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SAMPLING AND ANALYSES OF GEOTHERMAL STEAM AND GEOTHERMOMETER APPLICATIONS IN KRAFLA, THEISTAREYKIR, REYKJANES AND SVARTSENGI, ICELAND

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ABSTRACT

Krafla, Theistareykir, Reykjanes and Svartsengi are high-temperature geothermal areas in Iceland. In this report the results of sampling and analyses of fumaroles in Krafla, Theistareykir, and wells and fumaroles in Reykjanes and Svartsengi are presented. The results of the chemical gas analyses of samples from fumaroles and wells in these fields were used to estimate the temperature of reservoirs using selected gas geothermometers. Gas geothermometer temperatures were also calculated for wells in Reykjanes and Svartsengi. The estimated reservoir temperature for the Krafla sample is 315°C. The gas geothermometers predicted temperatures ranging between 227 and 406°C with a median value of about 290°C. The estimated reservoir temperature for Theistareykir is 280°C. The gas geothermometers predicted temperatures ranging between 220 and 395°C with a median value of about 310°C. The estimated reservoir temperature for the Reykjanes fumarole samples is 295°C. The gas geothermometers predicted temperatures ranging between 240 and 430°C with a median value of about 280°C. Geothermometer results for wells in Svartsengi (SV-11, 14, 19) range between 122 and 430°C whereas the measured well temperature is 240°C. The median of the geothermometer results for the Svartsengi wells ranges from 229°C for well 19 to 289°C for well 14. The measured temperature in well 12 at Reykjanes is about 290°C but the range of temperatures obtained from gas geothermometers is 192-447°C with a median value of 256°C. The best fit between predicted and observed/estimated temperatures was obtained by different gas geothermometers for individual samples, but Giggenbach´s CH_4/CO_2 geothermometer consistently predicted temperatures that are 100-200°C above estimated reservoir temperatures.

1. INTRODUCTION

The Reykjanes, Svartsengi, Krafla and Theistareykir geothermal fields are all active high-temperature systems, located in the active volcanic zone in Iceland. Krafla and Theistareykir are in NE-Iceland, characterized by dilute geothermal solutions, while Reykjanes and Svartsengi are in SW-Iceland and influenced by seawater (Figure 1). Krafla volcanic system consists of the Krafla central volcano

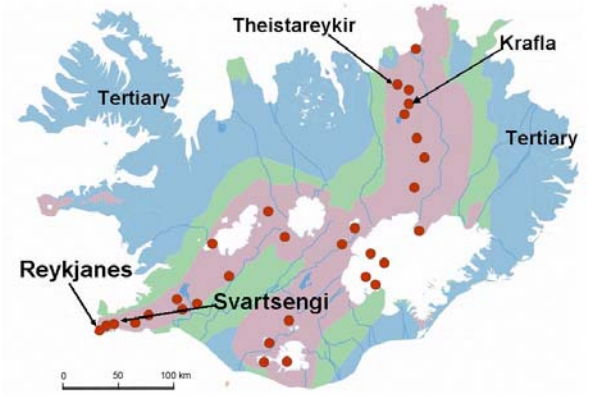

FIGURE 1: Geological map of Iceland and place of sampling

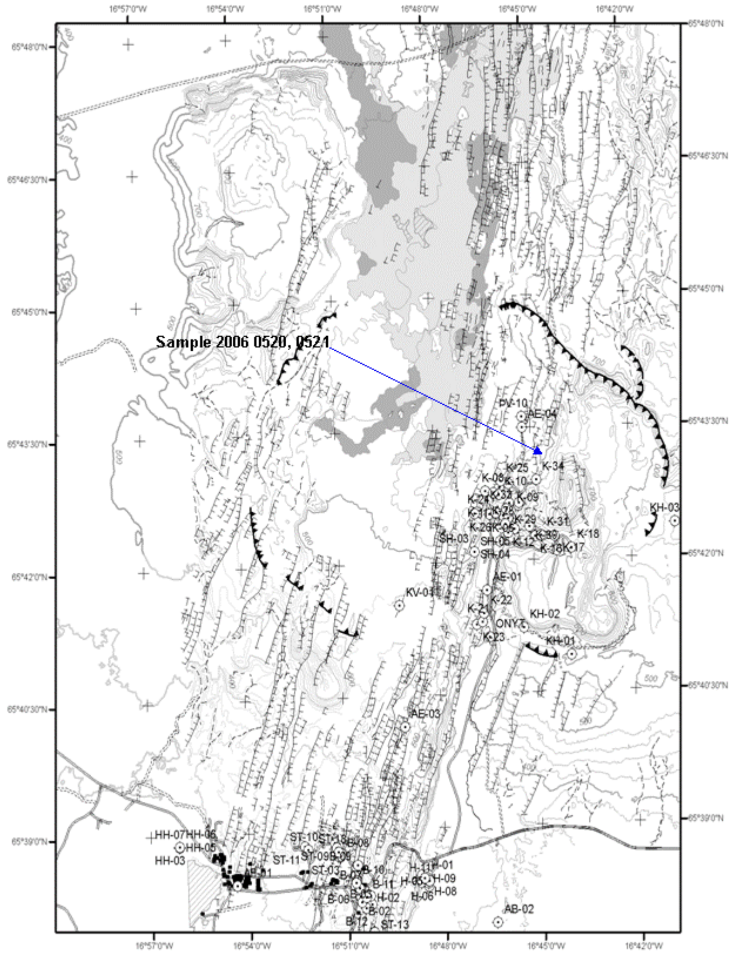

FIGURE 2: The Krafla volcanic system and sampling locations (modified from Saemundsson, 1991)

and a 100 km long transecting fissure swarm. It was last active between 1975 and 1984 when lava erupted from, and to the north of, the central volcano, and dykes were injected along most of the fissure zone (Saemundsson, 1991; Björnsson et al., 1979). The Krafla volcanic system forms part of the Northern volcanic rift zone in Iceland, which is a N–S trending region of active spreading along the axial rift boundary between the European and American plates. The mean spreading rate is 10 mm/year. An 8×10 km caldera has been identified at Krafla (Figure 2) and is thought to have been formed during an explosive eruption of acidic rocks and the formation of rhyolite and dacite ridges during the last inter-glacial period, about 0.1 Ma ago (Saemundsson, 1991). Post-collapse features such as hyaloclastite ridges and postglacial activity, including some 35 fissure eruptions (Björnsson et al., 1979), have largely obliterated the surface evidence for the caldera, although exploratory drilling and petrologic data (Ármannsson et al., 1987) have provided evidence in support of the presence of the caldera.

Samples were also collected at Theistareykir. The Theistareykir field is located in the volcanic rift zone in N-Iceland and has abundant surface geothermal manifestations (Slater et al., 2001).

The Reykjanes Peninsula, SW-Iceland (Figure 1) is the subaerial continuation of the Reykjanes Ridge section of the Mid-Atlantic Ridge, and as such the boundary between the European and American tectonic plates. Volcanism takes place mainly within five fissure systems (Pálmason and Saemundsson, 1974). A high degree of obliquity between the ridge axis at ~90°E and the plate spreading direction of ~110°E induces a right-stepping, en-echelon arrangement of the fissure systems (Jakobsson, 1972), spaced on average approximately 5 km apart, and having an average strike of 40°E. Associated with the volcanic systems are high-temperature geothermal systems. These systems are localized at the surface by spreading-direction-parallel fractures, producing alteration which varies from basalt ‘spotting’ to complete replacement by clay minerals. There are four main geothermal fields on the Reykjanes Peninsula (Arnórsson, 1978), which show a decrease in fluid salinity with distance from the southwestern part of the peninsula. This may result from a decreasing seawater contribution to the geothermal fluids or a decrease in the evaporation rate of the fluid (Sveinbjörnsdóttir et al., 1986). The Reykjanes geothermal system is the outermost, located at the tip of the Reykjanes Peninsula, while the Svartsengi geothermal system is found about 10 km to the west-northwest. Fluids in Reykjanes (Figure 3) have seawater salinity and those in Svartsengi have about 2/3 of the salinity of seawater. The Svartsengi high-temperature area has an area of 2 km^2 and shows only limited signs of geothermal activity at the surface (Thórólfsson, 2005).

Geochemistry is one of the most effective ways of studying geothermal reservoirs, both in the exploratory and production stages. Chemical composition of the thermal water has proven very useful in evaluating subsurface temperature, determining water origin, observing mixing and predicting scaling and corrosion. During the 1970s and 1980s, various solute geothermometers were proposed and revised. Some of these have been used extensively in geothermal fields with great success.

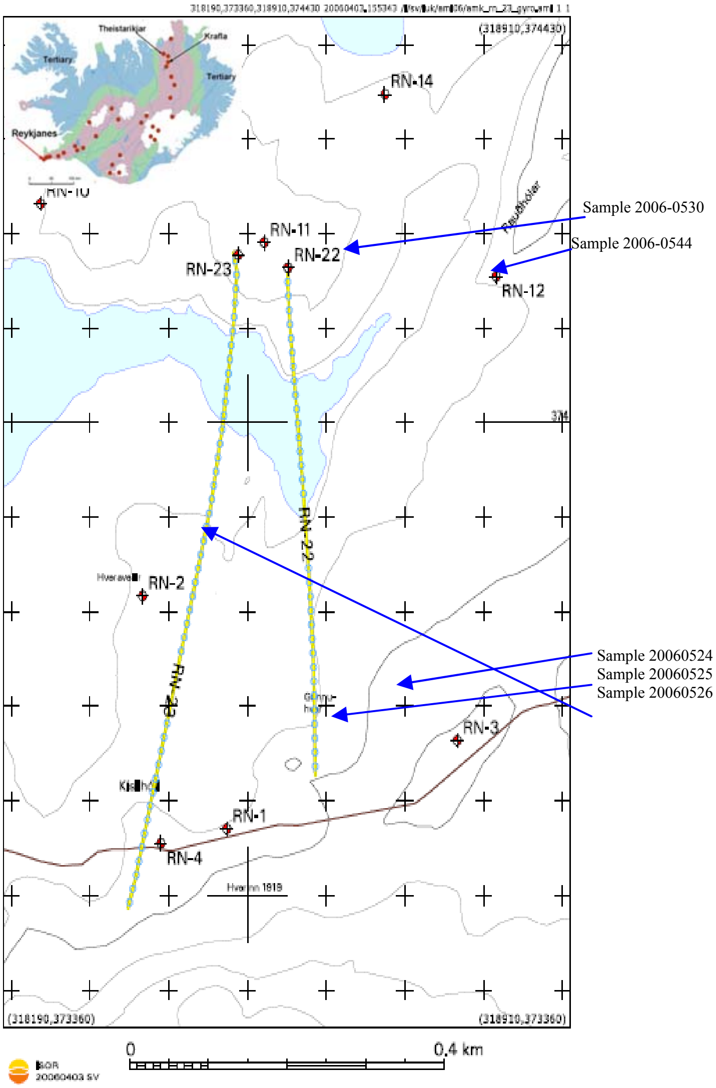

FIGURE 3: Wells and fumaroles in Reykjanes field, with sample locations

Ellis (1957) pointed out that gas constituents, e.g. NH_3 and CH_4, in natural magmatic steam could theoretically be used to predict temperature. The first gas geothermometers were suggested in the 1970s (Tonani, 1973). Several empirical and thermodynamic methods were subsequently proposed (D´Amore and Panichi, 1980; D´Amore et al., 1982; D´Amore and Truesdell, 1985; Arnórsson, 1987; D´Amore et al., 1987). The composition of gas and/or steam from fumaroles can be used to predict subsurface temperature, locate upflow zones and map the flow direction of boiling water. The composition of steam from discharging wells has been used to evaluate the inflow temperature and the steam fraction, as well as boiling and multi condensation processes. The isotopic composition of steam can be used both to identify its origin and the equilibrium temperature.

In this study steam samples were collected from selected fumaroles and four wells which characterize geothermal systems in Iceland. Comparisons were made between different sampling techniques and the results of the chemical analyses of steam were used to compute reservoir temperatures using selected gas geothermometers.

2. GAS GEOTHERMOMETRY

2.1 Composition of steam

The major gases in geothermal steam are CO_2, H_2S, H_2, CH_4, N_2, NH_3, CO, He, Ar and Ne. CO_2 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 areal 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 experiment with reservoir data from several geothermal fields. Organic reactions in meteoric water may be a source of CO_2 in thermal fluids. The hydrogen sulphide concentration of the geothermal fluids varies widely, but is thought to be formed from iron and/or silica minerals. Hydrogen sulphide commonly decreases as the steam ascends to the surface due to interaction with wall rocks, and 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 redox processes in geothermal studies (D´Amore and Nuti, 1977). Truesdell and Nehring (1978) suggested that hydrogen is produced by high-temperature reactions of water with ferrous oxides and silicates contained in reservoir rocks. Methane concentration is relatively low in the steam. Nitrogen originates from meteoric water saturated with atmospheric air in Iceland but may be of organic origin in the subduction zone environments.

2.2 Empirical gas geothermometer

In the 1970s the first empirical gas geothermometer was proposed by Tonani (1973). Relative gas concentrations were used for calculations and P_{CO2} was assumed to be controlled by external factors. Three different functions were given for different P_{CO2} conditions in the reservoir. Because gas geothermometers are generally most useful in the early stages of exploration when relatively little is known about the nature of the geothermal system, the requirement for knowing the P_{CO2} in advance is a great disadvantage. Later, D´Amore and Panichi (1980) suggested a semi-empirical gas geothermometer based on gas composition of fluids from 34 thermal systems. They found that there was a relationship between the relative concentration of H_2S, H_2, CH_4, CO_2 and reservoir temperatures. The following two chemical reactions were considered:

$$CaSO_4 + FeS_2 + 3H_2O_{(aq)} + CO_2 = CaCO_3 + 1/3\ Fe_3O_4 + 3H_2S_{(aq)} + 7/3\ O_2 \tag{1}$$

$$C + CO_2 + H_2 = 2CH_4 + 2H_2O \tag{2}$$

However, this thermometer also requires that the user knows the P_{CO2} beforehand.

Nehring and D’Amore (1984) developed gas geothermometers based on thermodynamic data for gas and mineral solubilities. In this study two of these are considered, i.e., the H_2-CO_2 and the H_2S-CO_2 gas geothermometers. The temperature functions for these geothermometers, as reported by D’Amore and Arnórsson (2000), are

$$T_{(HC)} = 190.3 + 55.97Q_{HC} - 0.14Q_{HC}^2 \tag{3}$$

and

$$T_{(SC)} = 194.3 + 56.44Q_{SC} + 1.53Q_{SC}^2 \tag{4}$$

where Q_{HC} $= \log m_{H_2} + 0.5 \log m_{CO_2}$; and

$Q_{SC} = \log m_{H_2S} + 1/6 \log m_{CO_2}$ (concentrations in mmol/kg).

Arnórsson (1983) suggested an empirical geothermometer based only on the CO_2 concentration of the steam, and later proposed five gas geothermometers which were calibrated with data from selected wells (Arnórsson and Gunnlaugsson, 1985). These geothermometers are based on the assumption that the geothermal reservoir is a one-phase system. Three of these geothermometers are based on the total concentration of CO_2, H_2S and H_2 in steam, respectively, and two are based on ratios, CO_2/H_2, and H_2S/H_2. Different functions for different temperature ranges and chloride concentrations were given for the H_2, H_2S and CO_2/H_2 geothermometer, because different mineralogical studies of wells showed that different gas concentrations prevailed at different temperatures for dilute water and brine. They pointed out that it is often advantageous to calibrate geothermometers using geothermal rather than thermodynamic data, particularly when silicate mineral equilibrium is involved. Small errors in thermodynamic data for these minerals may produce unacceptable deviations in predicted temperatures even if the error is less than one thousandth of the enthalpy of mineral formation. Below are the temperature functions for the gas geothermometers from Arnórsson and Gunnlaugsson (1985) that are considered in this study, all concentrations are in mmole/kg:

$$T_{(CO_2)} = -44.1 + 269.251 \log m_{CO_2} - 76.88(\log m_{CO_2})^2 + 9.52(\log m_{CO_2})^3 \tag{5}$$

$$T_{(H_2S)} = 246.7 + 44.811 \log m_{H_2S} \tag{6}$$

$$T_{(H_2)} = 277.2 + 20.99 \log m_{H_2} \tag{7}$$

$$T_{(H_2S/H_2)} = 304.1 - 39.481 \log m_{H_2S} / m_{H_2} \tag{8}$$

$$T_{(CO_2/H_2)} = 341.7 - 28.571 \log m_{CO_2} / m_{H_2} \tag{9}$$

Arnórsson (1987) developed a N_2/CO_2 gas geothermometer which is based on the assumption that the N_2 in the reservoir fluids is derived from local meteoric water in equilibrium with atmospheric air. Later, Arnórsson et al. (1998) revised this thermometer, presented similar thermometers based on H_2S/Ar and H_2/Ar and added new theoretical calibrations for the CO_2, H_2S, and the H_2 thermometers. The temperature functions for these thermometers are (all concentrations are in mmole/kg):

$$T_{CO_2} = 4.724\left(\log m_{CO_2}\right)^3 - 11.068\left(\log m_{CO_2}\right)^2 + 72.012\left(\log m_{CO_2}\right) + 121.8 \tag{10}$$

$$T_{H_2S} = 4.811\left(\log m_{H_2S}\right)^2 + 66.152\left(\log m_{H_2S}\right) + 177.6 \tag{11}$$

$$T_{H_2} = 6.630\left(\log m_{H_2}\right)^3 + 5.836\left(\log m_{H_2}\right)^2 + 56.168\left(\log m_{H_2}\right) + 227.1 \tag{12}$$

$$T_{CO_2/N_2} = 1.739\left(\log m_{CO_2}/m_{N_2}\right)^3 + 7.599\left(\log m_{CO_2}/m_{N_2}\right)^2 + 48.751\left(\log m_{CO_2}/m_{N_2}\right) + 173.2 \tag{13}$$

$$T_{H_2/Ar} = 0.640\left(\log m_{H_2}/m_{Ar}\right)^2 + 43.260\left(\log m_{H_2}/m_{Ar}\right) + 170.0 \tag{14}$$

$$T_{H_2S/Ar} = 4.108\left(\log m_{H_2S}/m_{Ar}\right)^2 + 42.256\left(\log m_{H_2S}/m_{Ar}\right) + 137.6 \tag{15}$$

Giggenbach (1991) proposed gas geothermometers based on simple gas ratios in a paper on chemical techniques in geothermal explorations. The temperature functions of these geothermometers are (all concentrations are in mole %):

$$T_{H_2/Ar} = 70\left[2.5 + \log(H_2/Ar)\right] \tag{16}$$

and

$$T_{CH_4/CO_2} = \frac{4625}{10.4 + \log\left(CH_4/CO_2\right)} - 273.15 \tag{17}$$

3. COLLECTION OF STEAM SAMPLES

Interpretation of the steam composition has its basis in correct sampling and analytical methods. There are some differences in the methods used for sampling wells and fumaroles (Ólafsson, 1988; Ármannsson and Ólafsson, 2006). These methods are described below.

3.1 Sampling from wells

The collection of representative gas samples from discharging wells involves that of the steam phase and the water phase. This is done with the aid of a webre separator and a cooling device. Great care must be taken to separate steam completely from liquid. The separator is connected to the steam line and kept open to rinse and warm it up for at least 10 min. Then it is closed and the sampling pressure (Ps) is recorded from a pressure gauge installed in the separator. The geothermal fluids are separated completely by adjusting outlet valves. For steam sampling, a cooling coil is connected to the steam outlet on the separator. The steam outlet is opened just a little bit and the water outlet of the separator is opened completely in order to discharge a mixture of both steam and water. This ensures that only steam is discharged through the steam outlet. A cooling coil is connected to the steam outlet and allowed to rinse for few minutes before sampling. The condensed steam and the non-condensable gases are then collected to an evacuated double port bottle containing a concentrated solution of NaOH (40 wt%). The most abundant gases, CO_2 and H_2S, will dissolve in the caustic solution and the other gases will be collected in the head space. Figure 4 is a schematic diagram of the sampling procedure for geothermal wells.

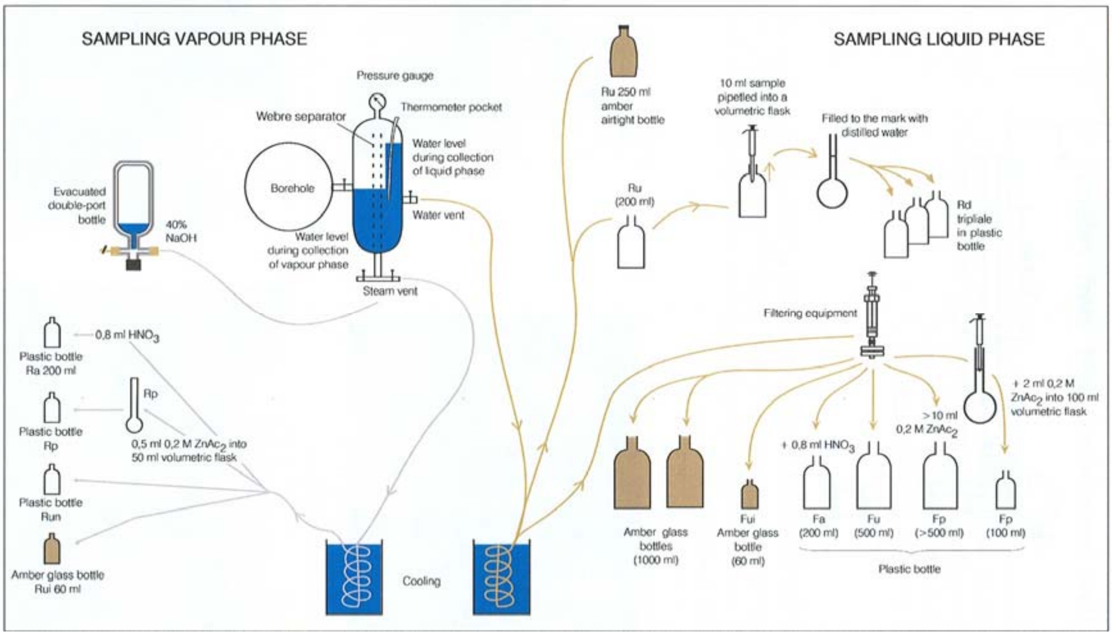

FIGURE 4: Collection of a sample from a two-phase geothermal well for chemical analysis (Ármannsson and Ólafsson, 2006)

3.2 Sampling from fumaroles

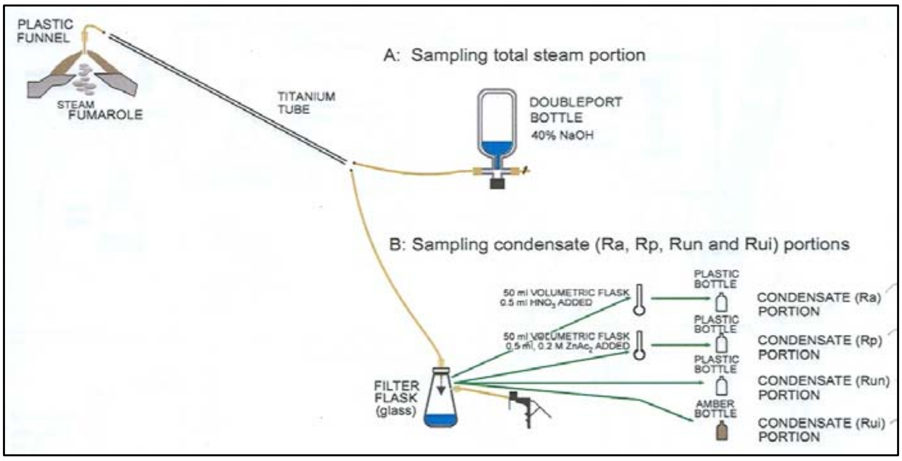

FIGURE 5: Collection of a steam sample from fumaroles (Ármannsson and Ólafsson, 2006)

Before sampling, it is necessary to measure the temperature in different locations and try to find the optimum spot for sampling. A funnel is placed upside down over the major upflow and tightly packed with mud and clay to prevent atmospheric contamination (Figure 5). The funnel is connected to an evacuated double port bottle with a concentrated NaOH (40-%wt) solution, either by a short silicon rubber hose or a titanium pipe. The rubber hoses are generally narrow and if the flow from the fumarole is weak the resistance of the hose may stop the flow. The wide titanium pipe has much less flow resistance allowing sampling from weaker fumaroles. However, because the titanium pipe is usually wider and longer than the rubber hose, there is a concern that some of the steam may condense in the pipe before it reaches the bottle. In this study, both methods of sampling were tested in order to determine if condensation in the titanium pipe was affecting the gas concentration of the sample. If possible, it is best to have a free flow of water from the sampling spot in order to cool the bottle during sampling; otherwise a bucket of cooling water will suffice.

3.3 Chemical analysis

The most convenient methods for determining CO_2 and H_2S by titration are with hydrochloric acid using a pH-meter, and with mercury acetate using dithizone as the indicator, respectively. The head space gases are analyzed using gas chromatography.

4. RESULTS AND DISCUSSION

4.1 Chemical analysis of the samples

Chemical analysis for geochemical investigation of geothermal systems routinely include gases like CO_2, H_2S, NH_3, H_2, CH_4, O_2, N_2 and Ar and often He as well. The present geochemical study is based on the collection of steam samples from fumaroles (Figure 6) in Krafla, Theistareykir, and Reykjanes, and on well samples from Reykjanes and Svartsengi. The samples from Krafla are (20060520, 20060521(Figure 2)), and from Theistareykir (20060522, 20060523). Samples 2006-0524, 0525, 0526 (Figure 3) are from Reykjanes, and samples 0527, 0528, 0529 are from Svartsengi wells (SV-11, 14 and 19). Samples 0530 and 0544 correspond to the Reykjanes wells RN-22 and RN-12. The samples from Krafla and Theistareykir were collected utilizing the two different techniques of sampling, the first utilizing a titanium pipe and the second using a rubber pipe (Section 3.2). The analyses of head space gases were carried out by gas chromatography at the University of Iceland and the CO_2 and H_2S were determined by titration at the ISOR laboratory.

4.2 Gas chromatography

Gas chromatography analyses were carried out using a Perkin Elmer Arner XL chromatograph in the laboratory of the Institute of Earth Sciences, University of Iceland. Chromatography is a technique for separating chemical substances that relies on differences in partitioning behaviour between a flowing mobile phase and a stationary phase to separate the components in a mixture.

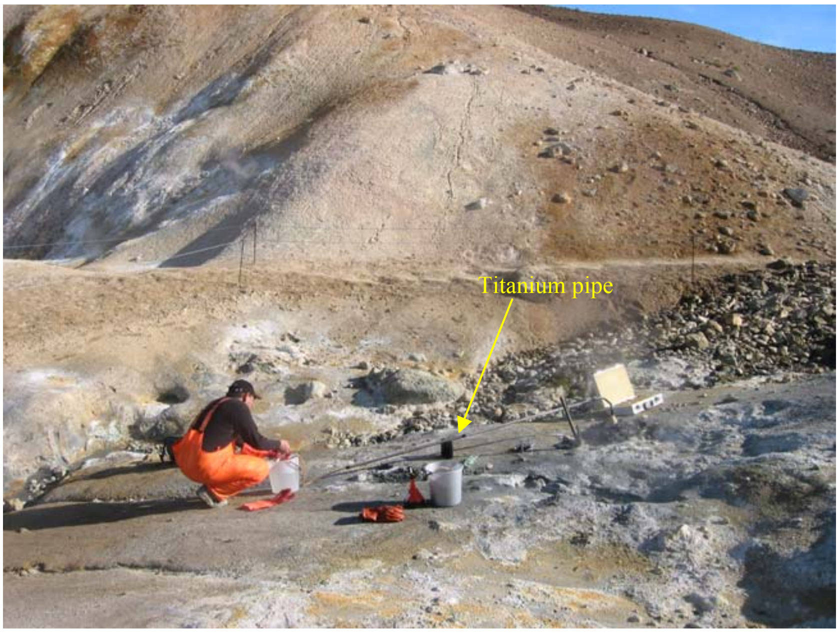

FIGURE 6: Steam sample collected using a titanium pipe

The sample is carried by a moving gas (mobile phase may be He or N_2) stream through a tube (chromatography column) packed with a fine solid. The analyses of head space gases of the samples were carried out. The chromatographic analyses were conducted in two steps; first H_2, N_2, CH_4, and Ar + O_2 were determined using the so called "light gas" method. It was necessary to run the sample again, using a different method, in order to quantify Ar. Typical results of a gas chromatography analysis are shown in Figure 7.

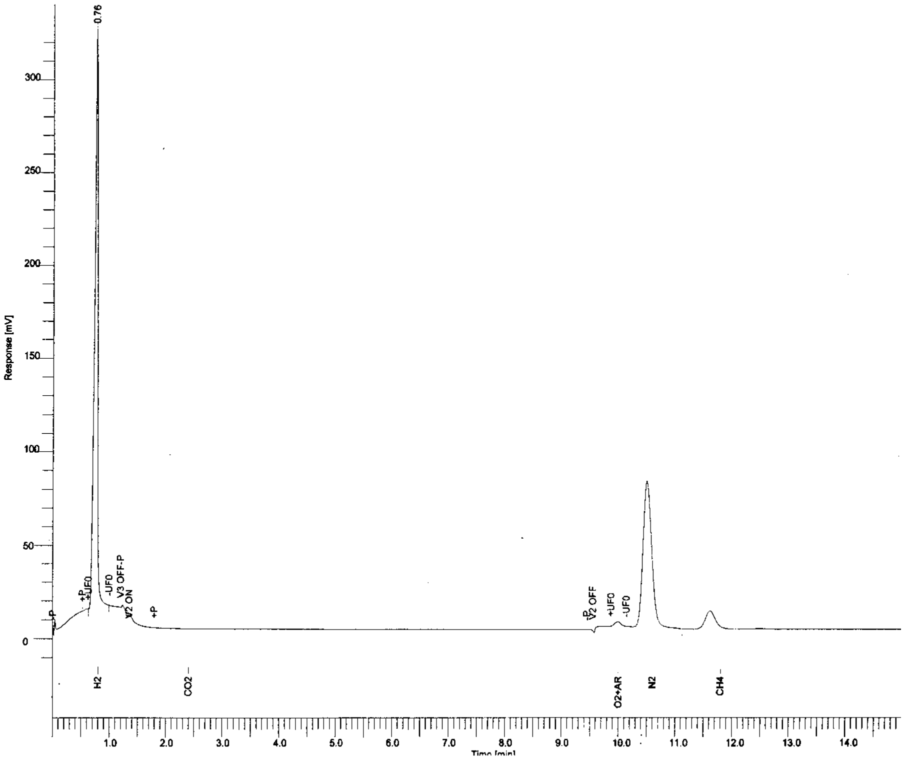

FIGURE 7: Typical results of a gas chromatograph analysis

The peaks in the chromatogram (see Figure 7) correspond to individual gas species in the sample and the area below the peaks of the chromatogram is a linear function of the concentration of the corresponding gas. The chromatogram is used to determine the concentration ratios of the gases in the head space. When the sample bottle is connected to the sample inlet line of the chromatograph the pressure is measured and, because the head space volume and the volume of the inlet line in known, this pressure can be used to compute

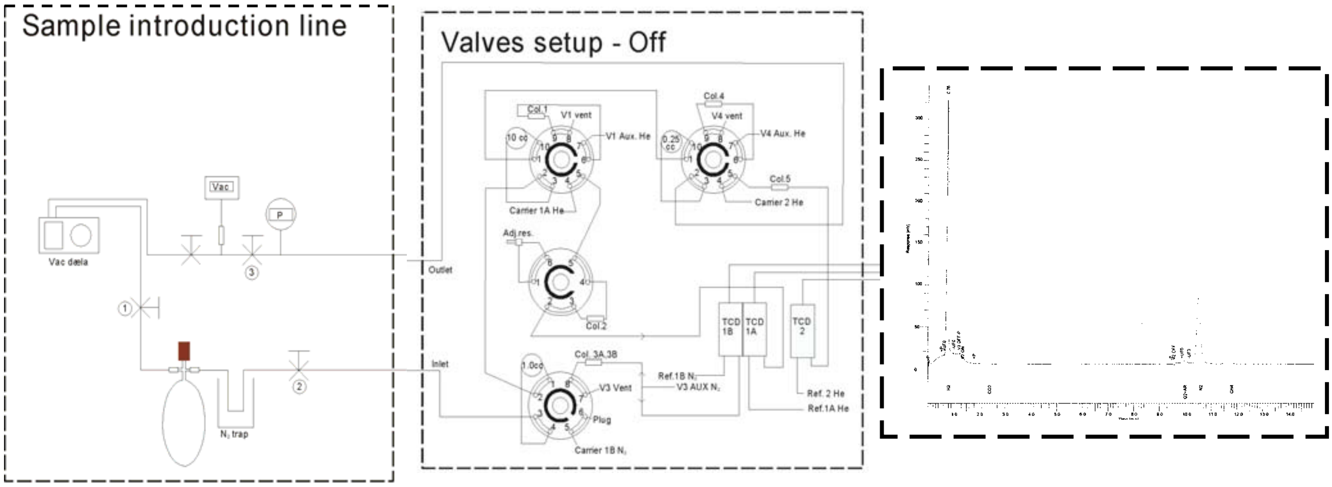

FIGURE 8: Schematic diagram of the chromatograph used,
Perkin-Elmer Arnel Model 4019 Analyzer

the total amount of head space gas in the sample. This is then used along with the amount of condensed water in the bottle to compute the concentration of the head space gases in the steam in mmole/kg of steam. Figure 8 shows a schematic diagram of the setup of the gas chromatograph used in this study. The results of these analyses are shown in Table 1.

4.3 Determination of CO_2 and H_2S in steam samples

Both CO_2 and H_2S dissolve in the NaOH solution in the Giggenbach bottle. After the head space gas had been analyzed by gas chromatography, the concentration of H_2S and CO_2 in the condensate was analyzed (H_2S by classic titration and CO_2 by potentiometer titration). The hydrogen sulphide (H_2S) was determined by titration with αHg $(CH_3COO)_2$ solution using a dithizone indicator. The end point is recorded when the colour changes from the yellow colour of dithizone in an alkaline solution to the pink colour of Hg-dithizonate.

The CO_2 concentration was determined by a pH titration. A small volume of the solution from the Giggenbach bottle containing the NaOH solution and the condensed steam is accurately measured and diluted to about 50 ml with deionized water. The pH is adjusted with 5 M and 1 M HCl solutions to about pH 9 and then titrated with 0.1 M hydrochloric acid using an automated *Metrohm 716 DMS Titrino* titrator (see Figure 9) to a pH of about 3. The equivalence points of the titration are at pH 8.20 and 3.80 and the volume of acid added between these points is used to quantify the concentration of CO_2 in the sample. A correction had to be made for the analyzed concentration of H_2S. The results of the titration of CO_2 and H_2S were processed with software called *Titrar* used in the laboratory of ISOR. A typical titration curve is shown in Figure 10 and the first and second derivatives of the titration curve are shown in Figures 11 and 12, respectively. The shapes of the derivative curves illustrate that the endpoints of the titration are very well defined.

4.4 Gas concentrations in steam samples

The gas concentrations of all the samples considered in this study are reported in Table 1. Titrations for CO_2 and H_2S for sample 20060526 were carried out but some of the analytical data were missing and, as a result, the concentrations of these gases were not reported for this sample. Similarly, the concentrations of the head space gases in sample 20060530 have not yet been determined due to a fracture in one of the ports of the bottle.

TABLE 1: Gas concentrations in the steam samples taken

Gas species	20060520 Krafla G-36 (mmol/kg)	20060521 Krafla G-36 (mmol/kg)	20060522 Theistareykir G-35 (mmol/kg)	20060523 Theistareykir G-35 (mmol/kg)	20060524 Reykjanes G-1 (mmol/kg)	20060525 Reykjanes G-2 (mmol/kg)	20060526 Reykjanes G-3 (mmol/kg)	20060527 Svartsengi well 19 (mmol/kg)	20060528 Svartsengi well 11 (mmol/kg)	20060529 Svartsengi well 14 (mmol/kg)	20060530 Reykjanes well 22 (mmol/kg)	20060544 Reykjanes well 12 (mmol/kg)
CO_2	664	658	108	114	155	135		41	263	378	141	224
H_2S	6.85	5.18	4.00	4.12	11.18	13.24		3.47	8.12	5.35	9.91	7.41
Ar	0.034	0.026	0.021	0.030	0.023	0.025	0.078	0.006	0.018	0.025		0.149
N_2	1.29	1.46	0.80	1.42	1.13	1.14	3.57	0.35	0.96	1.35		10.15
CH_4	0.17	0.18	0.07	0.05	0.02	0.02	0.06	0.00	0.03	0.06		0.02
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.13
H_2	2.94	3.16	29.86	25.18	1.83	1.78	1.22	0.04	1.44	3.46		0.47

FIGURE 9: Titration equipment Metrohm 716 DMS Titrino

Table 1 shows that CO_2 is always the most abundant gas species, ranging from 41 to more than 660 mmole/kg. CO_2 is followed in most cases by H_2S, which was generally between 5 and 10 mmole/kg. In the Theistareykir samples, however, H_2 is more abundant than H_2S. The Theistareykir samples have unusually high H_2 concentrations, close to 30 mmole/kg steam compared to the other samples that generally have H_2 concentrations between 1 and 4 mmole/kg. CH_4 is present in all samples in low concentrations, close to 0.2 mmole/kg in the Krafla samples but below 0.1 mmole/kg in other samples. The concentrations of N_2 and Ar are very consistent. N_2 is generally between 0.8 and 1.5 mmole/kg. The most notable exceptions to this were the samples from wells SV-19 and RN-12, and the Reykjanes fumarole G-3. SV-19 has very low concentrations of all gases which may possibly be a result of more extensive boiling of the deep fluid than in other wells. Reykjanes fumarole G-3 is on the periphery of the most active fumarole field in Reykjanes and the gas concentrations may have been affected by condensation, although the absence of CO_2 and H_2S analyses for this sample prevents further interpretation of its chemical composition. The sample from well RN-12 shows signs of atmospheric contamination. Ar is, in most cases (the exceptions being the abovementioned three samples), between 0.02 and 0.035, and the N_2/Ar ratio of all samples is in the range of 37-56 with the exception of the sample from well RN-12, which has a higher ratio due to atmospheric contamination. The expected N_2/Ar ratio for air-saturated water at 5°C is about 38 and the ratio of these gases in the atmosphere is 83.6.

In order to use well samples to compute gas geothermometer temperatures it is necessary to compute the gas concentrations of the samples at 1 bar. This was done to all the well samples, except for the sample from well SV-14 by computing the steam fraction at sampling from the reading of the manometer on the webre separator and the estimated deep fluid temperature and similarly the steam fraction at 1 bar. The concentrations of the individual gases at 1 bar were found by multiplying the observed gas concentrations at the sampling conditions by the ratio X_S/X_{1bar}, where X_S was the steam fraction at the sampling conditions and X_{1bar} was the steam fraction at 1 bar. This

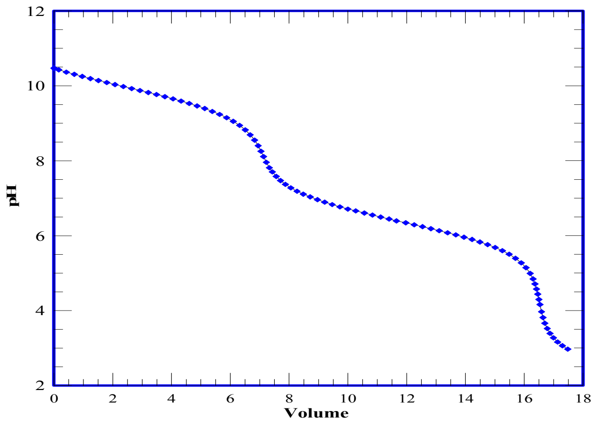

FIGURE 10: CO_2 titration curve of sample 20060520

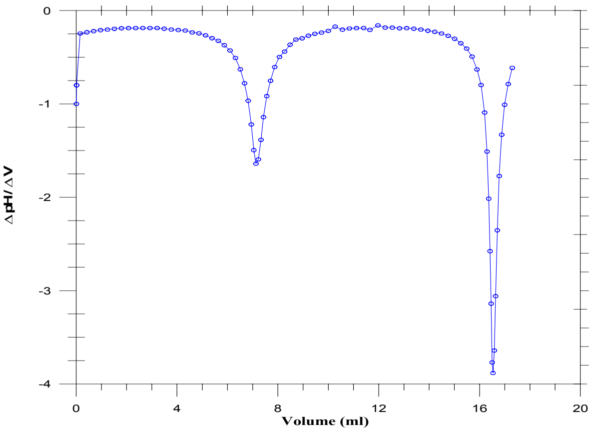

FIGURE 11: First derivate of the CO_2 titration curve of sample 20060520

correction was not made to the sample from SV-14 as this well produces only dry steam and the conditions where the steam is separated from the deep liquid are not accurately known. Table 2 lists the resulting steam concentrations at 1 bar for the well samples as well as the sampling conditions, the steam fractions at sampling conditions and 1 bar.

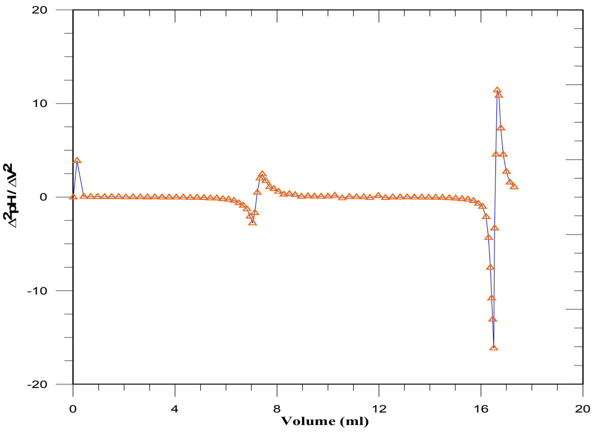

FIGURE 12: Second derivate of the CO_2 titration curve of sample 20060520

TABLE 2: Sampling conditions, steam fractions and gas concentrations corrected to 1 bar pressure for steam samples from two-phase wells

Sampling conditions	**20060527 Svartsengi well 19**	**20060528 Svartsengi well 11**	**20060530 Reykjanes well 22**	**20060544 Reykjanes well 12**
Separator pressure (bar)	13.5	18.4	44.8	33.5
Separator temperature (°C)	195.9	208.1	253.2	240.5
Reservoir temperature (°C)	240	240	305	295
Sampling steam fraction (X_S)	0.10	0.07	0.15	0.16
Steam fraction at 100°C (X_{1bar})	0.27	0.27	0.42	0.40
X_S/X_{1bar}	0.37	0.26	0.36	0.40
Gas concentrations at 1 bar	**(mmol/kg)**	**(mmol/kg)**	**(mmol/kg)**	**(mmol/kg)**
CO_2	15.49	68.83	50.19	89.02
H_2S	1.30	2.13	3.53	2.95
Ar	0.002	0.005		0.059
N_2	0.13	0.25		4.04
CH_4	0.001	0.007		0.009
O_2	0.000	0.000		0.051
H_2	0.015	0.376		0.188

Note that well 14 in Svartsengi is a dry steam well and therefore it was not attempted to compute the composition of the steam at 1 bar for that well.

4.5 Sampling through a titanium pipe versus a silicon tube

As noted above, two samples were collected from the same fumarole in Krafla (20060520 and 20060521) and similarly two samples were collected from the same fumarole in Theistareykir (20060522 and 20060523). In each of these places the samples were first collected using the titanium pipe and subsequently a sample was collected through a silicon rubber pipe. The objective of collecting two samples from the same fumaroles using two different sampling techniques was to check if the sampling technique would affect the result. The titanium pipe was long (~ 3 m) and wide (2.5 cm) and the titanium metal is a good head conductor. The rubber pipe on the other hand was short (< 1 m) and thin (~ 0.5 cm diameter), with the walls much thicker than in the titanium pipe. It was suspected that condensation might have more effect on the sample collected with the titanium pipe. If that were the case gas concentrations would be systematically higher in the sample collected through the titanium pipe.

It can be observed from Table 1 that the results obtained for sample 20060520 are fairly similar to the results for 20060521, but there is some discrepancy between samples 20060522, and 20060523. However, the discrepancy in not systematic, and thus it is not likely that it was caused by condensation in the pipe. Figures 13 and 14 depict the concentrations of individual gases in the samples collected through a silicon rubber pipe as a function of the concentration of the same gases in the samples collected through a titanium pipe. Also shown in the figures is a 1:1 line. It can be seen that the gas concentrations in the Krafla samples fall more or less on the 1:1 line whereas the Theistareykir samples are more scattered around it. The data points fall both above and below the 1:1 line. The scatter is most likely not a result of the sampling technique, but rather due to natural variations in gas concentrations, analytical accuracy, or sample contamination.

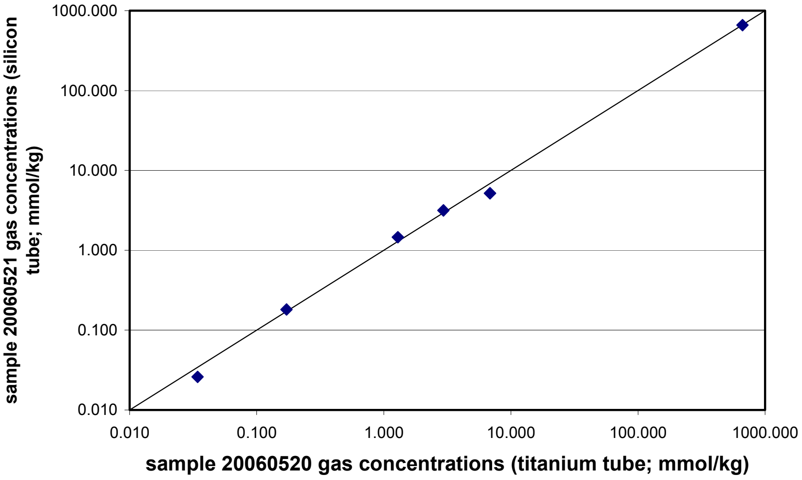

FIGURE 13: Comparison of the results of the gas chromatography analyses of the samples collected with different pipes in Krafla

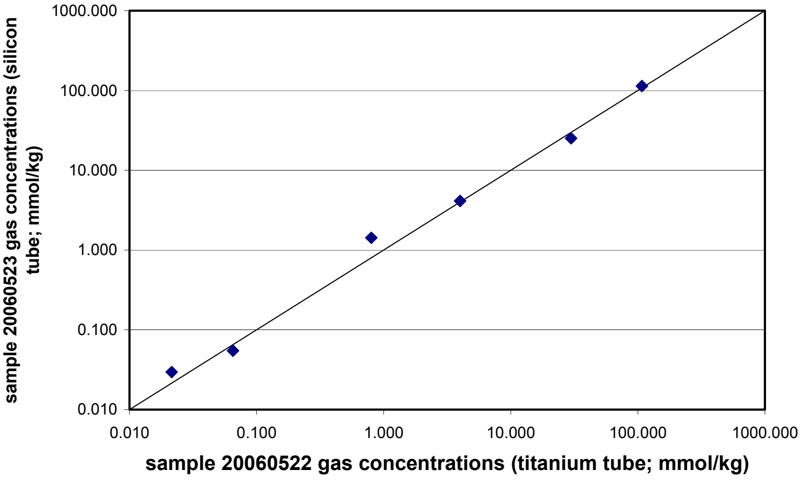

FIGURE 14: Comparison of the results of the gas chromatography analyses of the samples collected with different pipes in Theistareykir

4.6 Geothermometry result

After analysing the samples, the results were used to compute reservoir temperatures using different gas geothermometers. The geothermometers utilized for these calculations were those of Nehring and D'Amore (1984), Arnórsson and Gunnlaugsson (1985), Arnórsson (1987), Giggenbach (1991), and Arnórsson et al. (1998). The temperature functions for these geothermometers are given in Equations 3 through 17 and the results are shown in Table 3. Table 3 also shows the average and the median of the geothermometer results as well as the estimated reservoir temperature for each system. The geothermometry results that fall within 25°C of the estimated temperature for each system are highlighted in *italics*. Figures 15-22 show graphical representations of the results.

Table 3 shows that the H_2S and H_2 geothermometers from Arnórsson and Gunnlaugsson (1985) generally give the best results. Some of the other thermometers perform well in a few cases, whereas five of the geothermometers do not come within 15°C of the estimated reservoir temperature for any of the samples. These poor performers are the H_2-CO_2 geothermometer from Nehring and D'Amore (1984), the CH_4/CO_2 thermometer from Giggenbach (1991) and the H_2S, H_2, and the CO_2-N_2 geothermometers from Arnórsson et al. (1998). Of these the CH_4/CO_2 thermometer from Giggenbach (1991) is least reliable, commonly predicting temperatures that are 100-200°C higher than the estimated reservoir temperature.

It is interesting to note that the performance of the geothermometers in predicting the reservoir temperatures for the fumarole samples is significantly better than it is for the well samples. This is particularly striking for well RN-12 (20060544) where almost all the gas geothermometers predicted temperatures that were much lower than those measured in the well. But many of the geothermometers deviated significantly from the known temperatures in wells SV-19 and SV-11; in SV-19 they tended to predict too low temperatures and too high temperatures for well SV-11.

TABLE 3: Results of gas geothermometers

Geothermometer	**20060520** **Krafla** **G-36** **T (°C)**	**20060521** **Krafla** **G-36** **T (°C)**	**20060522** **Theistareykir** **G-35** **T (°C)**	**20060523** **Theistareykir** **G-35** **T (°C)**	**20060524** **Reykjanes** **G-1** **T (°C)**	**20060525** **Reykjanes** **G-2** **T (°C)**	**20060526** **Reykjanes** **G-3** **T (°C)**	**20060527** **Svartsengi** **well 19** **T (°C)**	**20060528** **Svartsengi** **well 11** **T (°C)**	**20060529** **Svartsengi** **well 14** **T (°C)**	**20060530** **Reykjanes** **well 22** **T (°C)**	**20060544** **Reykjanes** **well 12** **T (°C)**
N&A, 1984 - H_2-CO_2	295	297	329	325	266	264		121	218	292		204
N&A, 1984 - H_2S-CO_2	271	263	249	250	277	*281*		212	231	262	242	240
A&G, 1985 - CO_2	*317*	*317*	265	267	277	273		184	*250*	302	238	259
A&G, 1985 -H_2S	284	279	*274*	*274*	*294*	*297*		*252*	261	279	*271*	268
A&G, 1985 - H_2	287	288	308	307	*283*	*282*	*279*	*239*	268	289		262
A&G, 1985 - CO_2/H_2	274	275	326	323	*287*	*288*		255	277	283		265
A&G, 1985 - H_2S/H_2	290	296	339	335	273	270		*227*	274	297		257
G, 1991 - H_2/Ar	*310*	*321*	395	380	307	305	259	*230*	307			210
G, 1991 - CH_4/CO_2	406	403	371	380	433	432		459	448	430		447
SA et al. 1998 - CO_2	343	343	262	264	276	271		200	*246*		235	255
SA et al. 1998 - H_2S	236	227	219	220	252	258		185	200		215	210
SA et al. 1998 - H_2	255	257	344	335	242	242	232	103	204			187
SA et al. 1998 - CO_2/N_2	396	389	328	305	329	322		323	362			256
SA et al. 1998 - H_2S/Ar	257	257	255	247	*280*	*284*		284	278			221
SA et al. 1998 - H_2/Ar	256	263	312	302	254	253	223	204	*254*			192
Average	**299**	**298**	**305**	**301**	**289**	**288**	***248***	**216**	**259**	**286**	**240**	**235**
Median	**287**	**288**	**312**	**305**	**277**	**281**	***245***	**220**	**258**	**289**	**238**	**248**
Estimated temperature	**315**	**315**	**280**	**280**	**295**	**295**	**295**	**240**	**240**	**240**	**305**	**295**

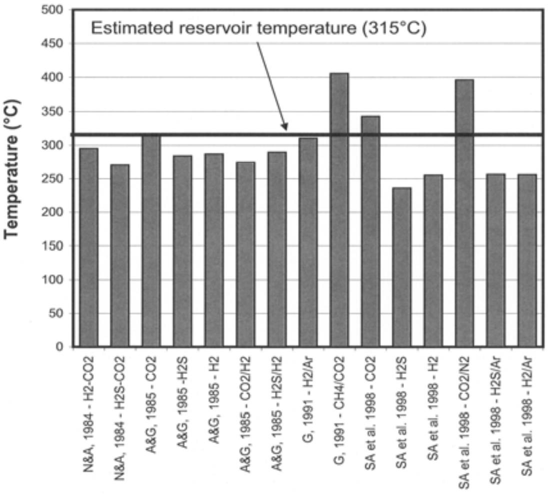

FIGURE 15: Results of gas geothermometers for sample 20060520 (Krafla G-36)

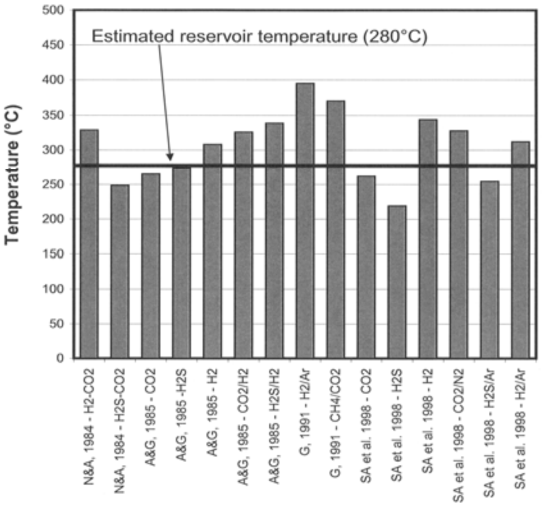

FIGURE 16: Results of gas geothermometers for sample 20060522 (Theistareykir G-35)

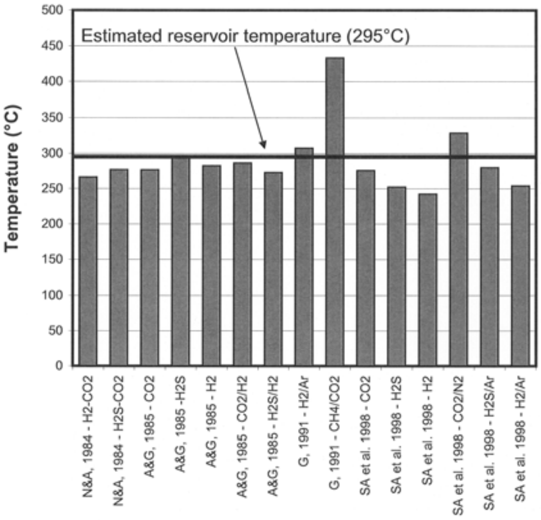

FIGURE 17: Results of gas geothermometers for sample 20060524 (Reykjanes G-1)

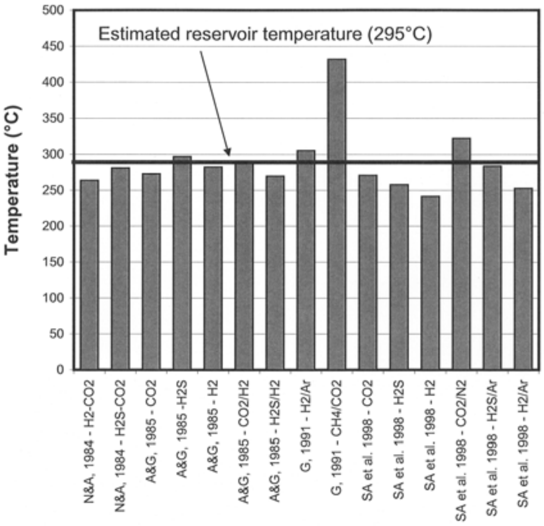

FIGURE 18: Results of gas geothermometers for sample 20060525 (Reykjanes G-2)

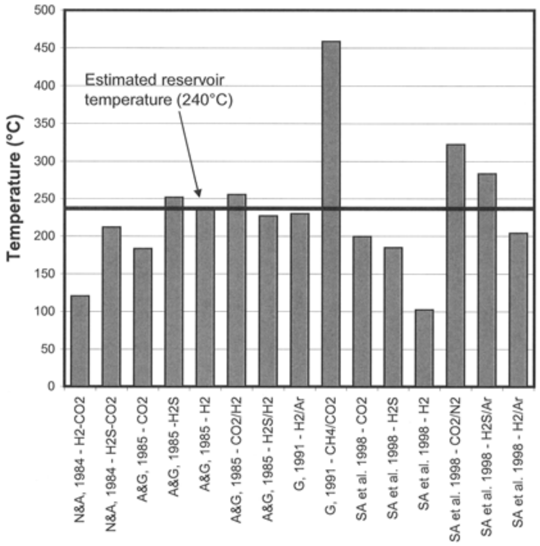

FIGURE 19: Results of gas geothermometers for sample 20060527 (Svartsengi well 19)

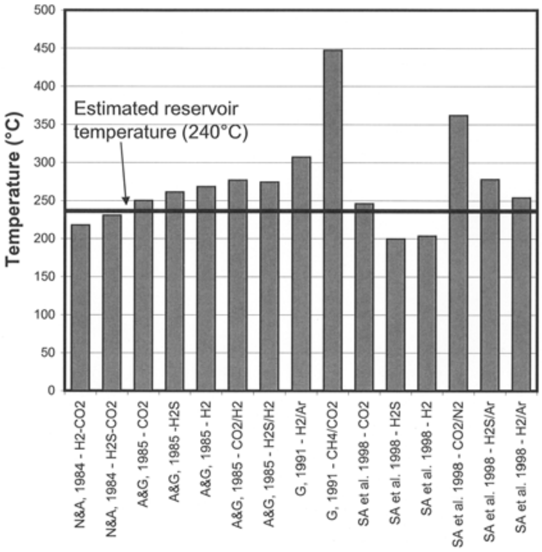

FIGURE 20: Results of gas geothermometers for sample 20060528 (Svartsengi well 11)

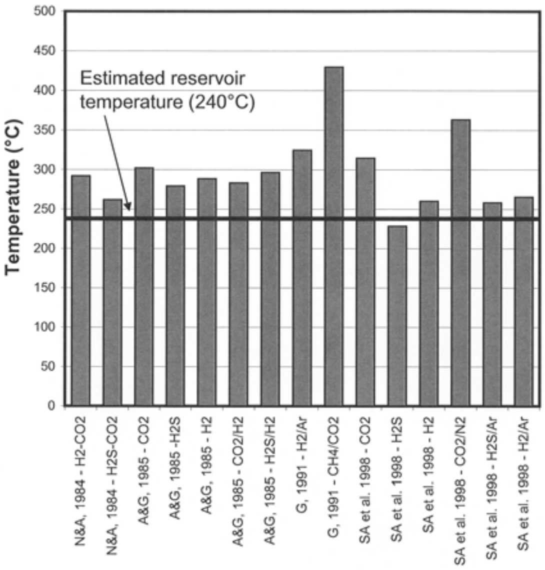

FIGURE 21: Results of gas geothermometers for sample 20060529 (Svartsengi well 149)

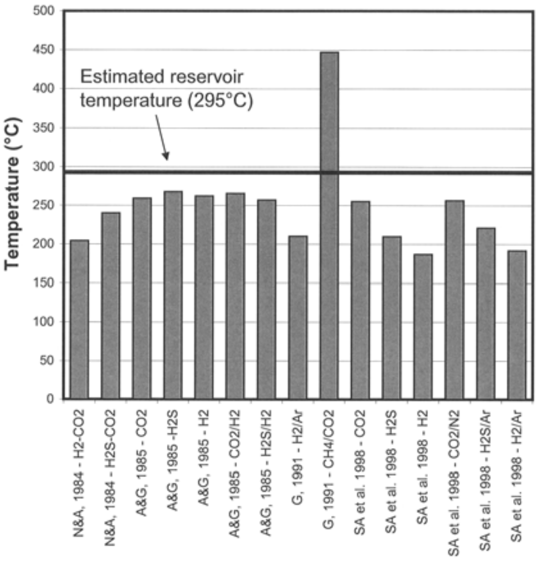

FIGURE 22: Results of gas geothermometers for sample 20060544 (Reykjanes well 19)

6. CONCLUSIONS

The main aims of this project were to collect steam samples from wells and fumaroles, compare two different techniques of sampling of fumaroles using a rubber pipe (silicone tube), and a titanium tube, and finally to calculate gas geothermometer temperatures and compare the results with the well temperatures. The main conclusions are the following:

- Fumaroles samples were collected in Krafla and Theistareykir using a long, wide Ti-pipe and a short silicon-rubber pipe. Analytical results do not indicate that the sampling technique affects the composition of the samples.

- The reservoir temperature was calculated using selected geothermometers. The geothermometers that were most often successful in predicting the reservoir temperatures were the H_2S and H_2 geothermometers from Arnórsson and Gunnlaugsson (1985). Five geothermometers never predicted temperatures within 15°C of the estimated temperature, including the H_2-CO_2 geothermometer from Nehring and D'Amore (1984), the CH_4-CO_2 thermometer from Giggenbach (1991) and the H_2S, H_2, and the CO_2-N_2 geothermometers from Arnórsson et al. (1998).

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