The United Nations University

GEOCHEMICAL STUDY OF THE GEYSIR GEOTHERMAL FIELD IN HAUKADALUR, S-ICELAND

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ABSTRACT

The Geysir geothermal field in Haukadalur, S-Iceland is one of Iceland's most famous tourist attractions and a treasured historical place. The geochemistry of the field was studied by the compilation of all older data and by sampling and analysis of two hot springs and three wells nearby. The main aim of the study was to evaluate the reservoir temperatures and geochemical properties of the field and assess possible changes over time. Further, the project aimed at studying the relationship between the Geysir geothermal field and exploited wells in the neighbourhood. The future protection of the field was also a point to be considered in the course of the study.

The geothermal waters are sodium chloride and bicarbonate waters with high contents of fluoride and boron indicating reactions with acidic volcanic rocks. The waters in the warm wells of Nedridalur and Helludalur are carbonate waters with high silica, typical for mixed waters on the boarders of high-temperature geochemical fields. The radioactivity of the water is also found to be 10-100 times higher than that encountered in most other geothermal fields in Iceland. The calculated quartz geothermometer values for water from the Geysir hot spring indicate minimum reservoir temperatures of 240°C. Other hot springs give lower values, probably due to starting precipitation of silica. The calculated mineral saturation indices for the waters show that water from Geysir itself is in near equilibrium at 220-240°C, whereas waters from the other hot springs show signs of boiling, condensation and mixing. The Na-K and Na-K-Ca geothermometers give mostly lower values for the hot spring waters than the quartz geothermometer gives but higher for the warm wells. Only minor changes, probably due to different sampling and analysing methods, are found in the chemistry of the hot spring waters during the last 30 years. The chemistry and isotopic studies of the warm waters from wells nearby indicate that they originate from mixing of run-off water from the Geysir geothermal field and local cold groundwater. The results of the study stress the need for enhanced reservoir research, increased protection and the monitoring of the effects of nearby exploitation.

1. INTRODUCTION

The Geysir geothermal field in Haukadalur is located in South Iceland, about 110 km from the capital, Reykjavik and 50 km from the sea, at approximately 100 m altitude. The Geysir area lies in a shallow valley and is elongated in a north-south direction. The Geysir hot spring itself lies at the bottom of the eastern slope of the hill Laugarfjall, which rises to 187 m. Further west are the Bjarnarfell mountain, which rises to 727 m and to the north, Sandfell, a lava shield of 610 m, forming the horizon, but to east and south glacially eroded planes slope gently southwards to the ocean.

Most of the geothermal activity occurs in an area which is only a few hundred metres across, but thermal manifestations, mostly in the form of warm springs, are spread over an area of approximately 6 km × 1 km, which is elongated in the prevailing tectonic direction within this region. Surface rocks of the area belong to the Brunhes magnetic epoch (younger than 700,000 years). They consist of interglacial basaltic lavas, pillow lava and hyaloclastite formations, also of basaltic composition, but have erupted under glaciers, and domes of spherulitic rhyolite. All the boiling hot springs within this field are located within intensively altered basalts. Springs are found at the foot of the cliffs on the west side of Laugarfjall and the alluvial plain to the south, as far as 4 km from the main hot springs. Warm and hot springs also occur in Haukadalur about 2 km to the north. Acid pools and small mud pots are found within the main hot spring area.

The oldest written accounts about the Geysir thermal area date back to the year 1294 AD when earthquakes caused great changes in the area and some hot springs disappeared and new ones were created. Once or twice each century large earthquakes occur in S-Iceland. In written annals it is reported that in 1630 the Geysir in Haukadalur erupted so violently, after having been dormant for some 40 years, that the area around it trembled during the eruptions. Since that time Geysir in Haukadalur, as well as the hot spring Strokkur, have attained world fame for their geyser activity and a large number of travellers and scientists have visited the area. Geysir has also become the international name for the phenomenon of an erupting hot spring (as the English word geyser attests). Before the last big earthquakes of 1896, the activity of Geysir had declined so much that months could pass between eruptions. At the same time, the activity of Strokkur had increased considerably. The earthquakes revived Geysir, erupting up to a height of about 60 m, sometimes once in an hour. After 1896 the activity declined gradually. In 1935 Geysir was reactivated when a narrow ditch was dug through the rim of the silica bowl that had accumulated around its vent, lowering the water table. This ditch was gradually refilled with silica, deposited from the water. In 1981 the ditch was cleared out and eruptions can now be stimulated by lowering the water level and putting in it a generous dose of soap.

Geochemistry is one of the most economical and efficient methods to study geothermal reservoirs during exploration, exploitation and utilization. Geothermal fluid which ascends from a geothermal reservoir and emerges at the surface provides information about the subsurface conditions. The ascending geothermal fluid from the reservoir to the surface may cool by conduction by adiabatic cooling (boiling), by mixing with subsurface cold waters or by any combination of these processes. The chemical composition of the surface discharge can be used to distinguish between these processes and to evaluate underground temperature.

The main parts of this study are sampling and analysis of the fluid, and interpretation of the results with comparison to previous work in the geothermal field. The main objectives are as follows:

1. To detect and explain possible changes in chemical composition and properties of the thermal fluids with time;
2. To evaluate reservoir temperatures and equilibrium conditions using chemical geothermometers and equilibrium calculations. Various chemical geothermometers such as silica, Na-K, Na-K-Ca and gas geothermometers are used. Comparison is made between the results of these and of the equilibrium temperature. Also the possible physical processes controlling the chemistry of the geothermal fluid in the field are assessed;

3. To assess the probable equilibrium temperatures, calculations made using the WATCH aqueous speciation program of Arnórsson et al. (1982);
4. To evaluate mixing and boiling processes;
5. To assess environmental effects of exploitation.

This report presents my work during the last 12 weeks of six months of geothermal training at the United Nations University in Reykjavik, Iceland.

2. THE GEOLOGICAL AND HYDROGEOLOGICAL SETTING

Iceland is located on the Mid-Atlantic Ridge, where the American and Eurasian continental plates are drifting apart and new crust is continuously forming. The geothermal areas in Iceland (Figure 1) are divided into two distinct groups. Low-temperature areas are found in Quaternary and Tertiary volcanics and have temperatures ≤150°C at 1 km depth. The high-temperature areas are confined largely to the central volcanoes of the active volcanic rift zones, and draw their heat from local accumulations of igneous intrusions located at a shallow level in the crust (Saemundsson,1979).

A simplified outline of the geology of the Geysir geothermal area is shown in Figure 2. It lies at the eastern margin of the southwestern volcanic rift zone, but no volcanic activity is accounted for during the last 10,000 years inside the area itself. The thermal area is heated by the intrusive roots of a now extinct central volcano, found at several kilometres depth in the crust. Laugarfell is a rhyolite dome and rhyolite is found in the southeastern and northern parts of the Bjarnarfell mountain, rising to the west. The mountain though consists mostly of basaltic lava flows and a brownish, crumbly rock type known in Icelandic as móberg (peat- or brown-rock), but the scientific name is "hyaloclastite".

FIGURE 1: The volcanic zones and geothermal areas in Iceland

Fractures strike SW-NE but there is some evidence of other fracture systems being connected with the geothermal area, probably related to the now extinct central volcano.

Most of the hot springs in the Geysir area and all of the most active ones lie on a fracture striking northeast. All the boiling hot springs within the field are found within intensively altered basalts (Arnórsson, 1969). The geological map shows, however, that the thermal activity in the area is much more wide spread. Warm springs occur at the foot of Laugarfjall both at its western side and on the alluvial plain to the south. Warm and hot springs also occur in the vicinity of the farm Haukadalur, about 2 km to the north at the eastern slope of Laugarfjall. In the slope above the most active area, where the water table is expected to be at deeper levels, spots of hot ground occur and fumaroles are also found in the talus on the northern slope of Laugarfjall. Acid pools and mud springs are found among the alkaline hot springs in the southern part of the main hot spring area. Extensive deposits of silica sinter have formed around many of the alkaline hot springs. From the distribution of the thermal activity and the high fluoride content of the thermal waters, it is concluded that the hot water ascends either along permeable contacts between the Laugarfjall dome and the basalts, or that the water ascends along permeable cracks within the rhyolite itself. Many records exist of changes in the hot springs during earthquake episodes (Thorkelsson, 1925). This indicates rejuvenation of permeability in the upflow zone
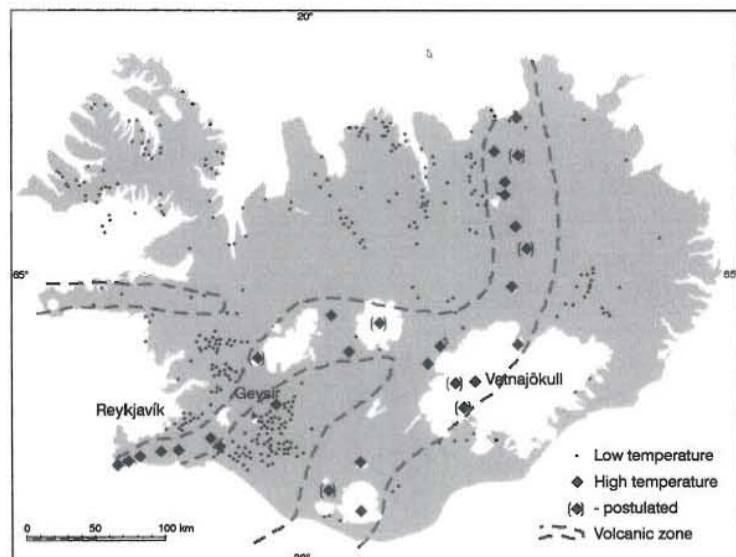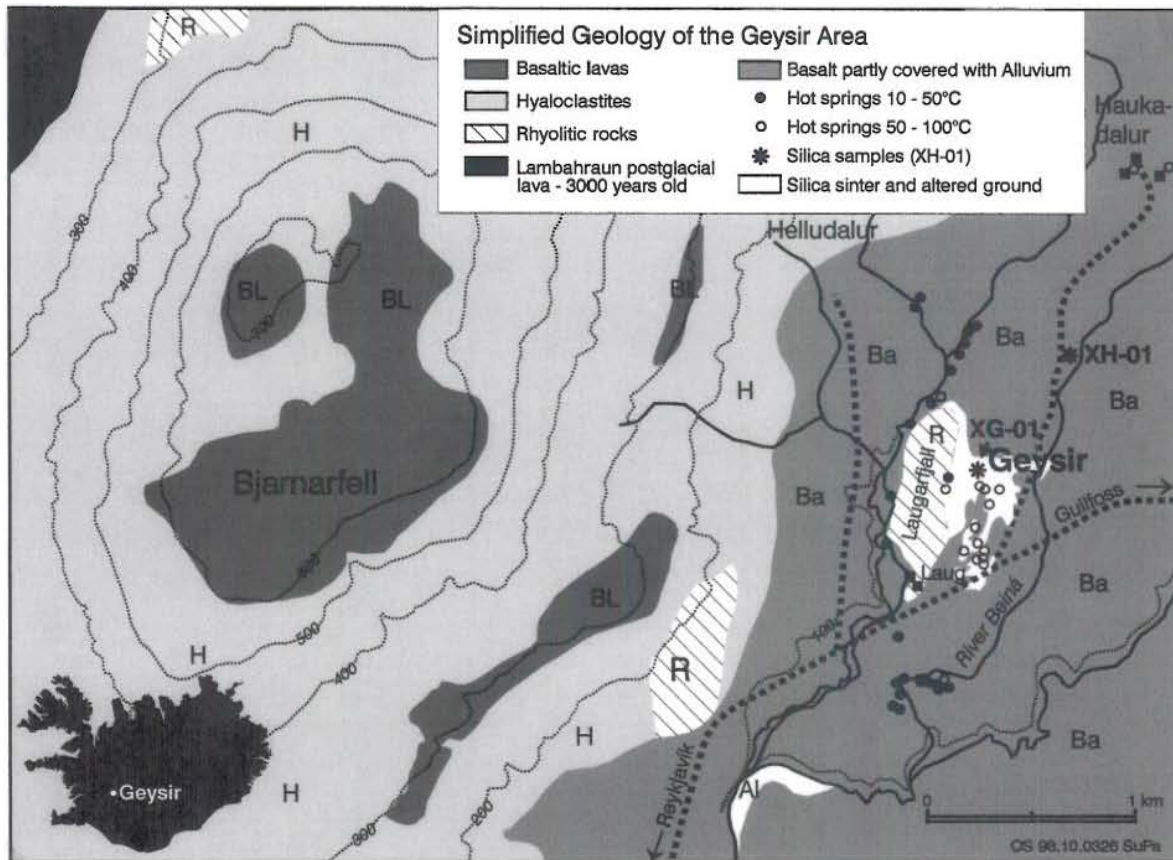
FIGURE 2:   A simplified geological map of the Geysir area and its surroundings (Torfason, 1985)

caused by tectonic movements. Drillholes have been sunk nearby, in Nedridalur and Helludalur (Figure 3). It is possible that they may have had some effect on Geysir and the thermal area. The deepest well
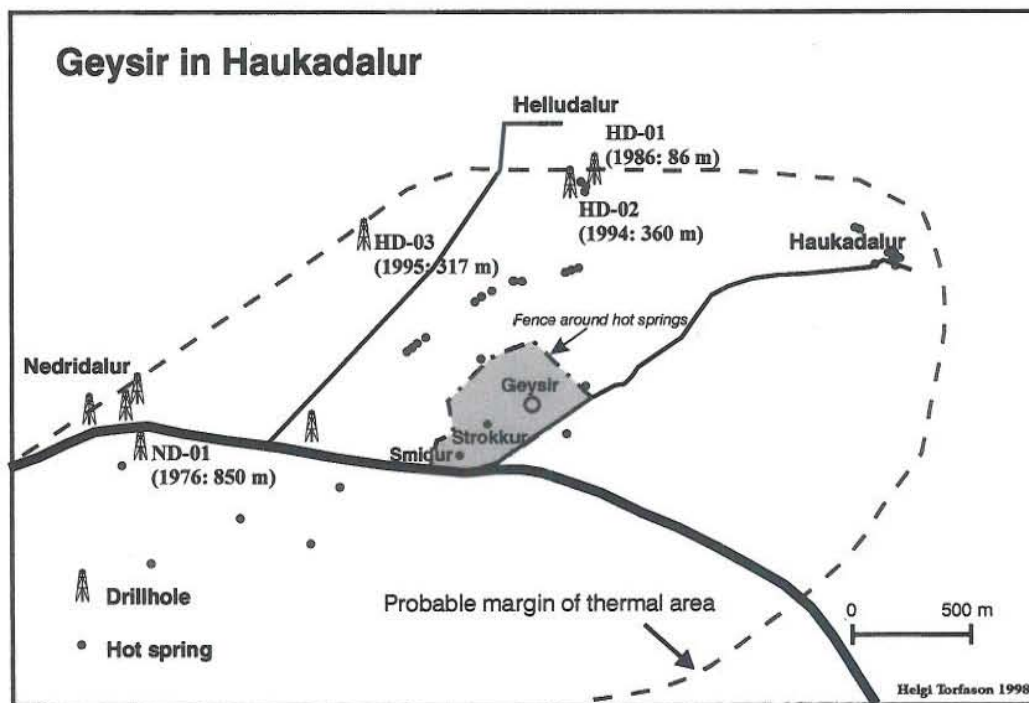

FIGURE 3:   The Geysir geothermal field, location of hot springs and drillholes (Torfason, 1985)

TAFLA 1: Flow rates from hot springs in Haukadalur, measured in 1994 by Helgi Torfason

Name	May 30 (l/s)	September 17 (l/s)
Geysir	1.7	1.8
Strokkur	1.3	1.9
Smidur	0.1	0.1

is 850 m deep and struck an aquifer at 386 m. The flow rate is 5 l/s and the bottom hole temperature is 173°C. There is a constant thermal gradient below the producing aquifer, equivalent to 220°C/km (Figure 4).

The flow rate from the Geysir field has been measured at least three times and individual hot springs have also been measured. The total flow amounted in 1967 to 14 l/s, in 1984 it was 13 l/s but only 9 l/s in 1994. It is not known whether this decrease in flow is related to drilling or other activities in the area. Table 1 gives flow rates for some of the hot springs in the field, measured in 1994.

The whole area is a geothermal park sitting on top of a vast boiling cauldron. A short distance away to the west rises the small Laugarfjall mountain with a panoramic view overlooking the Geysir area. The most famous hot springs in the Haukadalur geothermal field are:

The Great Geysir: The word geysir means "the spouter". The surface temperature may be as low as 72.8°C (measured in August 1998) but at a depth of 10 m it is 99.2°C. The Geysir hot spring is a regular hill, shaped of silica sinter, on top of which is a flat bowl or crater with a diameter of about 20 m. In the centre is a vent, extending at least 23 m downward and the highest measured temperature is 112°C at its bottom. Through the vent, columns of water and steam are shot as high as 60 m into the air during an eruption (Figure 5). The age of Geysir is not known but the build-up of the large hill of silica sinter must have taken thousands of years (Barth, 1940).

Strokkur: The main tourist attraction of the Geysir area is now the hot spring Strokkur
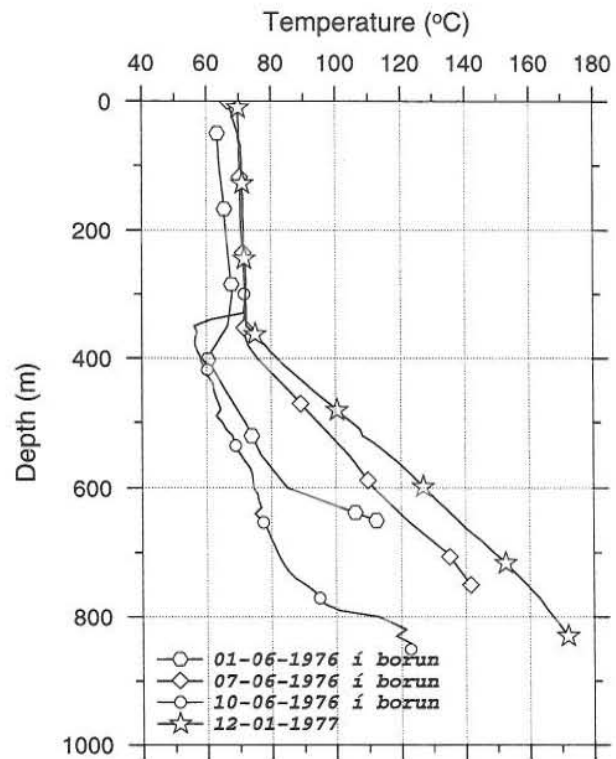

FIGURE 4: Temperature profile from the deep well ND-01 at Nedridalur (Orkustofnun database)

FIGURE 5: Eruption in the Great Geysir, the mount surrounding the bowl is made of silica (photo by Rafn Hafnfjörð)
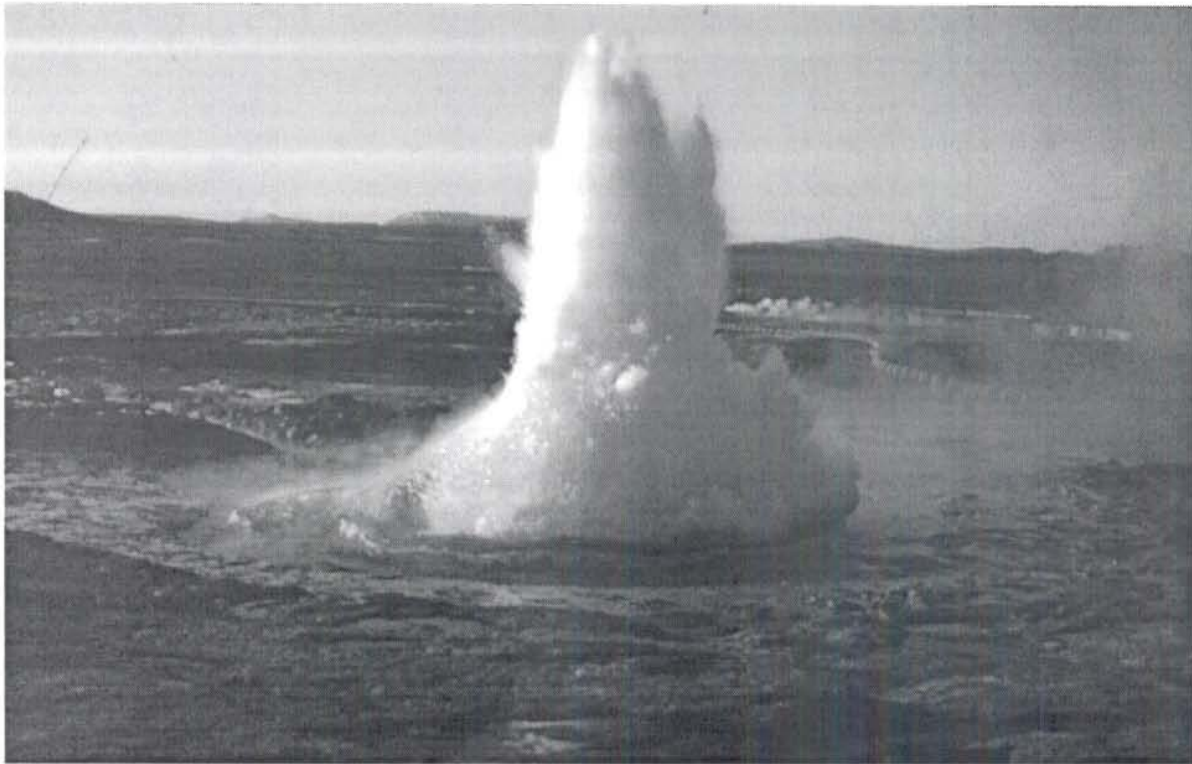
FIGURE 6: The Strokkur hot spring starting to erupt (photo by Benedikt Steingrímsson)

(the churn). It lies 100 m south of the Great Geysir, erupting every 5-10 minutes to a maximum of 30-35 m (Figure 6). It was reborn in an earthquake in 1789, but declined greatly in another earthquake, in 1896. It was artificially reawakened in 1963 by the drilling of a 40 m deep well down through its bottom.

Smidur: Means "the craftsman" or "the carpenter", because a carpenter working in the area in 1907 "dug it out". Smidur erupts small jets of water, but larger ones if treated with soap. It has a very nice silica bowl surrounding its vent. The basin measures 0.9 x 0.8 m. The measured temperature 1 m below the surface is 99.7°C.

3. THE MECHANISM OF GEYSIR

The Great Geysir erupts very irregularly and today it hardly erupts unless treated with soap. In the beginning of the 18th century Geysir erupted three times each day, but its activity declined between earthquake episodes and an interval of several days or weeks between eruptions became common. When Geysir was at its best, eruptions reached heights of 70-80 m with a thundering noise. For several tens of minutes afterwards a thick column of steam persisted. In 1894, a young pharmacist put ten pounds of soap in Geysir in order to trigger an eruption. This method had been used successfully in Yellowstone, USA. It also proved to be very successful at Geysir and since then soap has usually been effective in rousing Geysir from its slumber.

The uppermost part of Geysir's plumbing system has been probed with scientific instruments. Geysir has formed a large bowl in the sinter, 20 m in diameter and 1 m deep. In the centre of this bowl, the upflow channel is about 1 m wide. This pipe starts to get irregular in shape about 0.8 m from the rim, varying between 0.4 and 1.0 m in width down to 23 m depth, where it becomes too narrow or irregular to be probed (Figure 7). At sea level water boils at 100°C, but at higher altitudes the boiling point is
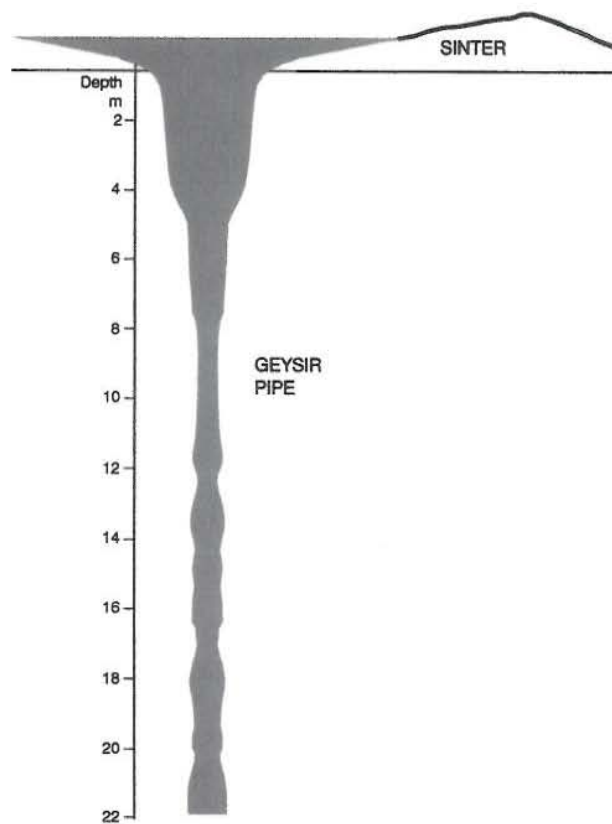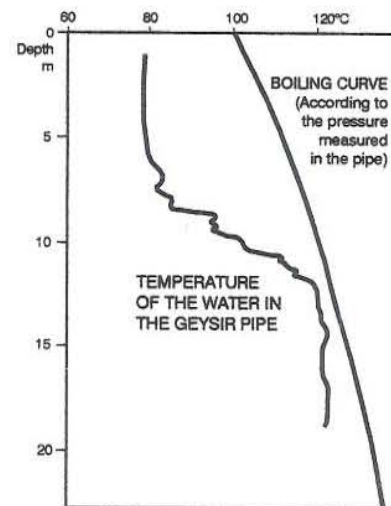
FIGURE 7: The Geysir pipe (Torfason, 1985)

FIGURE 8: The temperature in the Geysir pipe (Torfason, 1985)

lowered as the air pressure decreases. Similarly, the boiling point is raised with increasing pressure, as exerted by a column of water. This relationship is known as "the boiling curve". Therefore, the temperature of water under hydrostatic pressure at depth in the earth's crust, much higher that 100°C.

The famous German chemist, Robert Bunsen, visited Iceland in 1846. After studying the eruptions of Geysir and measuring the increasing temperature down the pipe, he produced the theory on the eruptive mechanism that still prevails with only minor changes. The temperature in the Geysir plumbing system rises from 85-90 °C in the bowl to around 120°C at 23 m depth, which is still below boiling point (Figure 8). At a depth of around 15 m the temperature is very close to boiling and thus the water column is very unstable. Because of this instability, water in some parts of the pipe may start to boil and trigger an eruption. The eruptions in Strokkur are simple; intermittent jets of water are shot into the air without warning, and little steam is produced. The pipe of Strokkur is not emptied so it does not have to fill again and the next eruption occurs several minutes later. The eruptions in Geysir are quite different. They begin with rumbles, while the water in the Geysir bowl gradually gets more vigorous, and jets of water are thrown 10-20 m into the air. This lasts for some 10-15 m minutes or more. Some of the water is thrown out of the bowl and sometimes great quantities of water are ejected from the bowl as the water bulges up. Suddenly the water is sucked down into the pipe and the geyser becomes quiet for some 30-60 seconds. Then the water shoots out, forming a column 60-80 m high. The water drains from the pipe and gradually the column changes from being mostly jets of water to a violent steam. This phase lasts for 5-10 minutes. The vigour of the steam decreases gradually and dies out at last as the pipe starts filling again.

4. METHODOLOGY

The composition of geothermal fluids depends on many factors. The most important are temperature dependent reactions between host rock and water. Leaching plays an important role when the amount of a particular constituent is too small to attain equilibrium or does not participate in any temperature dependent mineral /solute equilibria. Processes such as mixing, boiling and cooling may also have significant influence on the final composition of the geothermal water.

4.1 Collection of analytical data

The present geochemical study is mostly based on 7 samples selected from a few representative hot springs in the area including Geysir, Strokkur, Smidur and wells ND-01 in Nedridalur and HD-02 and HD-03 in Helludalur and a cold water sample from Kaldilaekur and a gas sample from a boiling spring in the eastern part of the field. Five of these samples were collected in 1998. The results are compared with older data.

The fluid samples were collected in several sub- fractions in different containers and treated accordingly (Ólafsson,1988) as described in Table 2. Before sampling it is necessary to measure the temperature in different locations in order to select the optimal site. A funnel is placed upside down over the major upflow and stabilised by weight to prevent atmospheric contamination. If possible, it is best to have a free flow of water from the sampling spot through the cooling device; else a vacuum pump is used. Before collection begins, the containers should be rinsed thoroughly with the fluid collected. Only one gas sample was collected, from boiling spring 0424 in the Geysir geothermal field.

TABLE 2:   Analytical methods used for the constituents determined

Consti-tuent	Frac-tion	Method	Brief description	Standard	RSD%	D.1. ($\mu g/l$)
pH	Ru	Electro-metric	A glass electrode combined with a reference potential is inserted into the sample, pH and temperature values recorded.	Merck titrisol, pH 4, 7, 10	±0.1 pH unit	
CO_2	Ru	Electro-metric titration	Sample pH adjusted to 8.2 with HCL/NaOH, then titrated to pH 3.8 with 0.1N HCL using a pH meter.	Merck titrisol 0.1N HCL	3.6 for 5-1500 ppm	1000
H_2S	Ru	Titration	NaOH added to make sample basic. Titrated with 0.001 M HgAc, dithizone as indicator.		3.9 for 0.03-800 ppm	20
O_2	Ru	Colorimetric	Measurements with chemmetric ampules.			1
SiO_2	Rd	Spectro-photo-metry	Iodine and thiosulphate added to destroy H_2S, ammonium heptamolybdate and HCL added. Absorption determined at 410 nm.	Spóastadir thermal water, SiO_2 conc. (104 ppm) determ. gravimetrically.	1.8-2.5 for 0.87-67.3 mg/l	500
F	Fu	Selective electrode	TISAB buffer added, electrode inserted and potential read.	Merck 1000 mg NaF/H_2O	3.5 for 0.85 ppm	2
Cl	Fu	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. Cl determined using a conductivity detector.	Merck titrisol HCl/H_2O	2.9 for 10 mg/l	25
SO_4	Fu/Fp	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. SO_4 determined using a conductivity detector.	Merck titrisol H_2SO_4/H_2O	1.5 for 98.5 mg/l	20
B	Fu	Spectro-photo-metry	Sample buffered with $NH_4Ac/Na_2EDTA/$ HAC Azomethine - H/ascorbic acid reagent added. Absorption determined at 420 nm.	Merck titrisol H_3BO_3/H_2O		5
Na	Fa	AAS DA	Small amount of Cs solution added and sample directly aspirated into oxidizing an air acetylene lame. Absorption read at 589.6 nm.	Merck titrisol $NaCl/H_2O$	1.2-1.5 for 8.2-52 mg/l	1
K	Fa	AAS DA	Small amount of Cs solution is added and the sample directly aspirated into an oxidizing air acetylene flame. Absorption read at 766.5 nm.	Merck titrisol KCl/H_2O	7.9 -12.5 for 1.6-6.3 mg/l	1
Mg	Fa	AAS DA	A small amount of La solution is added to water sample which is directly aspirated into an oxidizing air-acetylene flame. Absorption read at 285.2nm	Merck titrisol $MgCl_2/HCl$	2.4-4.8 for 21-82 mg/l	1
Ca	Fa	AAS DA	A small amount of La solution is added and the sample directly aspirated into an oxidizing air acetylene flame. Absorption read at 422.7 nm	Merck titrisol $CaCl_2/HCl$	1.7-3.3 for 9.36 mg/l	10

Consti-tuent	Frac-tion	Method	Brief description	Standard	RSD%	D.l. (μg/l)
Al	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 1500°C, atomized 3 s 2400°C. Purge gas Ar 309.3 nm	Merck Al(NO$_3$)$_3$ 0.5M HNO$_3$		1
Fe	Fa	AAS GF	Dried 30 s 140°C, ashed 30 s 1200°C, atomized 3 s 2100°C. Purge gas Ar 248.3 nm	Merck Fe(NO$_3$)$_3$ 0.5M HNO$_3$		0.1
Mn	Fa	AAS GF	Dried 30 s 140°C, ashed 30 s 1200°C, atomized 3 s 2400°C. Purge gas Ar.279.5 nm	Merck Cr (NO$_3$)$_3$ 0.5 M HNO$_3$		0.1
Cu	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 900°C, atomized 2 s 2000°C. Purge gas Ar.324.7 nm	Merck Cu(NO3)$_2$ 0.5 M HNO$_3$		0.1
Zn	Fa	AAS GF DA	Dried 30 s 125°C, ashed 30 s 1200°C, atomized 3 s 2300°C. Purge gas Ar.357.9 nm	Merck Zn(NO$_3$)$_2$ 0.5 M HNO$_3$	34-37 for 280-310 μg/l	0.1-20
As	Fa	AAS HG	Organic matter convert. with HNO$_3$-H2SO$_4$-HClO$_4$. As reduced and converted to AsH$_3$ using NaBH$_4$. The hydride swept into a heated cell in the beam of an As EDL lamp and As determined at 193.7 nm.	Merck H$_2$AsO$_4$ 0.5 M HNO$_3$	5.5-9 for 5-20 μg/l	0.1
Cr	Fa	AAS GF	Dried 30 s 125°c, ashed 30 s 1200°C, atomized 3 s 2300°C. Purge gas Ar.357.9 nm	Merck Cr(NO$_3$)$_3$ 0.5 M HNO$_3$	0.4-1 for 19-77 μg/l	0.1
Pb	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 750°C atomized 2 s 2000°c. Purge gas Ar. 283.3nm	Merck Pb(NO$_3$)$_2$ 0.5 M HNO$_3$	3.2-5.2 for 25-100 μg/l	0.1
Li	Fa	AAS DA AES	Sample directly aspirated into an oxidizing air-acetylene flame. Absorption read at 670.8 nm. Clay digests aspirated into air-acetylene flame and emission read at 670.8 nm.	Merck titrisol for 0.1 ppm. Na, K and Li after dilution to 1 l		0.5
Hg	Fu	AAS F1	For clay digest Hg is reduced and converted to HgH$_2$ with NaBH$_4$. Hydride is swept into a cell, placed in beam of an Hg EDL lamp and atomic abs. determ. at 2573.7 nm. At collection KMnO$_4$ / K$_2$S$_2$O$_8$/ HNO$_3$ added to water sample, At start of determ. H$_2$NOH, HCl and SnCl$_2$ added. The resulting gaseous Hg is amalgamated with gold and heated to be released into a cell for flameless AAS determ. at 253.7 nm	Merck Hg(NO$_3$)$_2$ 0.5 M HNO$_3$	4-16 for 2.5-18.1 ng/l	0.001
TDS	Fu	Gravimetric	Sample evaporated and dried at 105°C		2.6-3.8 for 190-1680 ppm	2500

AAS	= Atomic absorption spectroscopy		DA	= Direct aspiration
GO	= Graphite furnace		D.l.	= Detection limit
Fa	= Filtered, acidified		Ru	= Raw, untreated
Fu	= Filtered, untreated		RSD	= Relative standard deviation
Fp	= Filtered, precipitated		Rd	= Raw, diluted

4.2 Chemical analysis

The fluid temperature was measured at the site and for H$_2$S determination, a 5 N NaOH solution was added to the sample and analysed in the field. The remaining analyses were made in the geochemical laboratory of Orkustofnun by Mr. Kristján Sigurdsson. The most convenient method to determine CO$_2$ and H$_2$S is by titration with hydrochloric acid using a ph-meter and with mercuric acetate using dithizone as the indicator, respectively. Non-condensable gases were analysed using gas chromatography in the chemical laboratory of Orkustofnun. The credibility and usefulness of geochemical data depends on the methods used and the care taken in the collection of the samples. If the sample conditions are not well known, the significance of analytical results may not be fully appreciated. The analytical methods and analytical procedures are described briefly in Table 2. The analytical results of the laboratory are summarized in Table 3 and for comparison data from 1968-1993 are presented in the same table.

TABLE 3: Analytical data of geothermal fluids of the Geysir geothermal field in Haukadalur, S-Iceland (concentrations in mg/l)

Samp. No.	Location	Date	Temp. (°C)	pH/°C	SiO_2	Ca	Mg	Na	K	Cl	SO_4	CO_2	H_2S	F	B	Fe	Mn	Cu	Zn	Al	As	Hg	Pb	Li	δD	δ^{18}O
683223	Geysir	1968-04-15	84	8.7/84	509	0.8	0.03	209	22	122	114.5	134.6	0.7	11.5	1.27	0.0125							0.5315			
793004	Geysir	1979-05-22	72	9.36/22	486	0.76	<0.01	248	26	132.4	117	136.8	0.86	8.66	0.95	0.0172										
820047	Geysir	1982-04-02	76.8	9.21/23	542	0.81	0.016	220	24.3	121	98	140	2.11	8.74												
920313	Geysir	1992-11-27		9.32/22	528	0.73	0.006	228	23	123	102	137	0.69	8.39	1.08	0.0006	0.0004			0.41					-83,3	-7,77
930217	Geysir	1993-10-03				0.78	0.007	234	23	128	104			8.48	1.07	0.002	0.0003			0.36				0.41		
980423	Geysir	1998-08-06	72.8	9.28/23	501	0.81	0.01	228	23.6	125	105	144	0.67	8.31	0.9	0.0024	0.0008	<0.0001	<0.0001	0.36	0.147	0.00009	0.0003	0.404	-83.5	-7.75
683227	Strokkur	1968-04-15	87	8.5/87	476	0.9	0.05	224	14	130	106	86	0.9	12.5	1.06	0.0346							0.244			
82009	Strokkur	1982-04-02	78	8.56/20	457	0.73	0.011	225	14.4	132	105	159	0.25	12.9	0.96										-77.4	-7.77
920311	Strokkur	1992-11-27	120	8.92/22	437	0.79	0.013	238	13.5	121	100	166	0.86	12	1.08	0.004	0.0007			0.55					-81.7	-8.31
920312	Strokkur R.	1992-11-27		9.26/22	448	0.77	0.013	243	15.2	130	108	146	0.07	11.4						0.381						
683231	Smidur	1968-04-15	100	9/100	374	0.9	0.14	212	9.8	110	121	75	1.9	12	1.09	0.645							0.109			
79006	Smidur	1979-05-22	98	8.93/22	325	0.68	0.006	228	12.0	115	150	92	0.59	10.9	0.82										-74	-6.14
980425	Smidur	1998-08-06	99.7	9.17/23	358	0.81	0.011	225	10.1	117	121	107	1.02	11.3	0.83	0.009	0.0007	0.0002	<0.0001	0.11	0.105	0.00021	0.0005	0.244	-82.1	-7.42
740068	Ned. ND-01	1974-07-24	62	7.3/20	167	5.5	1.62	260	31	40.1	27	399	<0.03	5.4												
82013	Ned. ND-01	1968-04-02	68	7.52/20	146	7.72	0.611	223	44	46	28	462.5	0.04	5.88	0.22									0.017	-68.4	-9.54
980426	Ned. ND-01	1998-08-06	68.5	7.55/22	182	11.5	1.04	210	44	44	30	449	0.04	5.23	0.32	0.054	0.0064	<0.0001	0.0002	0.005			0.0007	0.059	-72.1	-9.61
860104	Hel. HD-02	1986-07-22	54	7.73/22	139	3.35	0.5	174	22	40.6	27	302	<0.03	5.29	0.31	<0.025										-9.71
980422	Hel. HD-02	1998-08-06	58.8	7.56/22	125	4.13	1.37	165	17	38	25	279	<0.03	5.25	0.26	0.013	0.0006	0.0002	0.0002	0.01			0.0005	0.064	-72.4	-9.68
980421	Hel. HD-03	1998-08-06	38	8.18/22	84	2.79	0.178	74	9.8	18	11.0	123	<0.03	3.16	0.1	0.0028	0.001	0.0004	0.0143	0.005			0.0004	0.021	-64.9	-9.13
82011	Kaldilaekur	1982-04-02	5	8.01/20	31	3.22	0.461	11.8	0.96	7.4	0.5	16.6	<0.01	0.07	0.01									0.001	-66.0	-9.78

4.3 Fluid classification

4.3.1 Cl-SO$_4$-HCO$_3$ triangular diagram

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 Giggenbach diagrams is obtained by the summation of the concentration of all the three constituents

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

and calculating the percentage of individual constituents

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

4.3.2 Cl-Li-B triangular diagram

The Cl-Li-B triangular plot has been suggested to trace the origin of the thermal fluid. Of the three components, Li is probably least affected by secondary processes. Therefore, it may be used as a "tracer" for the initial deep rock dissolution process and as a reference for evaluating the possible origin of the other two important "conservative" constituents of thermal waters, Cl and B (Giggenbach,1991). Once added, Li remains largely in solution. Both Cl and B are added to the Li containing solution in proportions close to those in crustal rocks. At high temperatures Cl occurs largely as HCl and B is likely to have been introduced with the magmatic vapours which lead to the formation of the deep acid brine responsible for rock dissolution. At low temperatures, the acidity of HCl increases rapidly, and it is soon converted by the rock to the less volatile NaCl; B remains in its volatile or to be carried in the vapour phase even at quite low temperatures.

4.3.3 Cl/B ratio

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

of Cl and B from the rock becomes faster, and because of the low Cl content in Icelandic basalt, the B enrichment is greater (Arnórsson and Andrésdóttir, 1995). So a study of this ratio can yield valuable information on the origin of the water.

4.4 The WATCH computer program

The WATCH computer program (Arnórsson et al., 1982; Bjarnason, 1994) is used to calculate the speciation, ionic balance, geothermometer (quartz, chalcedony and Na/K) values and the log solubility products (log Q/K values) of minerals for deep water corresponding to the samples.

1. The ionic balance is a good tool for checking the analytical results. The value is near to zero if the analyses are accurate and high if the analytical results are not accurate. In dilute waters, values in the range of ± 10% are thought to be good enough.

2. The deep water temperatures were calculated with use of various geothermometers (quartz, chalcedony and Na/K). The quartz temperature was used as a reference temperature when the speciation of the waters was calculated. As the Geysir geothermal field is a high-temperature area, the use of quartz as a reference temperature is assumed to give the most reliable results.

3   The log solubility product of minerals was calculated for the six thermal samples collected during this study. As these samples are representative for the Geyser area, they were run on the WATCH program in the temperature range 50-300°C. The mineral equilibrium in a high-temperature area like Geyser, almost always lies in this temperature range.

Log Q/K values are obtained from the log solubility products of minerals in deep waters, where Q is the calculated ion activity product in the water and K is the equilibrium constant. The saturation index is given by

$$Saturation \ index \ (SI) \ = \ \log Q - \log K \tag{3}$$

The *SI* value plotted against temperature for each mineral gives an estimation of the equilibrium state of the fluid. *SI* higher than zero shows supersaturation, below zero shows undersaturation and equal to zero shows equilibrium. The point at which several minerals cross the saturation line is near reservoir temperature. The saturation index (log Q/K) was calculated for minerals assumed to be relevant like anhydrite, calcite, fluorite, amorphous silica, chalcedony, quartz, wairakite, albite-low, microcline, analcime and adularia for all six hot water samples.

4.5 Geothermometers

4.5.1 Silica geothermometers

The silica geothermometers used to predict subsurface temperature of reservoirs are based on experimentally determined solubilities of chalcedony and quartz. In Iceland, rocks are young but equilibrium with chalcedony seems to be attained at temperatures up to 180°C, and equilibrium with quartz at higher temperatures. The formation of quartz or chalcedony is considered to be determined by the rate of dissolution of silica from the primary constituents of the rock and the kinetics of precipitation. Since 1960, several formulae for the estimation of deep temperatures have been presented based on the concentrations of silica in thermal water. These formulae give more or less the same temperature results. The differences are in the quartz geothermometer for the same concentration of silica, due to their different equilibration solubilities.

Application of the silica geothermometer is based on that the activity of H_4SiO_4, is temperature dependent. At high pH such as for the geothermal waters in the Geysir area (with pH 8-9) a significant fraction of the dissolved silica ionizes, generating protons, and does not contribute to the activity of H_4SiO_4. For such water, allowing analysed silica to represent H_4SiO_4 is unsatisfactory, as dissolved silica is an important proton donor at high pH. The computer program WATCH was used to calculate the activity of H_4SiO_4 and the silica temperature. The calculated results are listed in the Table 4.

TABLE 4: Different geothermometer values calculated with the WATCH program

Location	T (°C)	Ionic balance	Log Q/K T (°C)	Na/K - T (°C)	Quartz - T T(°C)
Geysir	72.8	-9.09	100-200	194	241
Strokkur	120	-1.30		144	231
Smidur	99.7	7.45	150-200	125	217
ND-01 (Nedridalur)	68.5	-7.68	150-175	283	175
HD-02 (Helludalur)	58.5	-1.97	145	198	145
HD-03 (Helludalur)	38	-29.99	-	225	123

4.5.2 Cation geothermometers

The Na-K geothermometer is based on the exchange of Na^+ and K^+ ions between coexisting alkali feldspars with temperature-dependent equilibrium constant

$$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+ \qquad (4)$$
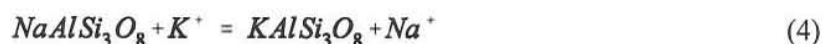
The equilibrium constant, K_{eq}, for Reaction 4 is

$$K_{eq} = \frac{[KAlSi_3O_8][Na^+]}{[NaAlSi_3O_8][K^+]} \qquad (5)$$

In the application of Equation 5, the usual simplifying assumptions are that activities of the solid reactants are unity and the dissolved species about equal to their molal concentration in aqueous solution. Thus, Equation 5 reduces to

$$K_{eq} = \frac{[Na^+]}{[K^+]} \qquad (6)$$

Many temperature functions have been presented for the Na-K geothermometers by various authors, but there is a large discrepancy between temperatures resulting from the different equations. The following formulae are used in this report (the concentration of Na and K are in mg /kg):

Na/K temperature of Fournier (1979):

$$t(°C) = \frac{1217}{1.483 + \log(Na/K)} - 273.15 \qquad (7)$$

Na/K temperature of Giggenbach (1988):

$$t(°C) = \frac{1390}{1.75 + \log(Na/K)} - 273.15 \tag{8}$$

Na/K temperature of Truesdell (1976):

$$t(°C) = \frac{856}{0.857 + \log(Na/K)} - 273.15 \tag{9}$$

Na/K temperature of Tonani (1980):

$$t(°C) = \frac{833}{0.780 + \log(Na/K)} - 273.15 \tag{10}$$

Na/K temperature of Arnórsson et al. (1983a and b):

$$t(°C) = \frac{933}{0.993 + \log(Na/K)} - 273.15 \tag{11}$$

The *K-Mg* geothermometer (Giggenbach,1988), based on the equilibrium between water and the mineral assemblage K-feldspar, K-mica and chlorite, is found to respond fast to changes in the physical environment and usually gives a relatively low temperature. This geothermometer is also reasonable for estimation of reservoir temperature (concentrations are in mg/kg):

$$t(°C) = \frac{4410}{14.00 - \log(K/\sqrt{Mg})} - 273.15 \tag{12}$$

The ratio *Li/Mg* can be used effectively as a geothermometer applied to geothermal waters (Kharaka and Mariner, 1989) (concentrations in mg/kg):

$$t(°C) = \frac{2200}{5.470 - \log(Li/\sqrt{Mg})} - 273.15 \tag{13}$$

The ratio *Li/Na* also can be used effectively as a geothermometer applied to geothermal waters (Kharaka et al., 1982) (concentrations are in mg/kg):

$$t(°C) = \frac{1590}{0.779 - \log(Na/Li)} - 273.15 \tag{14}$$

The *Na- K-Ca* geothermometers (Fournier and Truesdell, 1973) takes into account a reaction involving the exchange of Na^+, K^+ and Ca^+ with a mineral solid solution. For the calculation of the geothermometers above approximately 100°C and below, different constants are used:

$$t(°C) = \frac{1647}{\log(Na/K) + \beta[\log\sqrt{Ca}/Na] + 2.06 + 2.47} - 273.15 \tag{15}$$

1.   Calculate [$\log (Ca^{1/2}/Na) + 2.0$], if positive, calculate the temperature, t, using $\beta=4/3$.
2.   If $t < 100°C$, use the calculated temperature.
3.   If $t > 100°C$, or [$\log (Ca^{1/2}/Na) + 2.0$] is negative, then use $\beta=1/3$ to calculate the temperature.

The *Na-K-Mg* diagram (Giggenbach, 1988) gives an indication of the suitability of water for the application of ionic solute geoindicators. It is based on the temperature dependence of the reactions

$$K\text{-}feldspar + Na^+ = Na\text{-}Feldspar + K^+ \tag{16}$$

$$2\,albite + 0.8K\text{-}feldspar + 1.6\,water + Mg^{2+} = 0.8\,Mica + 0.2\,chlorite + 5.4\,silica + 2\,Na^+ \tag{17}$$

$$2.8K\text{-}feldspar + 1.6\,water + Mg^{2+} = 0.8\,Mica + 0.2\,chlorite + 5.4\,silica + 2K^+ \tag{18}$$
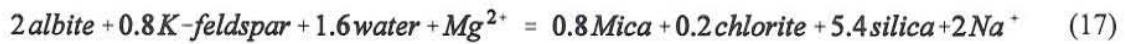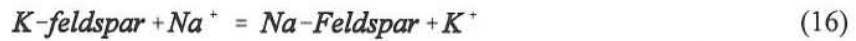
This diagram classifies waters as fully equilibrated with rock at given temperatures, partially equilibrated, and immature. The temperatures and compositions at which full equilibrium is shown may change significantly due to many Na /K geothermometer equation changes, and is most uncertain at low temperatures (Fournier, 1991). In geothermal waters the Mg concentration decreases with increasing temperature. As geothermal water flows from high-temperature rock formations to some low-temperature environment, it picks up a significant amount of Mg from the surrounding rocks and, thus, leads to a major ambiguity. To counteract this the application of the Fournier and Potter (1979) Mg-correction is required. Similar correction is also used for high-temperature waters, which pick up Mg during upflow and show lower reservoir temperatures. The coordinates for this triangular diagram are calculated as follows:

$$S = \frac{C_{Na}}{1000} + \frac{C_K}{100} + \sqrt{C_{Mg}} \tag{19}$$

$$\%Na = \frac{C_{Na}}{10S} ; \quad \%K = \frac{C_K}{S} ; \quad 100\%Mg = \sqrt{Mg/S} \tag{20}$$

This diagram gives Na-K (t_{kn}) and K-Mg (t_{km}) geothermometer values. The temperature drop in t_{kn} is minor but is major in t_{km}. This trend shows much greater speed for the K-Mg geothermometer adjusting to a change in temperature than the K-Na system. The shift in K-Mg temperature is a function of time taken by water to rise from the deep reservoir to the surface.

4.5.3 Gas geothermometers

The major gases in geothermal steam are CO_2, H_2S, H_2, CH_4, N_2, NH_3, CO and O_2. The noble gases in steam include He, Ne, Ar, etc. Carbon dioxide is generally the major gas component, often comprising more than 80% of the non-condensable gases and its concentration in total discharge increases with reservoir temperature. Barnes et al. (1978) found a very close correlation between CO_2 emanations and seismicity in certain areas, suggesting that the production of CO_2 is related to present tectonic activity. Kacandes and Grandstaff (1989) proposed that CO_2 in high temperature reservoirs is derived from either a deep magmatic or metamorphic source, comparing fluid composition resulting from water/rock experiments with reservoir data from several geothermal fields.

Organic reactions in meteoric water may be a source of CO_2 in thermal fluid. The hydrogen sulphide concentration of geothermal fluids varies widely, but is thought to be formed from reaction with iron and/or silicate minerals. Hydrogen sulphide concentration commonly decreases as the steam ascends to the surface due to reactions with the rock wall, dissociation to sulphur, or oxidation. The hydrogen concentration often changes with that of the hydrogen sulphide. The water dissociation is ubiquitous and of fundamental importance to all the redox processes in geothermal studies (D´Amore and Nuti, 1977). Truesdell and Nehring (1978/1979) suggested that hydrogen is produced by high-temperature reaction of water with the ferrous oxides and silicates contained in reservoir rocks. Methane concentration is relatively low in steam. The Fischer-Tropsch reaction has been applied successfully in some geothermal fields to explain its origin (Truesdell and Nehring, 1978). It also possibly derives from the decomposition of organic material and from the reaction between carbonaceous material and molecular hydrogen. Nitrogen originates from meteoric water saturated with atmospheric air. Ármannsson et al. (1989) argued that isotopic work involving ^{15}N suggests an atmospheric origin in some geothermal fields and the high nitrogen is caused by relatively low concentrations of other gases, e.g. CO_2. Another possible origin is ammonia dissociation (D´Amore and Nuti, 1977). The oxygen concentration is so low in uncontaminated samples that it can hardly be detected. The theoretical value is in the range of 10^{-32} -10^{-49} bar in some reservoirs (D'Amore and Panichi,1980).
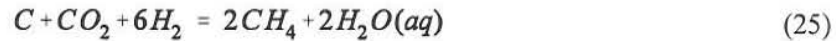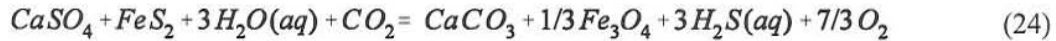
As early as in the seventies, the first empirical gas geothermometer was proposed by Tonani (1973; 1980). The relative gas concentrations were used for calculations and P_{CO_2} was assumed to be controlled by an external factor. The functions are as follows:

$$t_1(°C) = \frac{9150}{\log\dfrac{CH_4}{H_2} - 1 + 16.8} - 273.15; \quad for \quad P_{CO_2}=0.1 \ atm; \tag{21}$$

$$t_2(°C) = \frac{9150}{\log\dfrac{CH_4}{H_2} + 16.8} - 273.15; \quad for \quad P_{CO_2}=1.0 \ atm; \tag{22}$$

$$t_3(°C) = \frac{9150}{\log\dfrac{CH_4}{H_2} + 1 + 16.8} - 273.15; \quad for \quad P_{CO_2}=10 \ atm; \tag{23}$$

D´Amore and Panichi (1980) suggested a semi-empirical gas geothermometer based on the gas compositions of fluids from 34 thermal systems. They found that there was a relationship between the relative concentrations of H_2S, H_2, CH_4, CO_2 and reservoir temperatures. The following two chemical reactions were considered:

$$CaSO_4 + FeS_2 + 3H_2O(aq) + CO_2 = CaCO_3 + 1/3 Fe_3O_4 + 3H_2S(aq) + 7/3 O_2 \qquad (24)$$

$$C + CO_2 + 6H_2 = 2CH_4 + 2H_2O(aq) \qquad (25)$$

The oxygen partial pressure was assumed to be controlled by an external factor with the temperature function

$$\log PO_2 = 8.20 - \frac{23643}{T(°K)} \qquad (26)$$

The gas geothermometer was expressed by

$$t(°C) = \frac{24775}{\alpha + \beta + 36.05} - 273.15 \qquad (27)$$

where

$$\alpha = 2\log\frac{CH_4}{CO_2} - 6\log\frac{H_2}{CO2} - 3\log\frac{H_2S}{CO_2} \quad and \quad \beta = -7\log P_{CO_2} \qquad (28)$$

a) P_{CO_2} = 0.1 atm if CO_2 (% by volume) < 75;
b) P_{CO_2} = 1.0 atm if CO_2 (% by volume) > 75;
c) P_{CO_2} = 10 atm if CO_2 (% by volume) > 75 and $CH_4 > 2H_2$; $H_2S > 2 H_2$.

5. RESULTS OF CHEMICAL EXAMINATION

5.1 Analytical results

The water analysis from the research area, which were done in the period between 1968 until 1998, are shown in Table 3. The geothermal waters of Haukadalur generally have low concentrations of dissolved solids and electrical conductivity of the water samples ranges from 356 to 1106 μS/cm. There are no significant changes seen in the chemical composition of water during this period. However, a few minor differences in the analytical results were noted. The main reason is probably that the water was collected at different times and analysed by different methods. The water was also collected at different conditions and sampling methods have changed during the mentioned period. The chemical composition of the samples is rather similar. Generally the following can be stated:

Sodium and potassium concentrations in the hot spring waters reaching the surface range from 43.5 to 10.1, respectively, and for the warm waters about 74 ppm and 9.75 ppm.
Calcium concentration is very low in all the hot water springs and is influenced by water temperature, pH and carbonate concentration. The low calcium concentrations may have resulted mainly from low salinity and consequent high pH of the water (Ellis and Mahon 1977).
Magnesium concentrations are also very low in the springs (0.01 to 1.04 ppm), but higher in water from the wells.

Chloride and sulphate concentrations have increased in Geysir, Strokkur and Smidur while decreasing in other parts of the Haukadalur geothermal field.

The concentration of **fluoride** has increased from Geysir, Strokkur to Smidur. The high fluoride concentration may be related to unusually low concentrations of calcium in the waters. Maximum concentrations are influenced by underground temperatures and the solubility of calcium fluoride. Except for Nedridalur and Helludalur thermal fields, changes are minor.

Boron, lithium, mercury, copper and arsenic are low in thermal waters of Haukadalur. Arsenic in Icelandic waters ranges between 6×10^{-3} and 0.3 mg/l (Hrefna Kristmannsdóttir, pers. communication).

Schoeller diagrams can be used to show general changes with time or between locations. The Schoeller diagrams are prepared according to the milliequivalent value percentage of ions. According to Figures 9-10 both slopes that connect the ions to each other for the hot water of Geysir through a period of 30 years, as well as for Geysir, Strokkur, Smidur and the Nedridalur and Helludalur wells and the Kaldilaekur cold water are similar. They suggest that the groundwater comes from local precipitation and has passed through similar rock types, i.e. confirm that the water comes from the same lithology and aquifers. They are in general higher in some constituents, particularly Na, K, Cl and HCO_3. Also the cold water lines intersect the thermal water line, suggesting that the thermal water of Haukadalur in particular is mixed with some cold water. These results support our use of the 1998 analytical results, which were done according to today's conditions. On that basis we will explain the geochemistry of the waters of the Geysir field.
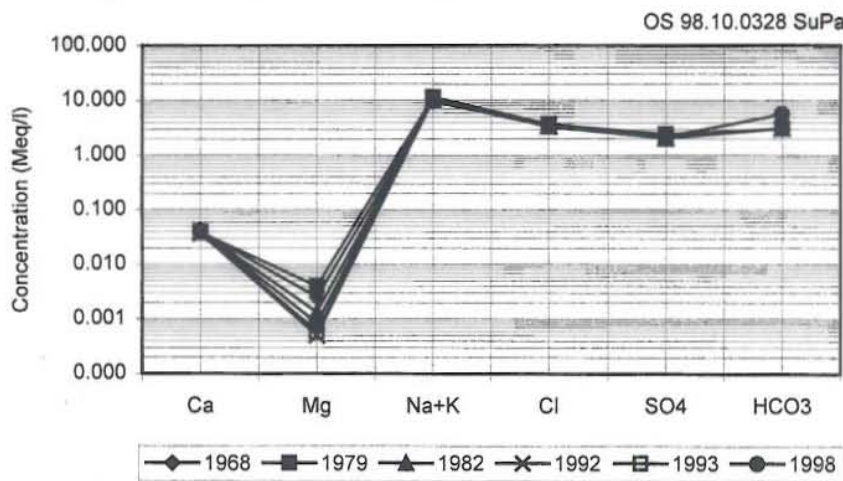

FIGURE 9: Schoeller diagram for the Geysir hot spring showing changes in the period 1968-1998
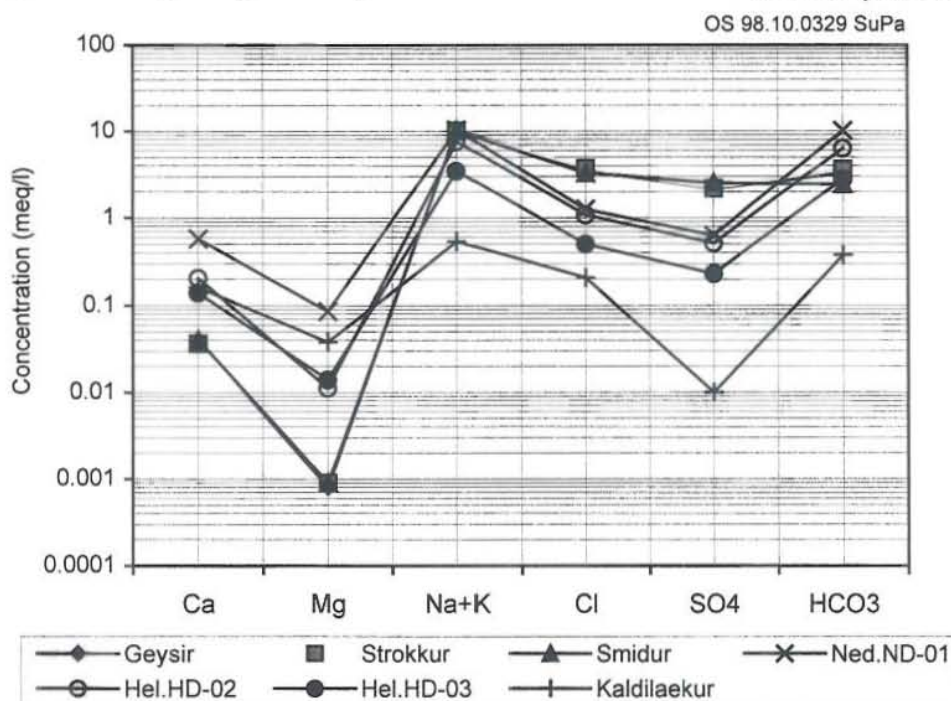

FIGURE 10: Schoeller diagram for recent samples from the Geysir geothermal field

The alignment of the ions in the water samples of the study area have been cross-plotted in a semi-logarithmic Schoeller plot (Figure 11). The relationship is as follows: $rNa+rK > Ca > Mg$; $rCl > rHCO_3 > rSO_4$. As seen from the plots for Geysir, Strokkur and Smidur, they have water of similar composition. Waters from Nedridalur and Kaldilaekur have the following relationship: $rNa+rK > rCa > rMg$; $rHCO_3 > rCl > SO_4$.

The classification of the International Association of Hydrogeologists (IAH), has been used for the waters. Geysir, Strokkur and Smidur all derive their water from sources that contain sodium, chloride, bicarbonate, sulfide, fluoride and carbon dioxide, while others contain sodium bicarbonate and fluoride. Thus, they can be considered thermal water. According to the Schoeller classification, Geysir, Strokkur, Smidur are hot water sources. The wells in Helludalur have common chloride and common carbonate water. The Nedridalur well, however, has common chlorine and hyper carbonate water. The Nedridalur and Helludalur waters are highly carbonated as often encountered in groundwater near to the borders of high-temperature geothermal fields or volcanic areas.

FIGURE 11: A Schoeller diagram for the Geysir, Strokkur and Smidur hot springs

The gas chemistry of Haukadalur geothermal field is characterised by high CO_2 and low concentrations of H_2S and H_2 compared to most other high-temperature geothermal field in Iceland. The low H_2S concentration is due to loss of H_2S by oxidation. Also CH_4, Ar and O_2 are generally less than 1% of total gases. The results of gas composition in the Geysir field are shown in Table 5.

TABLE 5: Calculated gas composition at atmospheric pressure for a boiling spring in the Geysir field in Haukadalur and results of gas geothermometers

Sample No: 98024		Gas geothermometer	Results
pH	5.47	D'Amore & Panichi (1980)	123
CO_2 (ppm)	532	CH_4-H_2, $P_{CO_2} = 0.1$ (Tonani, 1973,1980)	228
Cond.(μS/cm)	676	CH_4-H_2, $P_{CO_2} = 1.0$ (Tonani, 1973,1980)	258
Vol% H_2	0.26	CH_4-H_2, $P_{CO_2} = 10$ (Tonani, 1973, 1980)	290
Vol% CO_2	73.58		
Vol% H_2S	0.07		
Vol% (O_2+Ar)	0.63		
Vol% N_2	24.74		
Vol% CH_4	0.72		

5.2 Classification of the water

The chemical composition of the thermal water provides for the identification of the nature of the hot springs system. Fairly high ratios of Ca/Mg, Na/Ca, and low ratios of HCO_3/Cl, which were observed in the water of the Geysir area, are typical of hydrothermal systems having moderately high reservoir temperatures.
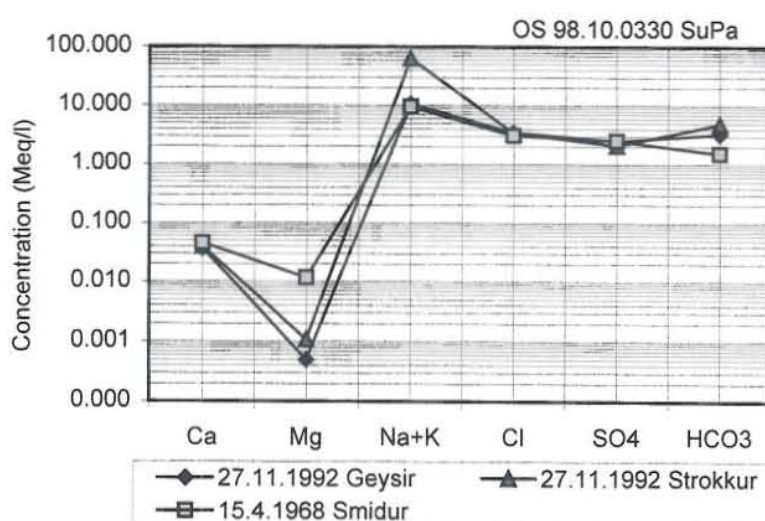
FIGURE 12:   The Cl-SO$_4$-HCO$_3$ diagram for the water
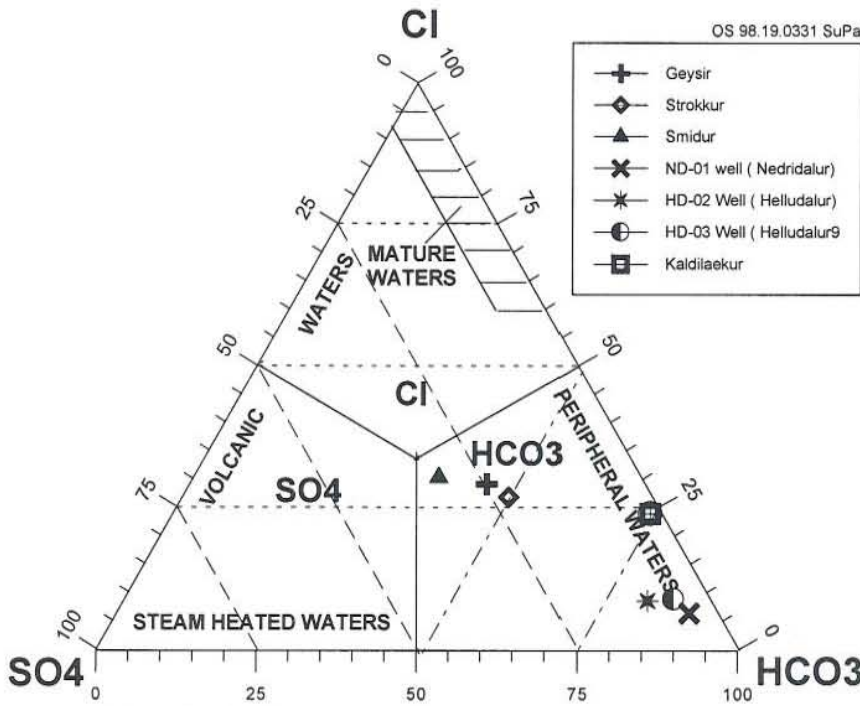from the Geysir geothermal field

FIGURE 13:   The Cl-Li-B diagram for the water
from the Geysir geothermal field

In a Cl-SO$_4$-HCO$_3$ triangular diagram (Figure 12) the data points for Haukadalur waters plot in the area of peripheral water. Samples from wells (Nedridalur, Helludalur) with cold water are located in the HCO$_3$ corner. Samples from Geysir, Strokkur, and Smidur are close to chloride and sulphate water, but are still in bicarbonate water range which suggests some degree of mixing.

Mass ratios like the Cl:B, Na:K, and Na:Li show a narrow range for each group of spring waters suggesting a homogeneous fluid source at depth. A plot of relative chloride, lithium and boron concentration (Figure 13) plot in the field classified as water originating from an old hydrothermal system. The boron content of thermal fluids reflects to some degree the maturity of a geothermal system. Like As, Sb and Hg, B is expelled during the early heating up stages because of its volatility. Therefore, fluids from "older" hydrothermal systems can be expected to be depleted in B. A slight deviation towards the upper left hand side of the Cl-Li-B plot can be seen, affecting Geysir, Strokkur and Smidur fluids. This is an indication that absorption of low B/Cl magmatic vapours may be taking place.

With the exception of cold water, the Cl/B mass ratio for all the samples is rather similar in the range of 112 to 177 (Table 6), indicating the origin of chloride and boron to be mainly dissolution from host rocks.

TABLE 6: Cl and B concentrations, pH and mass ratios for the Geysir geothermal field

Sample No.	Location	Date	T (°C)	pH	Cl	B	Cl/B
980423	Geysir	6.8.1998	72.8	9.28	124.8	0.9	139
920311	Strokkur	27.11.1992	120	8.92	121	1.08	112
980425	Smidur	6.8.1998	99.7	9.17	117	0.83	141
980426	ND-01	6.8.1998	68.5	7.55	44.3	0.33	134
980422	HD-02	6.8.1998	58.8	7.56	38.4	0.26	148
980421	HD-03	6.8.1998	38	8.81	17.7	0.1	177
82011	Kaldilaekur	1982	5	8.01	7.4	0.01	740

5.3 Geothermometry

The Na-K-Mg triangular diagram (Arnórsson, 1983) is used to see whether there is equilibrium between the hot water and rocks at depth. Results are shown in Figure 14. As seen from the diagram, samples from the Nedridalur and Helludalur wells and the Kaldilaekur cold water plot in the "immature area" indicating that these waters are unsuitable for the evaluation of Na/K equilibration tempera- ture. Samples from Geysir, Strokkur, and

FIGURE 14: The Na-K-Mg equilibrium diagram for the water from the Geysir geothermal field (based on Arnórsson, 1983)

Smidur plot above the equilibrium area, but that from Geysir falls very near to the equilibrium line. This might be caused by a steam loss which would increase the absolute solute concentration of samples.
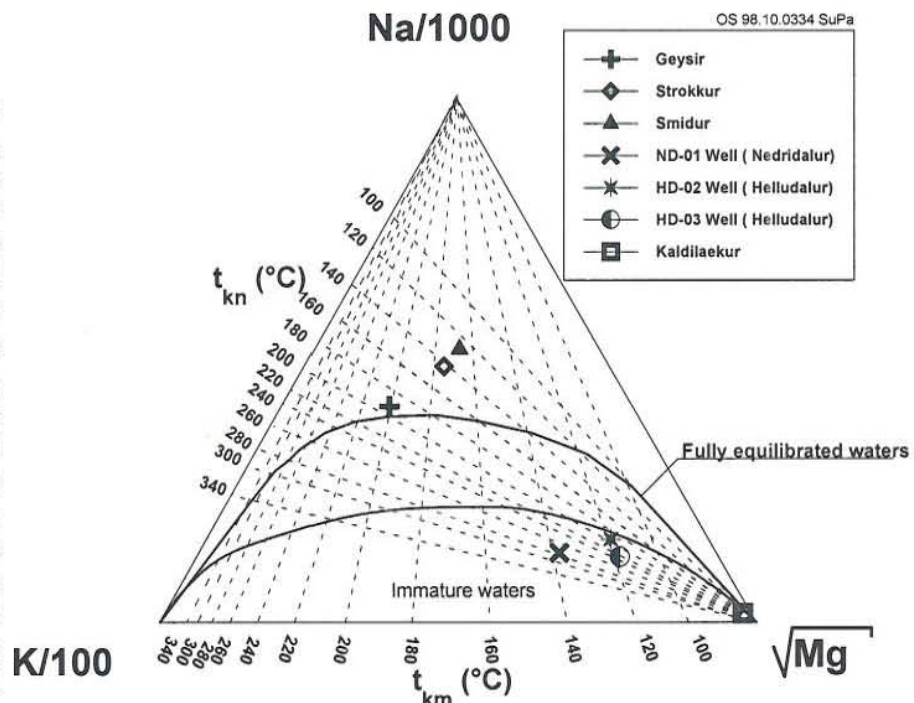
According to the Na-K-Mg Giggenbach diagram (Figure 15) the Geysir, Strokkur and Smidur water lies near to the fully equilibrated line and the rest of the samples fall in the immature water section, near the Mg corner. The Na/K geothermometer temperature values of this diagram (175-230°C) and (130-200°C) of the Arnórsson diagram show that both diagrams have limitations in one respect or another.

The chemical geothermometers are used on the water from the hot springs and wells to evaluate subsurface temperatures of the geothermal field. Table 7 shows the results for different solute geothermometers. All the samples lie in the temperature range of 123-241°C for quartz, 157-288°C for Na/K (Fournier, 1979), 122-281°C for Na/K (Arnórsson at al., 1983a and b), 191-298°C for Na/K (Giggenbach, 1988), 115-282°C for Na/K (Truesdell, 1976) and 142-259°C for Na/K (Tonani, 1980). For the Na-K-Ca temperature (Fournier and Truesdell,1973), all samples lie in the range of 201-273°C, the Li-Mg temperature of Kharaka and Mariner (1989) is 80-179°C and the Na-Li temperature (Kharaka et al.,1982) is 94-205°C.
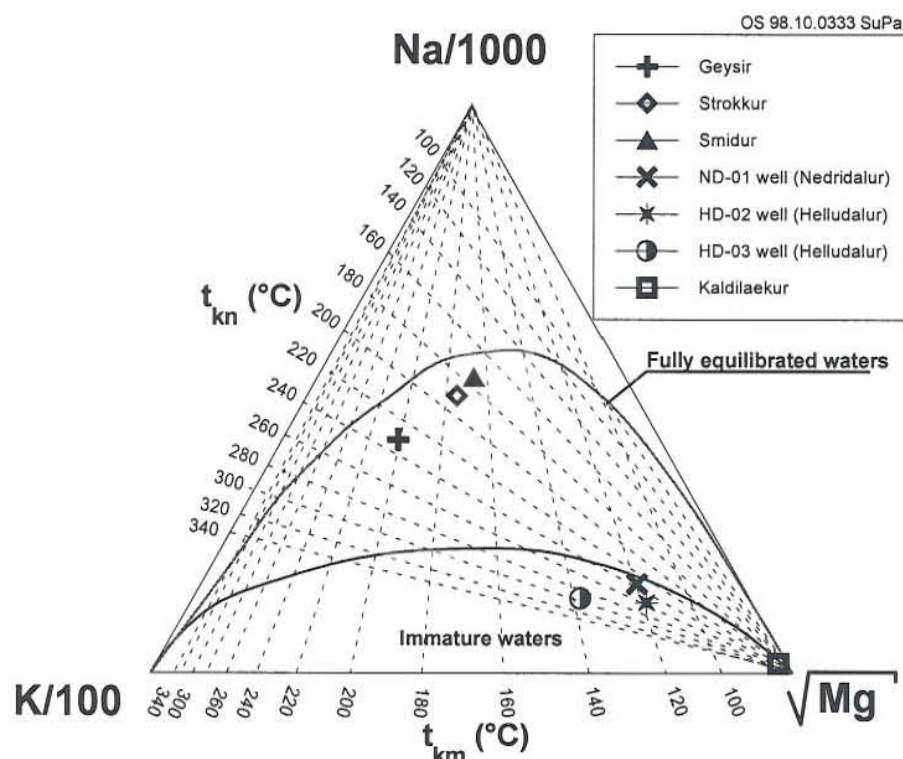
FIGURE 15: The Na-K-Mg equilibrium diagram for the water from the
Geysir geothermal field (based on Giggenbach, 1988)

For Geysir the quartz geothermometers gives a bit lower value than Na-K-Ca but all other geothermometers give lower values. For Smidur and Strokkur quartz gives the highest values, but somewhat lower than for Geysir. The relationship between chloride on one hand and sodium and potassium on the other indicates that the lower Na-K temperatures, compared with quartz, are due to a loss of potassium from the solution in the upflow (Figure 16).

The Na-K-Ca geothermometer usually gives slightly higher temperature than the Na-K one for the boiling hot spring water. Loss of potassium from solution will, of course, lower the Na-K-Ca temperatures but this tends to be counteracted when boiling occurs, by loss of calcium through calcite precipitation. The different results obtained by these two cation geothermometers are not necessarily due to the net effect of the two counteracting processes, (loss of potassium and loss of calcium); systematic deviation relating to their calibration may just as well be the cause.

The relationship between the chemical geothermometry results is different for the warm water wells than for the boiling springs. Here, the Na-K temperatures are equal to or higher than the quartz equilibrium temperatures in the warm water and they are also about equal to or higher than the Na-K temperatures of the boiling hot spring water.

FIGURE 16: Chloride vs. sodium and potassium
for water from the Geysir geothermal field

The major cation concentrations in the warm water are governed by leaching after mixing. It is concluded that the Na-K temperatures, as well as the Na-K -Ca temperatures, are unrealistic for the warm water as the assumption of mineral/solute equilibrium with respect to sodium and potassium does not seem to be valid. Like the Na-K-Ca geothermometer, the Na-Li and Li/Mg geothermometers of Kharaka and Mariner (1989) tend to give less misleading results for water of mixed origin than the Na-K geothermometer, the reason probably being that the sodium/lithium ratios in basaltic and acidic rocks are comparable with those of equilibrated warm water. For the warm water from wells, those geothermometers give though widely varying values and are obviously not useful for our purpose.

Figure 17 is composed of six graphs representing the calculations which were performed using the WATCH aqueous speciation program (Arnórsson et al.,1982; Bjarnason, 1994) to construct the mineral
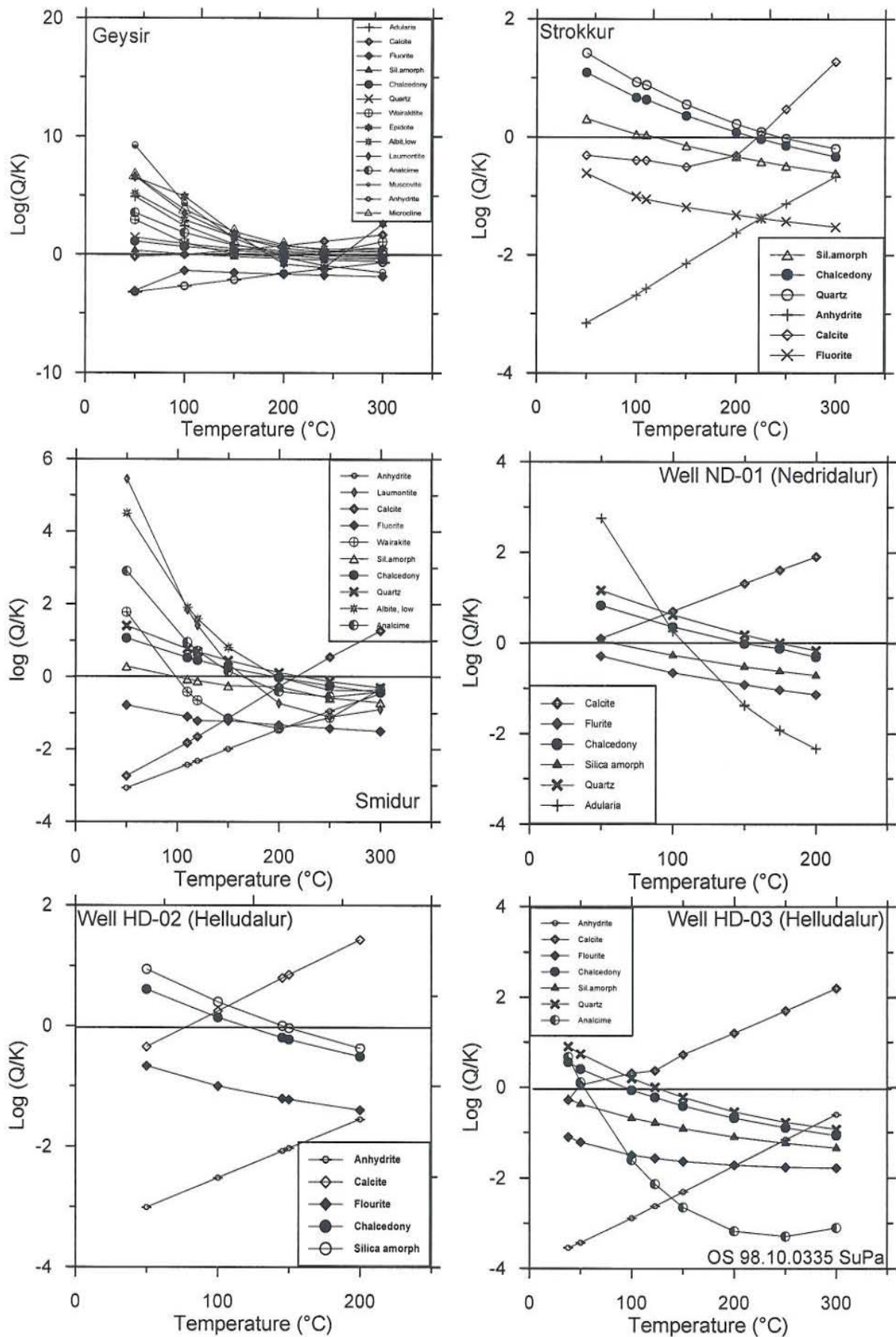
FIGURE 17: Mineral equilibria diagrams for waters from the Geysir geothermal field

equilibrium diagrams showing the saturation index, log (Q/K), from the temperature range 50-300°C for Haukadalur samples. It is the temperature at which the SI curves intersect the zero line that determines the equilibrium temperature for each mineral.

Generally, the calcite, quartz and chalcedony reach saturation in equilibrium in the temperature range 150-300°C. Anhydrite and fluorite are undersaturated at these temperatures. The hot springs also indicate some mixing even if they appear nearer to equilibrium than the warm water. The interpretation of samples from Nedridalur and Helludalur (ND-01, HD-02, and HD-03) suggests some mixing of cold groundwater with thermal fluid during its upflow.

The intersection of various mineral curves stretches over a range of temperatures, making it difficult to draw any definite conclusion about the most probable reservoir temperature. However, this temperature range is helpful to confirm the validity of the temperatures calculated from other geothermometers. Where such intersections appear at two or three places with a large difference in temperature, the values near to those obtained by the quartz geothermometer are considered best (Table 7). Lack of apparent equilibrium with respect to many minerals at a particular temperature is common in mixed water and surface water.

The hot spring waters of Geysir, Strokkur, and Smidur attain equilibrium with many of the minerals but all the other waters are undersaturated with the most common hydrothermal alteration minerals. However, the waters of Geysir, Strokkur and Smidur do not show a single point of equilibrium, but rather a range of tens of degrees, Geysir appears to be closest to equilibrium, at 200-250°C. The others show signs of mixing and more diffuse graphs, but a similar range in temperature is indicated. For the water of Nedridalur and Helludalur no apparent equilibrium can be defined from the graphs.

TABLE 7: Different geothermometer temperatures for the 1998 samples from the Geysir field

Geothermometer (°C)	Geysir	Strokkur	Smidur	ND-01 well	HD-02 well	HD-03 well
$T_{measured}$	72.8	120	99.7	68.5	58.5	38
Quartz $_{Four,Trues}$	241	231	217	175	145	123
Na/K $_{Arnórsson}$	194	144	125	283	198	225
Na/K $_{Giggen.}$	232	191	176	298	235	255
Na/K $_{Four.}$	216	173	157	288	220	242
Na/K $_{Trues}$	187	134	115	282	191	220
Na/K $_{Tonani}$	222	163	142	330	227	259
Na-K-Ca $_{Four,Trues}$	253	216	201	273	230	232
K/Mg $_{Giggen.}$	106	97	94	-	84	76
Li-Mg $_{Kharaka\ \&Mariner}$	179	-	159	55	80	108
Na-Li $_{Kharaka\ et\ al.}$	177	-	152	94	106	205

In many high-temperature geothermal fields, surface manifestations consist only of fumaroles, steam-heated water, and hot altered ground. The solute geothermometers are not applicable for the exploration of such fields. Since the 1970´s, studies have successfully demonstrated that gas components from fumaroles or hot water springs can be used as geothermometers. In this report, the two geothermometers were applied for the boiling spring sampled in the Geysir high-temperature field.

The results of the gas geothermometers are given in Table 5 together with the analysis of the gas. The results indicate that the discrepancy between the estimated subsurface temperature by various gas geothermometers may be explained by a combination of condensation and removal of H_2S and by oxidation in the upflow. Gas geothermometers based on gas ratios such as the Tonani and D'Amore and Panichi geothermometers, have generally not been so useful for Icelandic geothermal fields. The last

one has been used though in a few places. As there are no data available of total concentrations of the gas in the steam, those gas geothermometers are the only ones which can be calculated.

In the Geysir field, the estimated temperature by the gas geothermometer of D'Amore and Panichi (1980) yields the temperature value 123°C, the reason probably being that oxidation occurs in the upflow and boiling. The gas geothermometers of Tonani give temperature values with an average of 258°C.

6. ISOTOPE HYDROLOGY

Craig et al. (1956) first discussed the possibility of using combined δD and $\delta^{18}O$ measurements on thermal water to determine whether such water is of meteoric origin and whether it has undergone any isotopic changes during its passage underground. The deuterium concentration of the precipitation in Iceland varies significantly from one place to another. This suggests the possibility of using deuterium as a natural tracer to locate recharge areas for groundwater systems and to study their flow patterns. When a sample of groundwater is discharged from either a cold or a hot spring whose deuterium value is similar to the mean value of the local precipitation, it indicates a local origin for the groundwater (Árnason, 1976). The use of deuterium as a natural tracer in groundwater studies is based on the assumption that groundwater is derived from precipitation and that the deuterium content of the water does not change underground. Furthermore, the method assumes that the deuterium value of the precipitation has not changed significantly during the time the water has remained underground. Árnason (1976) concluded that the D vs. $\delta^{18}O$ relationship obtained for hot and cold water in Iceland supports the contention that the groundwater is almost entirely of meteoric origin. He further suggested that the stable isotope ratios of the precipitation have not changed greatly during the last 8000 years, so that deuterium values for groundwater younger than 8000 years should be comparable to the values of the deuterium map of precipitation which he presented for Iceland. However, the results of deuterium measurements suggest that most groundwater in Iceland is younger than 8000 years. Comparison of the deuterium content of a deep ice core from Greenland with the δD content of a more recent ice core, indicates that precipitation deposited between 10,000 and 60,000 years ago had δD -50‰ to -100‰ lower than today. When "ice-age water" is present in the geothermal water, deuterium cannot be used as a tracer to locate the recharge areas to geothermal areas and in this way draw conclusions about regional groundwater flow (Arnórsson, 1995).

6.1 Sampling and isotope analysis

The samples were collected from the field on August 6,1998 according to sampling principles defined by IAEA (International Atomic Energy Agency). By sampling for analysis of ^{18}O and Deuterium, the 60 mg glass bottles and their lids were washed with the water sample and completely filled so that no space remained for air. After closing the taps and lids of the bottles very tightly, the bottles were kept in a cold place until they were sent for analysis. The isotope analyses were done at the University of Island, Institute of Sciences, Isotope laboratory by Mrs. Árný Sveinbjörnsdóttir. The isotope analysis results are given in Table 8 with older isotopic results, but the conventional analytical analyses are given in Table 3.

6.2 Results and explanation

Isotope analysis of water samples from the Geysir field done in the period 1967-1998 show no significant changes in $\delta^{18}O$ and δD (Table 8). Figure 18 shows the relationship between δD and $\delta^{18}O$ values for the water. The results show that samples collected in the Geysir geothermal field have δD. values ranging from -83.3‰ to -64.9‰ with an average δD = -75.1‰. The data points from the Geysir field show a minor scattering. Water from boiling hot springs shows distinct oxygen shift do to reaction to
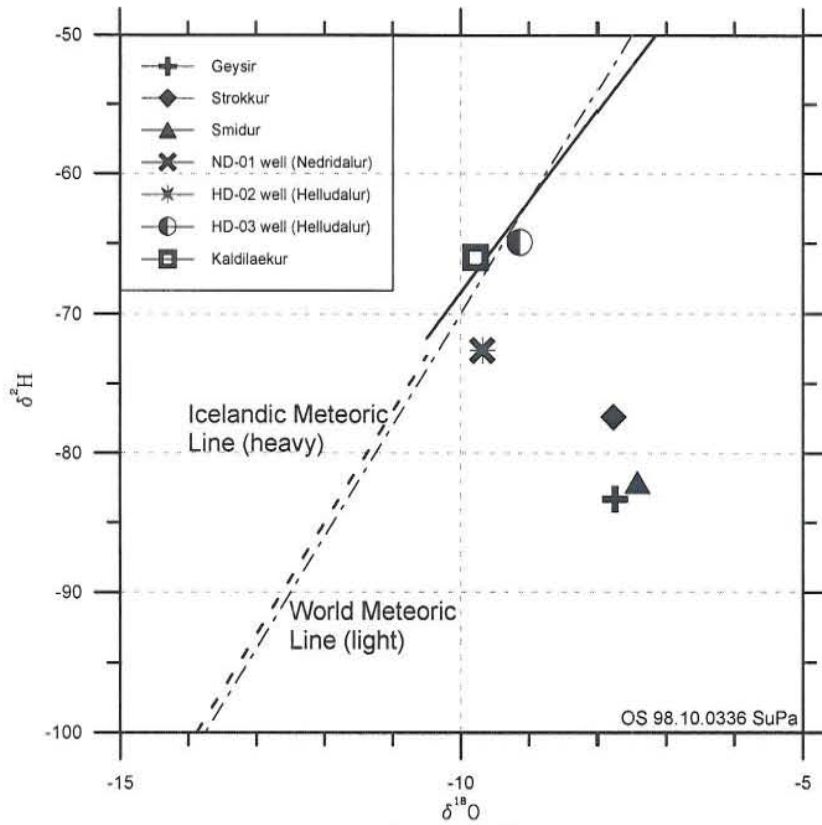
FIGURE 18: δD (δ ²H) vs. δ ¹⁸O for the water
from the Geysir geothermal field

rocks and a gentle slope. This shift may be explained by steam loss. The deuterium levels indicate that the water is not local precipitation, but may be derived from the southern part of the Langjökull ice-sheet, some 50 km to the north (Árnason, 1977). With two exceptions, the warm spring water from the Geysir field plots close to the meteoric line. According to the deuterium precipitation map of Árnason (1977), the deuterium content of the warm water is compatible with being largely local precipitation. Two mixed water samples, wells ND-01 and HD-02 plot in the same position and are intermediate between the boiling hot spring water and the meteoric line. This is considered to be due to the fact that this water contains a rather large portion of the hot water component, as indicated by the chloride content.

TABLE 8: The isotope composition of the samples collected from the study area

Sample No.	Location	Date	T(°C)	pH	Ec	‰¹⁸O	‰ D
	Geysir	4.7.1957	Boiling			-7.75	-85
79004	Geysir	22.5.1979	72	9.36	1010	-7.6	-75.6
920313	Geysir	27.11.1992				-7.77	-83.3
980423	Geysir	6.8.1998	72.8	9.28		-7,75	-83.5
	Strokkur	23.6.1967	98			-7.75	-85.4
82009	Strokkur	1982	78	8.56		-7.77	-77.4
	Smidur	24.6.1967	Boiling			-7.75	-85.2
79006	Smidur	1979	98	8.93	901	-6.14	-74.0
980425	Smidur	6.8.1998	99.7	9.17		-7.42	-82.1
82013	Well ND-01	1982	68	7.52		-9.54	-68.4
980426	Well ND-01	6.8.1998	68.5	7.55		-9,61	-72.1
860104	Well HD-02	22.7.1986	54	7.73	773	-9.71	
980422	Well HD-02	6.8.1998	58.8	7.56		-9.68	-72,4
82019	Well HD-03	1982	30	7.94		-9.35	-60.7
980421	Well HD-03	6.8.1998	38	8.81		-9.13	-64.9
82011	Kaldilaekur	1982	5	8.01		-9.78	-66

7. RADIOACTIVITY

Thorkelsson measured radon concentrations in 1906-1940 in gas samples from numerous hot springs in Iceland (Thorkelsson, 1910; 1925). The highest concentrations he found in the springs at Geysir were in Litli Strokkur, where he observed 186 and 260 nC/l gas. Sveinbjörn Björnsson measured radon concentrations in many hot springs in 1965 and his results confirmed the observations of Thorkelsson with 187 nC/l gas in Litli Strokkur, and in Sódi 28.4 nC/l gas (Björnsson, S., 1998).

Radon is a radioactive inert gas. The most common isotope ^{222}Rn (T $\frac{1}{2}$ = 3.825 days) is a decay product of radium, ^{226}Ra (T $\frac{1}{2}$ = 1622 years). The other naturally occurring isotopes ^{220}Rn (thoron, T $\frac{1}{2}$ = 54.5 s) and ^{219}Rn (actinon, T $\frac{1}{2}$ = 3.9 s) are relatively short-lived. Radon decays by the emission of an α-particle. The daughter products decay in a cascade of short-lived α- and β- emitters and end as stable isotopes of lead.

Gas concentrations are not a direct measure of the amount of radon being released. Radon is generated by the decay of radium in the rock. Radon diffuses into the geothermal fluid and mixes there with other types of dissolved gases. The hydrostatic pressure is reduced within gas bubbles formed in the water and most of the radon diffuses into the bubbles. In some extreme cases the water boils and practically all the dissolved gas goes into the steam phase. Given the same source rock for the radon, it is obvious that the concentration of radon in the gas or steam bubbles depends on the amount of other gases dissolved in the water.

The geothermal water is of meteoric origin. Rain water percolates down from the surface and carries with it dissolved gases from the atmosphere. These gasses are oxygen, nitrogen and traces of carbon dioxide and argon. The oxygen reacts with the rock and disappears from the water. Other gases added to the fluid from reaction with the reservoir rocks, are carbon dioxide, hydrogen sulphide and even hydrogen. Therefore, the concentrations of nitrogen in the geothermal gas can be used as an indicator of the amount of gases that has been added to the original atmospheric gas and to give a relative measure of the quantity of gas being released by the spring (Sveinbjörn Björnsson, 1998). A still better method for such estimates would be an analysis of the isotopic ratios of argon (Ar ^{36}/ Ar ^{40}) in the gas. This ratio is 0.0034 in atmospheric gas but only Ar ^{40} is generated underground and added to the dissolved gas in the atmosphere. If a spring issues gas with 80% by volume percentage of CO_2 and 20% N_2, the spring is yielding the same quantity of N_2 per litre of flowing water as a spring with 100% N_2, but in addition to that a four times greater volume of CO_2 gas. Given the same radon production in the source rock, the radon concentrations observed in the gas samples with 80% CO_2 present would show five times lower values than in a sample from the spring with 100% N_2. If we turn to the springs at Geysir we could correct for the dilution by added gas by taking into account the volume percentage of nitrogen in the gas samples. In Thorkelsson's sample that had 186 nC/litre gas, the volume percentage of nitrogen was 15%. Dividing that percentage into the radon concentration gives 186/0.15 = 1240 nC/litre gas per vol% N_2. The other sample with 260 nC/litre gas had a volume percentage of nitrogen of 21%, which gives 260/0.21 = 1238 nC/litre gas per vol% N_2. Similar applies to the sample from Litli Strokkur where the nitrogen percentage was 20%, thus, a normalized value of 187/0.20 = 935 nC/litre gas per vol% N_2. These values are higher than those observed in any other springs in Iceland. Typical normalized values are in the range of 1-10 nC/litre gas. Values of the same order as at Geysir were, however, found at the high- temperature fields of Krísuvík and Nesjavellir.

The discharge from the Geysir hot springs has 10-100 times higher concentrations of radon than most other springs in Iceland. Although the radioactivity is high for Icelandic waters, it is not sufficient to explain the heat source of the springs. The hot springs are closely connected with active volcanism as evidenced by the rhyolite mountain Laugafell. It is, therefore, considered certain that the springs derive their heat from magmatic sources. The high radon activity is, however, a peculiarity with an unknown explanation. It may be caused by a formation where the long-lived mother atom ^{226}Ra has become enriched to concentrations 10-100 times the average for Icelandic rocks. The most likely locations for such an enrichment are scales in shallow feeders of the springs or the silica sinter precipitated from the water at the surface.

Radon, like other gases, is quickly dissolved in water. When the flow of underground water is towards the surface, the concentration of [222]Rn at the surface will be high (Pasvanoglu, 1996). Because of this, [222]Rn concentration is low in deep flowing water. The reason is that the [222]Rn has a short half life period. In the water [222]Rn concentration can come from silica rich underground rock at shallow depths. Accordingly, the Fata hot spring reservoir may represent deeply flowing waters, poor in Radon, whereas Geyser and Litli Strokkur may represent shallow flowing waters.

8. MIXING MODELS

Geothermal water which ascends from geothermal reservoirs and emerges at the surface in hot springs may cool on the way, either by conduction, boiling, or mixing with shallow cold water, or by any combination of these three processes as suggested by Arnórsson (1985). Thus, the chemical composition of this water in surface discharge, as well as the gas content in associated fumaroles, may be used to evaluate underground temperatures, applying mixing models.

8.1 Evidence of mixing

Water formed by the mixing of geothermal water and cold ground or surface water possesses many chemical characteristics which serve to distinguish it from unmixed geothermal water. The chemistry of geothermal water is characterized by equilibrium conditions between solutes and alteration minerals, whereas the composition of cold water appears mostly to be determined by the kinetics of the leaching process. The main chemical characteristics of mixed water, which serve to distinguish them from equilibrated geothermal water, include relatively high concentrations of silica in relation to the discharge temperature, and high total carbonate, at least if the mixing has prevented boiling and the temperature of the hot water component exceeds some 200°C.

The relationship between chloride on one hand and sodium and potassium on the other indicates that the lower Na-K temperatures, compared with quartz, are due to loss of potassium from the solution while in the upflow (Figure 16). For this field, there is approximately a linear relation between sodium and chloride and extrapolation passes close to the point of origin (Figure 16), suggesting that the sodium variations in the boiling spring water are due to dilution and/or steam loss. Potassium concentrations are lower than would be expected if only the processes of dilution/boiling were operative. Extrapolation of the data points for potassium and chloride intersects the chloride concentrations. Potassium appears, thus, to have been lost from solution, perhaps by precipitation of K-feldspar, but absorption by clays is also possible.

Chloride and boron levels in cold water are, as a rule, low but much higher in geothermal water. As these constituents are not considered to be incorporated in geothermal minerals, mixing involves simple lowering of concentrations without affecting the Cl/B ratio. If mixing of geothermal water with cold water is responsible for variable chloride concentrations, it is to be expected that the intersection at "0" ppm boron of a line through the data points is in the range of 10 ppm chloride, as cold water (and precipitation) contains chloride in that range and less then 0.01 ppm boron.

Figure 19 shows the chloride-boron relationship for the water from Geysir field. In every case there is a rather good linear relationship. The point of intersection corresponding with 0.01 ppm boron is some 10 ppm for chloride. Thus, the chloride boron relationships of water from the field are taken as strong evidence of mixing of geothermal water and cold water.

The water from the Geysir field displays a rather good linear relationship between chloride and silica

(Figure 20). If the dilution process is not followed by dissolution of silica from the rock, nor with precipitation, a linear silica-chloride relationship is to be expected and the line through the data points should pass close to the point of origin. If the unmixed geothermal water was in equilibrium with quartz and re-equilibrium with that phase occurred after mixing, considerable amounts of silica would have to precipitate from the water.

Sulphate concentrations show a good relationship with chloride in water from the Geysir field. It might be expected that the boiling hot spring waters, especially Geysir, with large surface areas, had relatively high sulphate content due to oxidation of hydrogen sulfide by atmospheric oxygen. And steam condensation gives us more SO_4, not more chloride.

The Na/K ratios in cold water and in the warm mixed water from the Geysir field, tend to be similar to or lower than those in the boiling hot springs. This indicates that the water is not in equilibrium as pointed out in the discussion of Figures 14 and 15.

8.2 Silica enthalpy mixing model

Truesdell and Fournier (1977) used a plot of dissolved silica vs. enthalpy of the liquid water to estimate the temperature of the mixed water. Enthalpy is used as a coordinate rather than temperature. This is because the combined heat contents of two waters at different temperatures are conserved when those waters are mixed (neglecting small heat of dilution effects), but the combined temperatures are not. This model is based on the assumption that no conductive cooling has occurred after mixing. If the mixed water has cooled conductively after mixing, the

FIGURE 19: B vs. Cl graph for the water from the Geysir geothermal field
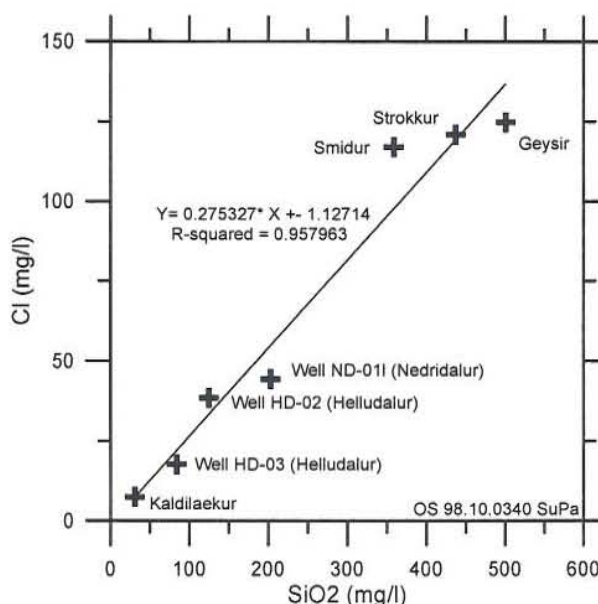
FIGURE 20: Cl vs. silica graph for the water from the Geysir geothermal field

calculated temperature of the hot water component would be too high. It is also assumed that no silica deposition took place before or after mixing and that quartz controls the solubility of silica in the hot water component. Figure 21 shows the results of the silica mixing model applied to the Haukadalur data. A sample from Kaldilaekur is used as reference cold water for the region. For the Haukadalur water, three mixing lines a, b and c are possible. Assuming no steam loss before mixing, a and c are drawn from the cold water sample through the Helludalur wells (HD-02, HD-03) and the Geysir spring which intersect the quartz solubility curve at points P and P′. Points P and P′ give the original silica content and enthalpy of the deep hot water. The estimated enthalpies for the deep hot water are 1120 and 1040 kJ/kg, which correspond to temperatures of 257 and 240°C, respectively. Mixing line b has a steep slope and would not intersect the quartz solubility curve. For this situation, we assume that a maximum amount of steam is lost from the water before mixing. The connection of the cold water sample to Strokkur and Smidur by a straight line, and an extension of this line to the enthalpy of the residual liquid
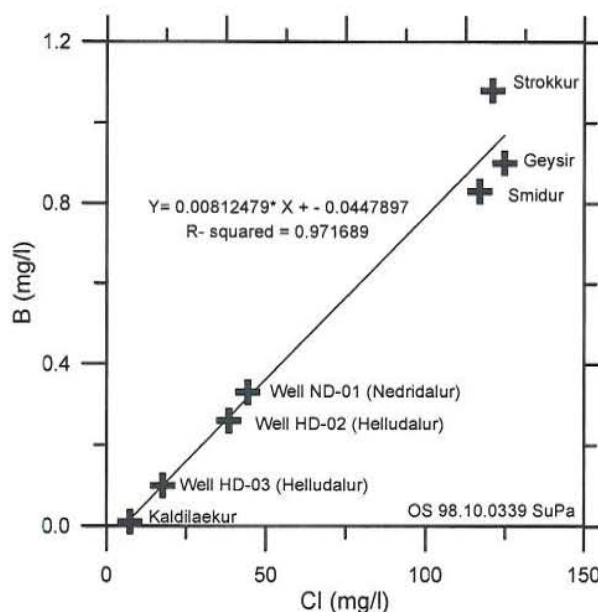
water at assumed temperature separation and escape of steam to ca. 100°C, gives point B and B′. B and B′ lines are drawn from points B and B′parallel to the x-axis, which intersects the curves of maximum steam loss at points C and C′. From points C and C′ a perpendicular to the x-axis is drawn which intersects the quartz solubility at points D and D′. These points give the original silica content and enthalpy of the Strokkur and Smidur hot water components, which are about 820 and 900 kJ/kg, corresponding to temperatures of 193 and 211°C, respectively.

FIGURE 21: Silica vs. enthalpy diagram for determining the temperature of thermal water mixed with cold water for the Geysir geothermal field

8.3 Enthalpy-chloride mixing model

Fournier (1977) suggested the use of an enthalpy-chloride diagram to predict underground temperature. This mixing model takes into account both mixing and boiling processes. Its application basically involves relating analysed chloride levels to water enthalpy which can be derived from measured discharge temperature, and silica-enthalpy mixing model temperature.

The enthalpy-chloride mixing model for the Haukadalur waters is shown in Figure 22. In this diagram most of the spring waters lie along the mixing line. This line connects the cold water sample and well warm water samples with hot water samples, which are affected by cooling probably by two processes, boiling and mixing with cold water and possibly conductive cooling. The enthalpy chloride mixing model gives a reservoir temperature of about 240°C.

Figure 23 shows that there is a relatively good relationship between chloride concentration and δ¹⁸O values supporting that the origin of the warm water is by mixing of cold water and discharge from the boiling springs.

FIGURE 22: Enthalpy vs. chloride diagram for cold and thermal water from the Geysir geothermal field

8.4 Silica-carbonate mixing model

Arnórsson et al. (1983b) found that the concentration of carbon dioxide in water in geothermal reservoirs is dependent on the temperature of these waters. At temperatures above about 200°C, most of the dissolved total carbonate is in the form of carbon dioxide, so it is a satisfactory approximation to allow analysed carbonate to represent carbon dioxide. It is well known that silica levels in high-temperature water are determined by quartz solubility. It follows, therefore, that it is a satisfactory approximation
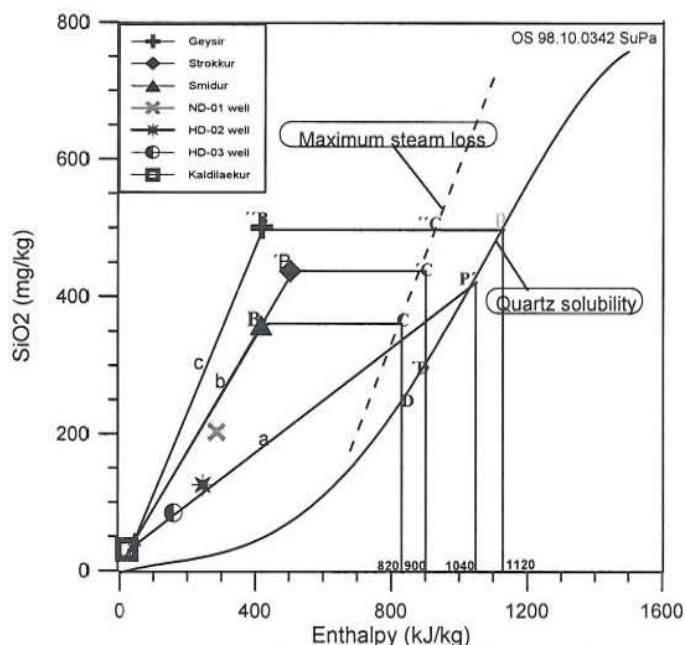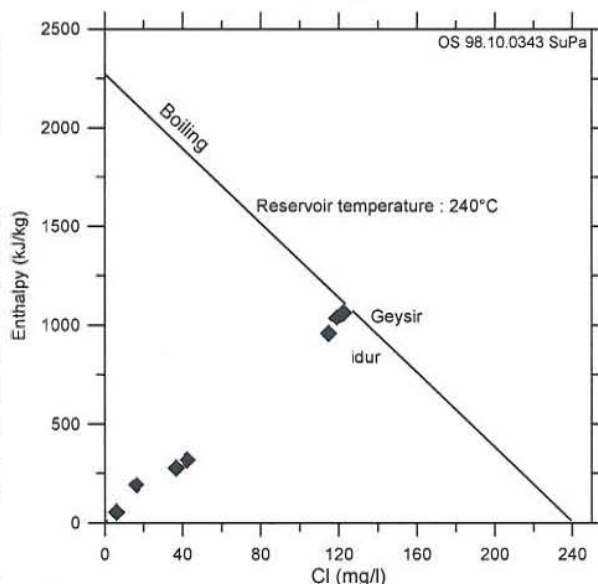
to assume a fixed relationship between silica and total carbonate in high- temperature geothermal reservoir water. Boiling of such water will lead to a drastic reduction in its carbonate content but mixing without boiling will, on the other hand, produce water with high carbonate/silica ratios relative to equilibrated water.

The silica-carbonate diagram may be used to aid interpretation of geothermometry. First, it serves to distinguish boiled water from conductively cooled water; mixed water contains an underground hot water component, assuming that boiling occurs between the points of last equilibrium with quartz and sampling. Secondly, if there are sufficient data available on warm water containing an unboiled water component, the diagram may be used to evaluate the temperature of the hot water component. Estimation of underground temperature by the silica-carbonate mixing model involves the extrapolation of a line through the data points for mixed and undegassed water and a demonstration of the intersection points with a silica-carbonate curve of equilibrated water. The quartz geothermometer is used to obtain the temperature from the silica concentration corresponding to this point.

In the Geysir geothermal field, a linear relationship between silica and carbonate is observed for most hot, warm and cold water (Figure 24) which indicates that the hot water component of the mixed water has not boiled. An extrapolation of a line through the data points indicates that the temperature of the hot water component is about 229°C. Geysir, Strokkur and Smidur contain relatively little total carbonate. This low concentration of carbonate might be due to near-surface boiling with CO_2 loss before sampling.
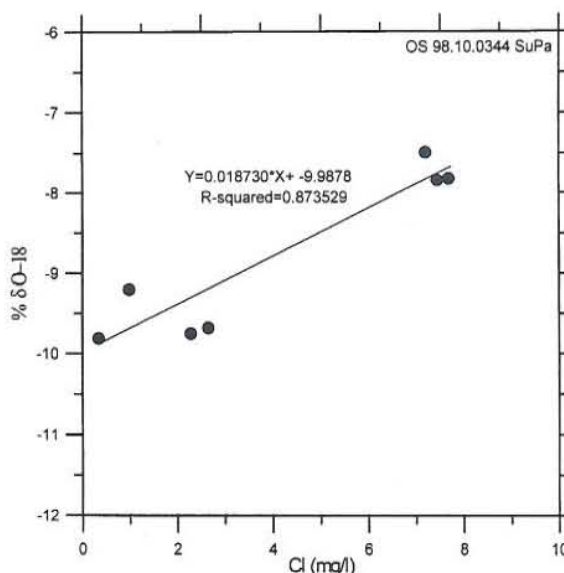

FIGURE 23: $\delta^{18}O$ vs. chloride diagram for cold and thermal water from the Geysir field
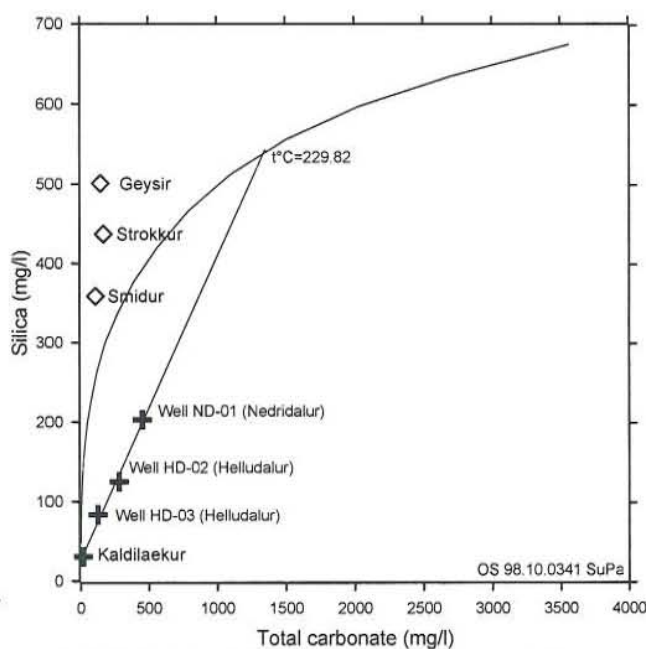

FIGURE 24: Silica vs. total carbonate (silica-carbonate mixing model) for water from the Geysir geothermal field

9. STUDY OF THE SILICA SINTER

Deposits are often formed around hot springs. The deposits may be composed of carbonates or silica sinter deposits which are indicators that the geothermal reservoir temperature is in excess of about 180°C (Ellis and Mahon, 1977). In the Geysir area, silica sinter is being deposited around many of the alkaline hot springs. Formerly there must have been considerable hydrothermal activity in the area between Laugarfjall and Haukadalur, as suggested by massive and fragmented silica sinter deposits in the soils.
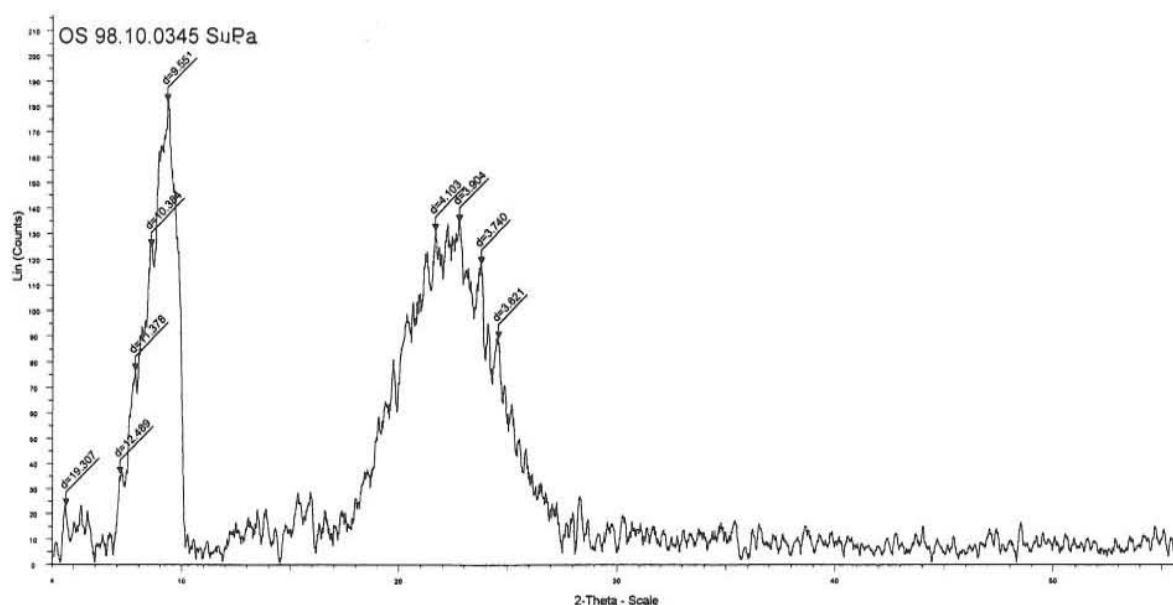
FIGURE 25: X-ray diffractometry for the silica sinter from the Geysir hot spring

In the cultivated fields of Haukadalur, snow and ice tend to melt on certain spots in the field during the winter time, indicating abnormally warm ground. Near one such spot a massive silica sinter deposit was found about one metre below the surface. This sinter deposit is covered by a brown layer which is found practically everywhere in soil profiles in the area. Surface hydrothermal activity has been insignificant for the last 3000 years or so in area. It seems possible that north of the presently most active part of the thermal area, silica sinter from the thermal water has inhibited the flow of water to the surface although high subsurface temperatures exist at shallow depths. Thorarinsson (1949) estimated the age of the silica sinter deposit exposed in a gully just west of the Geyser bowl to be 10,000 years. Arnórsson (1969) observed silicified vegetation in cemented talus exposed in the vertical cliffs forming the west side of Laugarfjall. This talus must have formed during the last glaciation. It is, thus, possible that there has been some thermal activity in the area since the last interglacial period.

X- ray diffractometry revealed that the sinter is composed of opaline silica. The diffractogram (Figure 25) reveals no well defined peaks, but a broad heap occurring at around d = 4Å is characteristic for amorphous silica.

A silica sample was collected from the Geysir silica sinter, about 10 m from the central pipe, and a second sample from the central pipe of an old geyser on the way to Haukadalur. These two samples were analysed with respect to Au, Ag, Bi, Cd, Co, Cu, Mn, Mo, and Ni (see Table 9, Hjalti Franzson, pers. comm.)

TABLE 9: Results of analysis silica sinter in the Geysir field

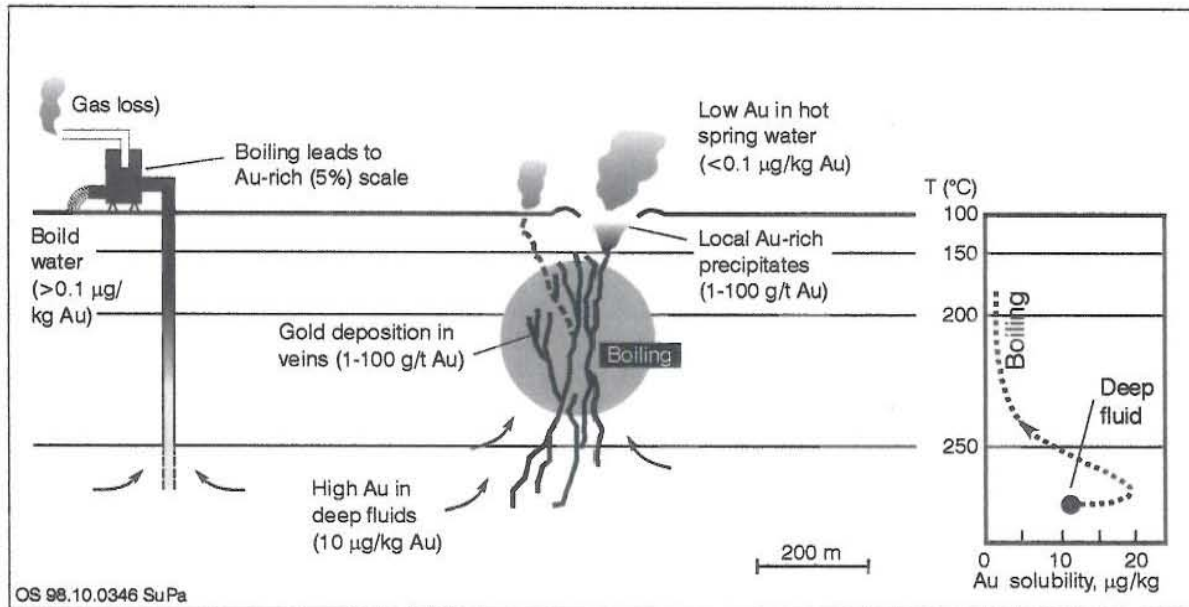| Sample location	Sample lab. no.	Au (ppb)	Ag (ppm)	Bi (ppm)	Cd (ppm)	Cu (ppm)	Co (ppm)	Mn (ppm)	Mo (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)
Geyser sinter, ca. 10 m from centre of sinter	XH-01	40	<1	<5	<1	5	18	342	<5	<5	4	21
Central part - old geyser at road-side to Haukadal.	XG-01	810	<1	<5	<1	7	<5	29	<5	<5	5	11

FIGURE 26:   Gold-rich scale in geothermal pipes indicates that gold concentrations
in deep waters (prior to boiling and gas loss) is about 10 mg/kg;
in contrast, hot spring water contains < 0.1 mg/kg of Au

Epithermal gold deposits form in hydrothermal systems related to volcanic activity. Due to the magmatic origin of the high-temperature geothermal fields, the fluid may carry relatively high concentrations of gold (Nesbit et al., 1987). These systems, while active, discharge to the surface as hot springs or fumaroles. Enrichment of gold in geothermal precipitates is, therefore, commonly encountered. On the way up the geothermal water carries gold that exists in a very little amount in the basaltic rocks (Figure 26). Some of the gold carried along will be left in the fractured and porous belts the water flows through, and there a gold enrichment of about 1-100 ppm occurs. Similar enrichment occurs in the surface precipitation, whereas only 0.1 ppb occurs in the sources. This process may continue for thousands or millions of years and, finally, economical gold deposits can be formed at shallow depths.

In the steam there is a considerable amount of HCl, HF and H_2S. Different mineral groups will form around the steam outlets. The first phase may be as magnetite, later phases galenite and sphalerite. Part of that crust will contain iron (Fe), lead (Pb), zinc (Zn), molibden (Mo), Cupper (Cu), arsenic (As), antimuan (Sb), tin (Sn), silver (Ag), nickel (Ni), cobalt (Co) and bismuth (Bi). Almost all of these can form volatile compounds and can be carried in a gaseous form.

10. CONCLUSIONS

The main objectives of this work were to study the geochemical characteristics of geothermal water from the Geysir geothermal area, to predict the subsurface temperature, study the changes in concentration with time, to evaluate the origin of the waters, and possible mixing and boiling processes during the evaluation. To obtain this, all older data were compiled. Seven samples from selected springs and wells were collected and analysed for comparison. The main conclusions of the study are:

1.   The change in the concentration of fluid composition with time is negligibly small.

2.   The most active hot springs in the Geysir area lie on a fracture striking northeast and the geology of the field suggests that geothermal activity is connected to the faulting of the area.

3. According to the classification of IAH, the thermal water is classified as follows: Geysir, Strokkur and Smidur are all hot water sources containing sodium, chloride, bicarbonate, sulfide, fluoride and carbon dioxide. The other water contains sodium bicarbonate and fluoride and, thus, all is considered as thermal water.

4. The geothermal water in Geysir geothermal field has concentration ratios of Ca/Mg, Na/K, F/Cl and Na/Cl that all exceed a value of 1. It also has high Na and K contents, high F and B together with high silica. This is strong evidence that the water has been in contact with acidic rocks. Mg concentration, as in all Icelandic thermal water, except carbonate water, is very low in the boiling hot springs. In the Nedridalur and Helludalur waters Mg is relatively high due to high carbonate concentration.

5. The Na-K and the Na-K-Ca geothermometers gives lower values for boiling hot spring water than do the quartz and the mixing models. This may result from loss of potassium from solution during cooling in the upflow. The Na-K-Ca temperatures tend to be somewhat higher than Na-K temperatures, probably because the effect of potassium loss is to some extent counter-balanced by loss of calcium from solution through calcite precipitation. The Nedridalur and Helludalur waters give high values for Na-K and Na-K-Ca geothermometers indicating mixing with cold water.

6. The δD-$\delta^{18}O$ relationship obtained for the samples of hot and cold water in Geysir geothermal field supports the opinion that the groundwater is almost entirely of meteoric origin. The deep circulating water in the Geysir high-temperature system has undergone oxygen isotope exchange with rocks as reflected by the samples from the hot springs. The δD levels indicate that the water is not local precipitation, but derived from the southern part of the Langjökull ice-sheet to the north. The deuterium content of the warm water is very close to that of local precipitation.

7. The Geysir hot spring has 10-100 times higher concentration of radon than most other springs in Iceland. The Fata hot spring reservoir may represent deeply flowing waters poor in radon, whereas Geysir and little Strokkur may represent shallow flowing waters.

8. Mixing of hot water with cold water occurs in the upflow zones of the geothermal system. Linear relationships between chloride, boron and $\delta^{18}O$ constitute the main evidence for mixing. A good relationship is also observed between chloride, silica and sulphate.

9. The run-off thermal water from the Geysir geothermal field is used for heating greenhouses, for district heating and for swimming pools and ponds in the vicinity of the Geysir area. In nearby areas, amongst others, the Nedridalur and Helludalur wells have been drilled. As the water source is ultimately from the Geysir field, the reservoir has to be monitored closely.

10. According to research in balneology, high amounts of radioactivity in water is very important in the renewal of cartilage tissue, and can also be used extensively for curing some illnesses like rheumatism (Nurten Özer, pers. comm.).

11. RECOMMENDATIONS

1. The hydrologic setting of the Geysir geothermal field in Haukadalur has to be further investigated. The recharge and flow of the geothermal system has to be better defined. Furthermore, additional work is required to determine the geothermal potential of the area in terms of possible direct and indirect applications of the thermal energy that could be extracted from the system.

2. In order to know whether the geothermal system has a wider areal extent, more detailed mapping with emphasis on the hydrothermal deposits should be done. Further study should include more detailed geological mapping, covering a wider area. Systematic sampling of hot springs and cold springs should be performed. In addition, reconnaissance geophysical surveys would be an aid in understanding the nature of the geothermal field.

3. For the isotopic evaluation of water, radioactive Tritium (^3H) isotope analysis is recommended. in addition to ^{18}O and deuterium isotopes analysis. This could determine the underground water distribution in the hydrogeological systems, the residence time and the water's visible age and whether it belongs to the same system or not.

4. The recharge area for the Geysir geothermal field is in the highlands to the north and its extent needs to be determined. Protection may have to be extended both to the discharge area and the feeding area, as determined by zones of high permeability in the ground.

5. I would advise the area close to Geysir be protected. During the summer time, some tourists settle their tents in the field too close to the Geysir area, which is environmentally unaesthetic. It should be not allowed. It would be desirable that the area be protected against such and similar negative influencing factors.

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