.25E-05	5.31E-04	5.35E-09
0.5	2.97E-04	3.25E-05	5.31E-04	1.22E-10	2.97E-04	2.68E-05	5.32E-04	5.69E-06
1	2.97E-04	-1.56E-06	5.32E-04	3.40E-05	2.97E-04	2.48E-05	5.32E-04	7.69E-06
10	2.97E-04	-3.09E-05	5.32E-04	6.34E-05	2.97E-04	-4.29E-05	5.32E-04	7.54E-05
50	2.97E-04	-5.09E-04	5.32E-04	5.41E-04	2.97E-04	-4.34E-04	5.32E-04	4.66E-04
100	2.97E-04	-5.28E-04	5.32E-04	5.60E-04	2.97E-04	-4.51E-04	5.32E-04	4.83E-04

Figure 16B shows the minerals which are present in the matrix during the water-rock interaction at 120°C. Clinochlore and daphnite are precipitated throughout all values of the water/rock ratio, from high to low; antigorite is formed at very high W/R from 1,000,000 to 100,000, and then dissolved. Hematite is formed with the W/R between 100,000 and 20,000, while calcite is precipitated at two stages, one is where W/R = 25,000, another where the W/R goes from 10,000 to 2000. Laumontite is precipitated during W/R in the range of 25,000-2000. Other minerals such as albite-low, diopside and hedenbergite are deposited at low W/R. At W/R = 10, minerals present in the matrix are clinochlore, daphnite, andradite, grossular, stilbite, albite-low, diopside and hedenbergite.

Some of the minerals have the same deposition behaviour due to their similar chemical compositions and, therefore, have the same index in the SOLTHERM database file of CHILLER. For example, clinochlore with daphnite, andradite with grossular, clinozoisite with epidote-ord, diopside with hedenbergite behave similarly.

Figure 17A shows the evolution of the fluid in for WRI at 140°C. All the components show a very similar behaviour as at temperature of 120°C. The formation process of the secondary minerals is shown in Figure17B. They are very similar to that at a temperature of 120°C. The main difference is that quartz is deposited at W/R around 45. Another difference is that some of the minerals are deposited in a different sequence. Calcite, for example, is deposited after W/R becomes < 10,000, when the temperature is 140°C, but it is deposited mainly during the W/R range of 2500-2000 when the temperature is 120°C.

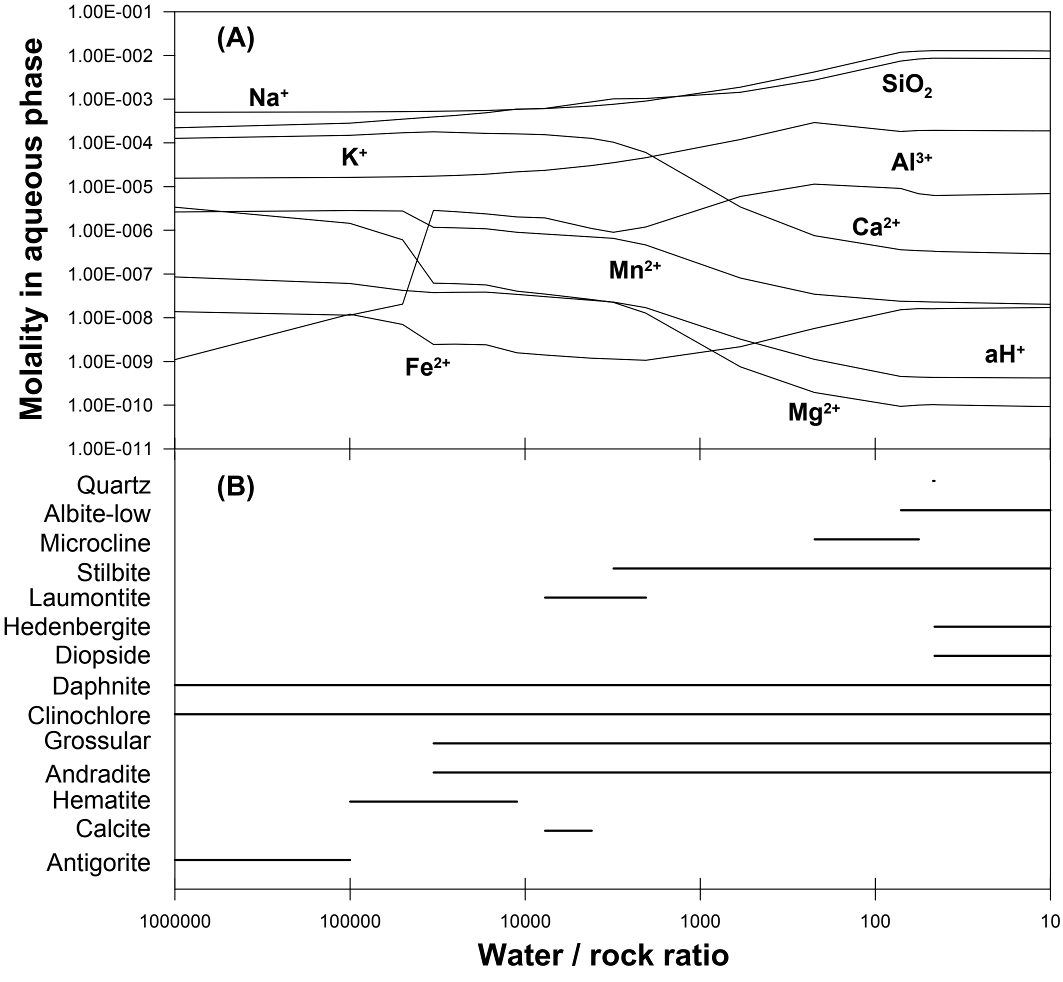

FIGURE 17: Water-rock interaction at the temperature 140°C, a) Evolution of cations in the fluid; b) Deposition of secondary minerals

The simulation studies show that at the low temperatures 120˚C or 140˚C, the main secondary mineral assemblages are calcite, laumontite, stilbite, clinochlore, daphnite and albite-low. The detected secondary mineral assemblages in the two studied wells are calcite, laumontite, quartz and stilbite. There may be different reasons for why other minerals were not found in the real section. Albite-low may not be found in this area due to dynamic reasons. Andradite and grossular may be present but have not been detected. We probably need much more detailed mineral study on the actual field to make a realistic comparison.

5.2 Modelling at high temperature

Due to the temperature changes from a high-temperature environment to a low-temperature one, the observed alteration is a mixture of relict alteration and that formed by the present temperature conditions. Therefore, another model run was executed imitating the high temperature at the condition 250˚C to try to understand the whole evolutionary processes of the geothermal field.

The fluid evolution is more or less similar to that at low temperatures. Na^+, Al^{3+}, K^+, Fe^{2+} and SiO_2 increase during decreased water-rock ratio, as they are dissolved from the rocks. Ca^{2+}, Mg^{2+} and Mn^{2+}, on the other hand, are fixed into the crystal structure of the secondary minerals such as calcite, epidote-ord, clinozoisite and clinochlore during the reaction, so their concentration decreased by decreased WR (Figure18A). The anions behave more or less similarly as at lower temperature (Figure18B), as neither andradite nor hematite was deposited. The concentrations of HS^- and SO_4^{2-} are positive, whereas they were negative in the low-temperature run. Figure 18C shows the alteration minerals which are deposited in processes at 250˚C. As would be expected, some of the typical relict minerals are formed at that temperature, such as epidote-ord and wairakite which are deposited in the matrix. Clinozoisite, was also formed at this temperature. Muscovite, instead of only microcline, is deposited now, while some of the low-temperature zeolites, like laumontite and stilbite, are not deposited at this temperature.

The simulation studies show that at 250˚C, the main secondary mineral assemblages are epidote-ord, clinozoisite, wairakite, calcite, clinochlore, muscovite and albite-low. Of those, at least the secondary mineral assemblages of epidote and chlorite are found in the two studied wells. Other minerals like clinozoisite and wairakite were found in other wells in the Ölfus area.

If we combine the present temperature model with the high-temperature model, most of the important minerals were identified both in the actual field and by geochemical modelling.

5.3 Discussion and summary

The modelling study suggests that the formation of alteration minerals depends on the temperature. Table 7 shows the main controlling reactions in the water-rock interaction and Table 8 shows minerals and equilibria controlling the composition of specific components of the fluid generated by water-rock interaction at different temperatures. For the major cation Na^+, the albite-low formation reaction is the only reaction which controls its concentration in the fluid at both the modelling temperatures. For K^+, the controlling reaction is the formation of microcline at low temperature, while the formation of both microcline and muscovite controls at high temperatures. The concentration of Ca^{2+} is controlled by the forming of the minerals andradite, calcite, diopside, grossular and laumontite at low temperatures, but andradite, calcite, clinozoisite, epidote-ord, grossular and wairakite at high temperatures. Mg^{2+} is controlled by the formation of antigorite and clinochlore both at low and high temperatures, and at low temperatures also by diopside. The concentration of Fe^{2+} is controlled by the formation of andradite, daphnite and hematite at low temperatures, but by andradite, daphnite and epidote at high temperatures. Al^{3+} is controlled by the formation of albite, clinochlore, laumontite, daphnite, grossular and microcline at low temperatures, and clinochlore, clinozoisite, daphnite, epidote, grossular, muscovite and wairakite at high temperatures. The concentration of SiO_2 is controlled by all the mineral formation reactions except

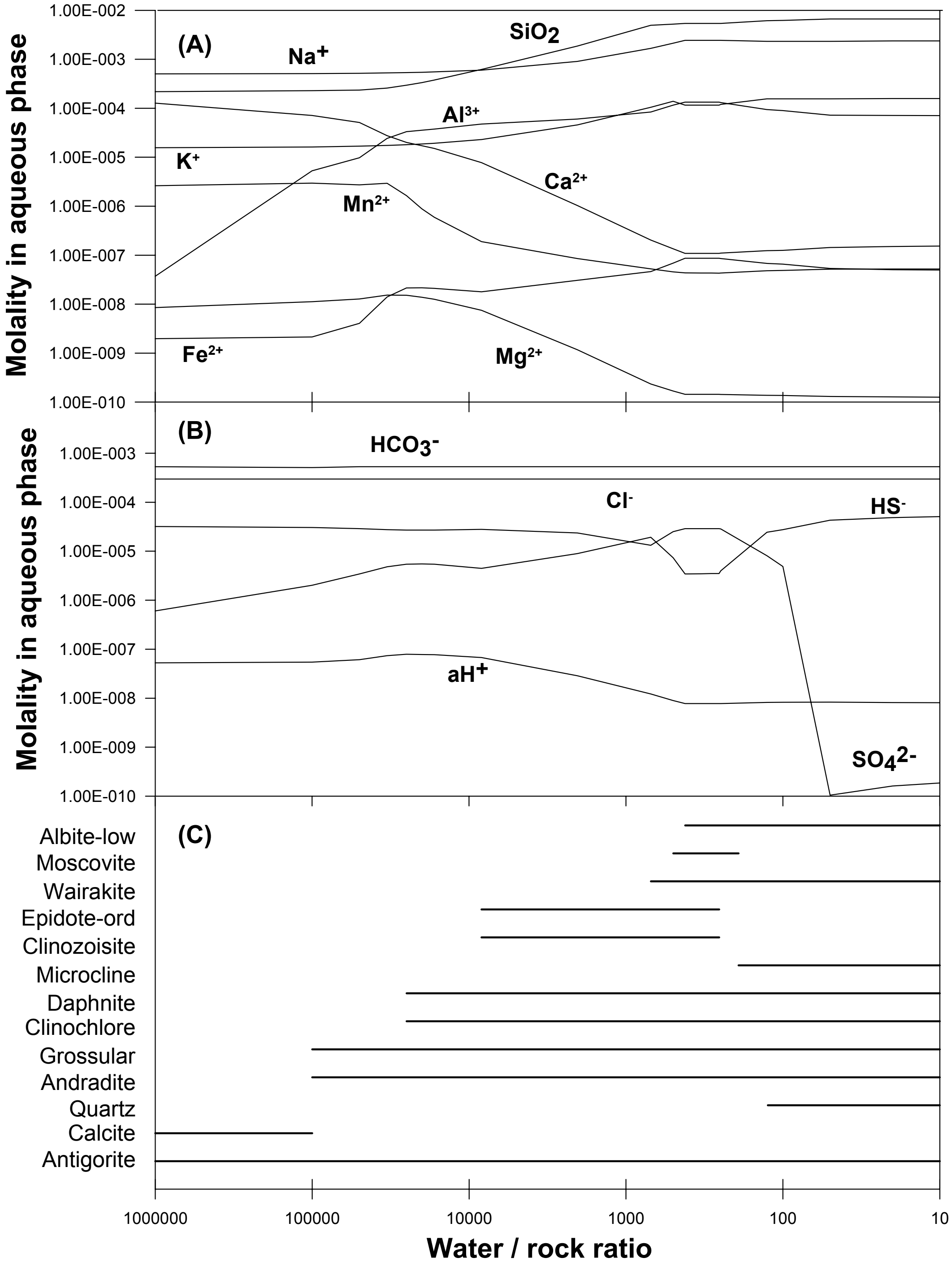

FIGURE 18: Water-rock interaction at the temperature 250°C, a) Evolution of cations in the fluid; b) Evolution of anions in the fluid; c) Deposition of secondary minerals

calcite and hematite. The formation of andradite and hematite is controlled by the concentration of HS^- and SO_4^{2-} in the fluid. The formation of calcite is controlled by the concentration of HCO_3^- in the geothermal fluid.

The results of the modelling study show that at low temperatures the main secondary mineral assemblages are very similar; there are calcite, laumontite, stilbite, clinochlore, daphnite and albite-low. The secondary mineral assemblage of calcite, laumontite, and stilbite is found in the two studied wells.

TABLE 7: Mineral controlling reactions which were used in this modelling study

Minerals	**Mineral controlling reactions equations**	
Albite-low:	*Alb-low* + $4H^+ = Na^+ + Al^{3+} + SiO_2(aq) + 2H_2O$	(11)
Andradite:	*Andradite* + $0.25HS^- + 9.75H^+ = 3Ca^{2+} + 3\ SiO_2(aq) + 5H_2O + 0.25SO_4^{2-} + 2Fe^{2+}$	(12)
Antigorite:	*Antigorite* + $6H^+ = 3\ Mg^{2+} + 2.125\ SiO_2(aq) + 4.938H_2O$	(13)
Calcite:	*Calcite* + $H^+ = Ca^{2+} + HCO_3^-$	(14)
Clinochlore:	*Clchl 7A* + $16\ H^+ = 5\ Mg^{2+} + 2\ Al^{3+} + 3\ SiO_2(aq) + 12\ H_2O$	(15)
Clinozoisite:	*Clinozoisite* + $13H^+ = 2Ca^{2+} + 3Al^{3+} + 3\ SiO_2(aq) + 7\ H_2O$	(16)
Daphnite:	*Dap* 14/2 + $8\ H^+ = 2.5\ Fe^{2+} + Al^{3+} + 1.5\ SiO_2(aq) + 6\ H_2O$	(17)
Diopside:	*Diopside* + $4\ H^+ = Ca^{2+} + Mg^{2+} + 2\ SiO_2(aq) + 2\ H_2O$	(18)
Epidote-ord:	*Epid-ord* + $11.875\ H^+ = 2Ca^{2+} + 2\ Al^{3+} + 3\ SiO_2(aq) + 0.125\ SO_4^{2-} + Fe^{2+} + 6.5\ H_2O$	(19)
Grossular:	*Grossular* + $12H^+ = 3\ Ca^{2+} + 2\ Al^{3+} + 3\ SiO_2(aq) + 6\ H_2O$	(20)
Hedenbergite:	*Hedenbergite* + $4\ H^+ = Ca^{2+} + Fe^{2+} + 2\ SiO_2(aq) + 2\ H_2O$	(21)
Hematite:	*Hematite* + $3.75\ H^+ + 0.25\ HS^- = 2\ H_2O + 0.25\ SO_4^{2-} + 2\ Fe^{2+}$	(22)
Laumontite:	*Laumontite* + $8\ H^+ = Ca^{2+} + 2Al^{3+} + 4\ SiO_2(aq) + 8\ H_2O$	(23)
Microcline:	*Micr-max* + $4\ H^+ = K^+ + Al^{3+} + 3\ SiO_2(aq) + 2H_2O$	(24)
Muscovite:	*Muscovite* + $10\ H^+ = K^+ + 3Al^{3+} + 3\ SiO_2(aq) + 6H_2O$	(25)
Quartz:	*Quartz* = $SiO_2(aq)$	(26)
Stilbite:	*Stilbite* + $6\ H^+ = Ca^{2+} + 2\ Al^{3+} + 7\ SiO_2(aq) + 10\ H_2O$	(27)
Wairakite:	*Wairakite* + $8\ H^+ = Ca^{2+} + 2\ Al^{3+} + 4\ SiO_2(aq) + 6\ H_2O$	(28)

At high temperatures, the main alteration mineral assemblages are epidote-ord, clinozoisite, wairakite, calcite, clinochlore, muscovite and albite-low. The secondary minerals, epidote and chlorite, are found in the two studied wells, and clinozoisite and wairakite are found in other wells in the Ölfus area. Most of the important minerals such as calcite, laumontite, stilbite, clinochlore, epidote-ord, clinozoisite, wairakite and muscovite are identified both in the actual field and by geochemical modelling, but the lack of albite-low in this area needs further study.

The evolution of fluid may suggest that most of the common cations found in the geothermal field have their origin in the dissolution of rocks. Cl is very stable due to its chemically conservative nature and the low concentration in added rocks, so the high concentration in the two studied wells is believed to have its origin from the dissolution of salt that formed by repeated submersion of the rocks into the sea during buildup of the formation.

6. CONCLUSIONS

The main conclusions and recommendations of this report may be summarized as follows:

The reservoir rocks in the Bakki geothermal field are mainly basalt lavas, basaltic hyaloclastites and clastic sediments of Quaternary age. The most abundant alteration minerals in the area include stilbite, laumontite, quartz, chlorite, pyrite and epidote. The occurrence of epidote in the area suggests a high-temperature geothermal activity which declined over time as the field drifted out of the active volcanic zone by spreading of the mid-ocean ridge.

Geothermal water from wells BA-01 and HJ-01 is utilized for the district heating system of Thorlákshöfn town. The wells were connected to the contribution system in 1979 and 1987, respectively. Chemical monitoring shows no significant changes for well BA-01, but continuous changes took place in well HJ-01 from the end of 1987 to 1990. After reparation of the well, it stabilized at the lower concentration level. The change included a calculated chalcedony temperature drop of 13°C and a one third decrease in salinity.

TABLE 8: Minerals and equilibria controlling the composition of specific components of the fluid generated by water-rock interactions at different temperatures

Component	T = 120˚C		T = 140˚C		T = 250¨C	
	Minerals	**Reaction**	**Minerals**	**Reaction**	**Minerals**	**Reaction**
Na^+	Albite-low	11	Albite-low	11	Albite-low	11
K^+	Microcline	24	Microcline	24	Microcline Muscovite	24 25
Ca^{2+}	Andradite Calcite Diopside, Grossular Hedenbergite Laumontite Stilbite	12 14 18 20 21 23 27	Andradite Calcite Diopside Grossular Hedenbergite Laumontite Stilbite	12 14 18 20 21 23 27	Andradite Calcite Clinozoisite Epidote-ord Grossular Wairakite	12 14 16 19 20 28
Mg^{2+}	Antigorite Clinochlore Diopside	13 15 18	Antigorite Clinochlore Diopside	13 15 18	Antigorite Clinochlore	13 15
Fe^{2+}	Andradite Daphnite Hedenbergite Hematite	12 17 21 22	Andradite Daphnite Hedenbergite Hematite	12 17 21 22	Andradite Daphnite Epidote-ord	12 17 19
Al^{3+}	Albite-low Clinochlore Laumontite Daphnite Grossular Microcline Stilbite	11 15 23 17 20 22 27	Albite-low Clinochlore Laumontite Daphnite Grossular Microcline Stilbite	11 15 23 17 20 22 27	Clinochlore Clinozoisite Daphnite Epidote-ord Grossular Muscovite Wairakite	15 16 17 19 20 25 26
SiO_2aq	Albite-low Andradite Antigorite Clinochlore Daphnite Diopside Grossular Hedenbergite Stilbite Laumontite	11 12 13 15 17 18 20 21 27 23	Albite-low Andradite Antigorite Clinochlore Daphnite Diopside Grossular Hedenbergite Stilbite Laumontite Quartz	11 12 13 15 17 18 20 21 27 23 26	Albite-low Andradite Antigorite Clinochlore Clinozoisite Daphnite Epidote-ord Grossular Quartz Wairakite	11 12 13 15 16 17 19 20 26 28
HS^-	Andradite Hematite	12 22	Andradite Hematite	12 22	Andradite Hematite	12 22
HCO_3^-	Calcite	14	Calcite	14	Calcite	14
SO_4^{2-}	Andradite, Hematite	12 22	Andradite, Hematite	12 22	Andradite Epidote-ord	12 19

The continuous change in chemistry and temperature appears to be due to dilution of the geothermal water with fresh local groundwater. A silica-enthalpy mixing model shows that the reservoir temperature may exceed 150˚C. The CHILLER mixing model suggests that in well HJ-01, the dilution ratio may have been around 0.5 to 0.6.

The log *Q/K* vs. temperature diagram for well BA-01 shows that the curves do not intersect the zero line at a fixed point, but most of them intersect in the temperature interval 100-160˚C. Part of them intersect below the line at still higher temperatures, indicating mixing with water of higher reservoir temperatures. For well HJ-01similarly, the curves cross the zero line in a temperature range, in this case at 100-140°C. There is also indicated mixing with water of still higher reservoir temperatures.

A water-rock interaction modelling study shows that at the temperatures 120 and 140°C, the main secondary mineral assemblages are very similar to each other; they are calcite, laumontite, stilbite, clinochlore, daphnite and albite-low. At higher temperature, the main alteration mineral assemblages are epidote-ord, clinozoisite, wairakite, calcite, clinochlore, muscovite and albite-low. The formation of the alteration minerals is temperature-dependent.

Most of the alteration minerals such as calcite, laumontite, stilbite, clinochlore, epidote-ord, clinozoisite, wairakite and muscovite were identified both in the actual field and by geochemical modelling, but the lack of albite-low in this area needs further study.

The evolution of the fluid may suggest that most of the common cations found in the geothermal field originate from the dissolution of rocks. Cl is very stable due to its chemically conservative nature and the low concentration in added rocks. The high Cl concentration in the two studied wells is derived from the dissolution of salt that formed by the repeated transgressions of the sea during formation of the reservoir rocks.

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