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GAS GEOTHERMOMETRY AND EQUILIBRIA IN ICELANDIC GEOTHERMAL SYSTEMS

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ABSTRACT

The gas geothermometer temperatures and gas equilibria in Icelandic geothermal systems were studied. Around 290 samples of fumarole vapour samples from six geothermal areas in Iceland, Geysir, Hveravellir, Hengill, Reykjanes, Krafla and Torfajökull, were considered. A large range of temperatures was often observed within a given geothermal system with temperatures ranging from <100 to >800°C. Based on the calculated temperatures it can be concluded that factors other than temperature dependent fluid-mineral equilibria must influence fumarole gas composition at surface, for instance magma gas flux, open system boiling and phase separation, vapour condensation, mixing and oxidation at shallow depth. Based on the observations made in this study it is concluded that gas geothermometery temperatures may in many cases not reflect subsurface reservoir fluid temperatures of geothermal system but rather the source(s) of the gases and secondary processes occurring upon fluid ascent to surface.

1. INTRODUCTION

1.1 Objective

Gas and solute geothermometry are commonly applied tools used in geothermal exploration to predict subsurface geothermal fluid temperatures. The objective of this study was to evaluate the reliability of such gas geothermometry from fumarole discharge using empirically and theoretically calibrated gas geothermometry formulas.

1.2 Gas geothermometry

Surface manifestations such as fumaroles are among the primary sources of gas from the deep geothermal fluid. Upon fluid ascent and depressurization boiling, geothermal vapour is produced, the vapour being enriched in volatile gases like CO_2, H_2S, H_2, CH_4, N_2 and Ar. The concentrations of these gases can be dominated by the source and/or processes occurring within the geothermal system. Among the major processes is interaction of the geothermal fluids with the host rock producing secondary alteration minerals. It has been demonstrated that fluid composition is commonly controlled by close equilibrium between the fluids and the secondary alteration minerals. At reservoir conditions, the primary variable affecting the fluid-mineral equilibrium is temperature (e.g., Giggenbach 1980; Arnórsson et al., 1983). It follows that fluid gas composition may reflect the temperature of the geothermal fluids. This is the basics behind any gas geothermometer.

Due to processes upon fluid ascent, including boiling, degassing and phase separation, the fumarole gas compositions may not reflect the subsurface gas concentrations. In order to correct for such processes, boiling needs to be taken into account (e.g., Arnórsson and Gunnlaugsson, 1985). The assumption made when applying gas geothermometry are many and include:

(i) That the gas composition reflects the fluid-mineral equilibrium at reservoir temperatures.
(ii) That the system is thermodynamically closed, i.e. there is no loss of gas by mineral formation, phase separation upon boiling, vapour condensation etc.
(iii) There is no mixing with colder shallower aquifers.

Geothermal systems are open natural systems, and many of these assumptions may not be valid and thus the application of gas geothermometers. In addition, the gas concentrations may be controlled by the source(s) of gases rather than fluid-rock interaction, this being often the case for CO_2 for example (Stefánsson et al., 2017).

Gas geothermometry has been primarily developed in two ways:

(i) Calibration or fitting data on gas concentrations in vapour phase for two-phase wells discharges where the reservoir temperatures are known (Arnórsson and Gunnlaugsson, 1985); hereafter termed empirical gas geothermometers.
(ii) Calculation of gas-mineral equilibria for given reactions (Arnórsson et al., 1998); hereafter termed theoretical gas geothermometers.

The former relies on data of natural fluid composition and downhole temperature measurements, whereas the latter relies on thermodynamic properties of gases and minerals. In this report, the two have been compared to establish the reliability of gas geothermometry.

About 290 samples of vapour fumaroles from six high temperature geothermal area of Iceland were considered. The areas are Reykjanes, Torfajökull, Geysir, Hveravellir, Hengill, and Krafla. For these samples, various gas geothermometry temperatures were calculated and compared. Gas geothermometers applied included single gas geothermometry (CO_2, H_2S and H_2) and gas ratio geothermometry (CO_2, H_2, H_2S, N_2, Ar) both empirical and theoretical gas geothermometers applicable to Icelandic geothermal systems.

2. GEOLOGICAL AND GEOTHERMAL SETTING

2.1 Geology

Iceland is a geologically young country located in the North Atlantic on the boundary between the Eurasian and the North American plates. The regional geology of Iceland is the result of both extension and migration of the Mid-Atlantic divergent plate boundary relative to the Iceland mantle plume. The plate boundary is migrating westwards relative to the mantle plume, causing the volcanic zones in Iceland to shift eastwards (e.g., Bjarnason, 2008). Recent volcanic activity is most intensive where these extensional zones cut across the plate boundary.

2.2 Geothermal activity and utilization

Geothermal activity in Iceland has been classified into low- and high-temperature systems (Bödvarsson, 1961; Fridleifsson, 1979). Most of the high-temperature geothermal systems are located in central parts of the belts of active volcanism and rifting. In the Eastern and Northern Volcanic Zones, the high-temperature geothermal systems are typically associated with volcanic complexes. In the Western Zone, between Langjökull and Lake Thingvallavatn, no high-temperature systems are present, whereas, between Lake Thingvallavatn and the Reykjanes Peninsula, there are several high-temperature systems. Low-temperature geothermal activity is widespread in the Quaternary and Tertiary formations of Iceland. The low-temperature activity is frequently associated with active fractures and faults. Some systems are located within the active fissure swarms that run into older formations, whereas others are placed in the crust where the build-up of stress by plate movements leads to deformation and fracturing (e.g., Arnórsson, 1995) (Figure 1).

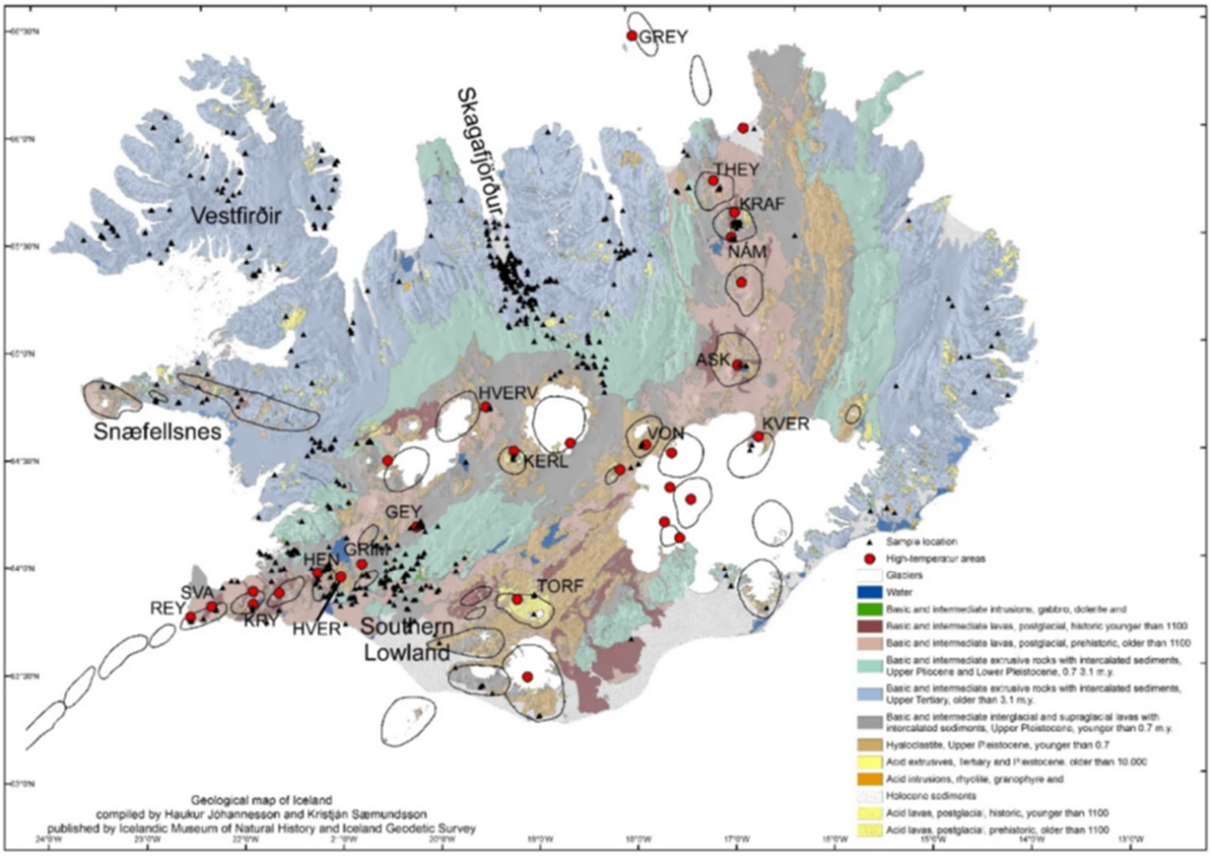

FIGURE 1: Geology and geothermal activity in Iceland and location of fluids in the GeoFluid database (Stefánsson et al., 2016a)

Geothermal system with temperature ≤150°C at 1000 m depth are defined as low temperature geothermal systems whereas systems with temperature of ≥200°C at 1000 m depth are termed high temperature geothermal systems. High temperature geothermal systems are distinguished by tectonic and magmatic settings. In Iceland, they can be divided in to three types of systems, such as systems occurring in a shallow intrusive complex heat source within calderas like in Krafla and Torfajökull, systems situated at the central volcanic complex of the fissure swarms such as in Nesjavellir, Hveravellir, Námafjall and Hengill, and finally systems with dyke swarms as intrusive heat source such as in Svartsengi, Eldvörp and Reykjanes (Arnórsson, 1995). Low temperature geothermal systems are located in Quaternary and Tertiary formations of the vicinity belts of the active rifting and volcanism in Iceland. Low temperature systems emerged where permeability is perpendicular to the topographic contour (Fridleifsson, 1979). Hydraulic gradient moves water from high lands to low lands through permeable underground rocks. Starting from the early twentieth century the low temperature geothermal areas in Iceland have been used in different ways. Currently they are mostly used for space heating, swimming pools, snow melting, industrial applications such as (drying, evaporation, washing, refrigeration and milk pasteurization), green house and fish farming. The total energy estimated from the direct uses annually is about 26,700 TJ (Ragnarsson, 2015). The high temperature geothermal system have been used to generate electricity as the most important source of energy next to hydro in Iceland. The total installed capacity in 2013 is 660 MWe and the annual generation in 2012 was 5,210 GWh, which is 30% of the total produced in the country (Ragnarsson, 2015).

2.3 Geothermal fluid chemistry

Icelandic thermal fluids are of meteoric and seawater origin or a mixture of the two, with temperatures between ~10 to ~450°C, pH of <2 to >10 and Cl concentrations of <1 to >20,000 ppm (Kaasalainen and Stefánsson, 2012; Ármannsson, 2015; Kaasalainen et al., 2015; Stefánsson et al., 2017). They have been divided into two groups: primary and secondary type fluids (Arnórsson et al., 2006). Primary fluids, sometimes referred to as reservoir fluids, are those reaching the deepest level within the geothermal system. With ascent to the surface, they can undergo chemical and physical changes leading to the formation of secondary geothermal fluids.

Wells over 2500 m deep, have been drilled into many of the geothermal systems in Iceland, thus allowing direct access to the reservoir fluid to study its chemical characteristics. Based on such well data, the primary fluids typically have close to a neutral pH value, with Na, Cl, S, C and Si being the dominant elements. The chemical composition of secondary fluids is much more variable. Processes like depressurization boiling, condensation and mixing may alter their composition from the reservoir to the surface. The boiled liquid that is typically discharged by hot springs is usually slightly enriched in non-volatile element concentrations and depleted in volatile element concentrations, such as CO_2 and H_2S, relative to the primary fluids. As the fluids have lost their main acids, their pH is typically alkaline. In contrast, the vapour phase formed upon boiling that is typically discharged at the surface by fumaroles is enriched in volatiles, including CO_2, H_2S, H_2, CH_4, N_2 and Ar relative to the boiled water and primary fluids. The vapour may also mix and condense with non-thermal water at shallow depths as well as surface steam-heated water. It follows that secondary fluids may have much more variable chemical composition relative to the primary fluids.

3. METHODOLOGY

3.1 The GeoFluid database

The current study relies on the newly published dataset on geothermal liquid water and vapour composition of Icelandic geothermal fluids. The complete database is named GeoFluids. It is divided into three parts (spreadsheets): (1) fumarole samples (GeoGas), (2) two-phase well samples (Two-Phase Wells) and (3) single-phase liquid samples (ThermalWater). The full dataset is published in Stefánsson et al. (2016a). In this study the composition of fumarole discharges was used, i.e. part of the GeoGas dataset. The sources of data are various and include reports, MSc and PhD theses, and published scientific journal articles. In many cases, there are multiple sources for a given sample (for details see Stefánsson et al., 2016a). The GeoGas dataset consists of around 800 samples, thereof around 290 samples were considered in this study.

For fumaroles, the common gases analysed include H_2O, CO_2, H_2S, H_2, CH_4, N_2 and Ar, whereas He, CO, NH_3 and light hydrocarbons (C_{2+}) other than CH_4 have not commonly been determined. Samples for SO_2 determination have rarely been collected, because of the low sampling temperatures of fumaroles (~100°C) and the non-magmatic reservoir temperatures (<350°C) of geothermal systems in

Iceland in general. The majority of the fumarole vapour samples have been collected in a similar manner. Plastic funnels have been placed over or a metal tube inserted into the vapour outlet and a gas bottle connected to the vapour stream using a silicone tube. The gas bottle ranged in volume from 50-250 mL and were evacuated prior to sampling and contained ~10mL of 50% KOH per 100 ml. The non-condensable gases, CO_2 and H_2S, were then analysed using modified alkalinity titration (Stefánsson et al., 2007) and Hg-acetate precipitation titration with dithizone as an indicator, respectively (Arnórsson et al., 2006). The non-condensable gases (H_2, CH_4, N_2 and Ar) were analysed using gas chromatography and the H_2O determined by gravimetry and mass balance.

3.2 Gas geothermometers.

The gas geothermometry formulas applied in this report have been previously published by Arnórsson and Gunnlaugsson (1985) and Arnórsson et al. (1998). The ones that were used have all been corrected for adiabatic boiling to 100°C. Two types of geothermometers were applied, empirical gas geothermometers and theoretical gas geothermometers. The gas geothermometers used and their formulas are given in Table 1. They include geothermometers involving single gas concentrations (CO_2, H_2S and H_2) and based on gas ratios (CO_2/N_2, CO_2/H_2, H_2S/H_2, H_2S/Ar, H_2/Ar).

TABLE 1: Geothermometry temperatures to be used for steam collected at 100°C and 1 bar

Reaction	Gas	Temperature function	Note	Ref.
1	CO_2	$-44.1+269.25Q-76.88Q^2+9.52Q^3$	Valid for all waters	Arnórsson and Gunnlaugsson (1985)
2	CO_2	$121.8+72.012Q-11.068Q^2+4.724Q^3$	Valid for all waters	Arnórsson et al. (1998)
3	H_2S	$246.7+44.81Q$	All waters >300°C and when Cl>500 ppm	Arnórsson et al. (1998)
4	H_2S	$173.2+65.04Q$	All waters <200°C and at 200-300°C when Cl<500ppm	Arnórsson et al. (1998)
5	H_2S	$173.2+65.04Q$	All waters <200°C and 200-300°C when Cl < 500ppm	Arnórsson and Gunnlaugsson (1985)
6	H_2S	$117.6+66.152Q+4.811Q^2$	Valid for all waters	Arnórsson et al. (1998)
7	H_2	$227.1+56.168Q+5.836Q^2+6.630Q^3$	Valid for all waters	Arnórsson et al. (1998)
8	H_2	$277.2+20.99Q$	All water > 300°c and 200-300°C when Cl > 500ppm	Arnórsson and Gunnlaugsson (1985)
9	H_2	$212.2+38.59Q$	All waters < 200°C and 200-300°C when Cl < 500ppm	Arnórsson and Gunnlaugsson (1985)
10	H_2S/H_2	$304.1-39.48Q$	All water > 300°C and 200-300°C when Cl >500ppm	Arnórsson and Gunnlaugsson (1985)
11	CO_2/H_2	$341.7-28.57Q$	All water > 300°c and 200-300°C when Cl > 500ppm	Arnórsson and Gunnlaugsson (1985)
12	CO_2/H_2	$311.7-66.72Q$	All waters < 200°C and 200-300°C when Cl < 500ppm	Arnórsson and Gunnlaugsson (1985)
13	CO_2/N_2	$173.2+48.751Q+7.599Q^2+1.739Q^3$	Valid for all waters	Arnórsson et al. (1998)
14	H_2S/Ar	$137.6+42.265Q+4.108Q^2$	Valid for all waters	Arnórsson et al. (1998)
15	H_2/Ar	$170+43.260Q+0.640Q^2$	Valid for all waters	Arnórsson et al. (1998)

4. RESULTS AND DISCUSSION

4.1 Gas composition and source(s) of gases

The gas chemistry of geothermal vapour from various geothermal systems in Iceland has recently been summarised and reviewed (Stefánsson, 2017). Vapour samples in Iceland are dominated by H_2O, accounting for 62-100 mol% of the gas and generally >98 mol%. The other gases of importance include CO_2, H_2S, H_2, CH_4, N_2 and Ar. Sometimes considerable O_2 is also detected, this is considered to be caused by air contamination. For the six geothermal areas considered in this report, the gas concentrations were: CO_2 ~6-13500 mmol/kg, H_2S ~0.1-150 mmol/kg, H_2 ~0.002-360 mmol/kg, CH_4 ~0.003-20 mmol/kg, O_2 ~0.001-4000 mmol/kg, N_2 ~0.001-17200 mmol/kg and Ar ~0.01-16 mmol/kg (Table 2). Of those, CO_2, H_2S, H_2 and CH_4 are reactive whereas N_2 and Ar are non-reactive.

TABLE 2: Chemical composition of selected samples of fumarole vapour considered in this report

#	Date	Area	Site	CO_2	H_2S	H_2	CH_4	O_2	N_2	Ar
	3.6.1982	Geysir area	Théttihver	129	0.945	0.002		0.1	124	0.019
1982-0008	3.6.1982	Geysir area	Geysir	190	0.372	0.018		5.41	28.3	0.590
1982-0011	5.6.1982	Hengill	Hveradalir	269	27.7	39.2	1.11		3.57	0.249
1982-0019	9.6.1982	Hengill	Gufudalur	124	6.32	1.04	0.197	0.013	5.56	0.216
1982-0031	11.6.1982	Hengill	Nesjavellir	219	33.0	29.1	0.826	0.020	5.35	0.146
1982-0043	16.6.1982	Hengill	Fremstidalur	184	9.81	25.8	0.728	0.031	2.13	0.122
1982-0060	21.6.1982	Hengill	Graendalur	170	8.27	2.03	0.042	0.082	2.26	0.068
1982-0064	21.6.1982	Hengill	Ölkelduháls	547	13.7	11.7	0.954	1.42	18.2	0.385
2014-0020	20.5.2014	Hengill	Hveragerdi, Stigagil	87.6	2.39	0.816	0.050	0.127	3.64	0.071
2014-0021	20.5.2014	Hengill	Hellisheidi	307	38.1	9.92	1.04	0.245	5.86	0.089
1982-0101	6.7.1982	Hveravellir	Strýtuhraun	58.2	2.00	0.153	0.076	0.126	3.71	0.066
1982-0103	6.7.1982	Hveravellir	Vid Braedrahver	46.1	1.95	0.048	0.039	0.67	9.24	0.118
1983-0007	1.1.1983	Krafla	Vítissvaedi	2310	62.1	19.2	0.024	0.624	7.10	0.120
1983-0019	29.7.1983	Krafla	Víti	2055	55.4	19.7	0.025	0.639	7.27	0.116
1984-0008	14.7.1984	Krafla	Sudurhlídar	1549	39.7	24.3	0.366	2.20	9.88	
1985-0024	5.8.1985	Krafla	Leirhnjúkur	2570	4.76	5.29	0.374	0.398	6.36	0.268
1995-0015	30.9.1995	Krafla	Leirhnjúkur	70.0	5.47	2.06	0.520	0.060	3.84	0.091
2010-0001	10.8.2010	Krafla	Vítissvaedi	2075	79.1	1.84	3.72	0.373	15.3	0.297
2010-0005	11.8.2010	Krafla	Vesturhlídar	2231	68.9	16.1	0.376	0.482	4.08	0.089
2013-0001	20.8.2013	Krafla	Leirhnjúkur	120	13.5	16.6	1.32	0.004	2.48	0.078
2013-0002	20.8.2013	Krafla	Tvíburavötn	549	53.7	22.5	1.07	0.004	2.81	0.087
2013-0003	20.8.2013	Krafla	Graenagil	720	46.4	20.7	1.07	0.005	0.900	0.044
1950-0003	6.6.1950	Reykjanes	Reykjaneshverir	115	2.08	0.83				
1982-0065	24.6.1982	Reykjanes	Holuhver	130	3.06	0.50	0.079	2.41	15.8	0.308
1982-0078	29.6.1982	Torfajökull	Brennisteinsalda	138	11.41	16.6	0.349	0.001	1.15	0.097
1995-0010	19.9.1995	Torfajökull	Sunnan Hrafntinnuskers		1.91	12.0	0.075	24.9	2.49	0.295
1997-0002	10.9.1997	Torfajökull	Vid Stórahver	43.7	4.53	4.28	0.062	0.191	0.004	0.005
1997-0003	11.9.1997	Torfajökull	Sudvestan Hrafntinnuskers	370	21.1	41.8	0.190	0.576		0.011
1997-0004	12.9.1997	Torfajökull	Vestan Torfajökuls	1797	8.50	12.5	0.310	1.62		0.025
1997-0005	12.9.1997	Torfajökull	Vestan Torfajökuls	2669	9.69	1.62	0.409	2.52	0.099	0.041
1997-0006	13.9.1997	Torfajökull	Háuhverir	199	17.2	12.9	0.223	7.15	1.66	0.088
2014-0058	1.8.2014	Torfajökull	Vondugil	40.3	3.38	0.354	0.144	1.16	8.45	0.134
2014-0059	1.8.2014	Torfajökull	Vondugil	43.8	3.65	0.386	0.157	1.31	8.49	0.148
2014-0062	1.8.2014	Torfajökull	Brennisteinsalda	264	7.78	26.1	0.402	0.242	2.31	0.028
2014-0063	1.8.2014	Torfajökull	Brennisteinsalda	160	10.4	15.0	0.332	0.439	3.44	0.037

The relationship between the major reactive gases, CO_2, H_2S and H_2, are shown in Figure 2. Carbon dioxide is the predominant gas in all cases followed by H_2S and H_2. The relative rations of CO_2-H_2S-H_2 is usually similar for all systems studied, except that H_2 is observed at low concentrations at Geysir and Hveravellir.

The relationship between the reactive gases, CO_2, H_2S and H_2, and the non-reactive gases, N_2 and Ar, are shown in Figure 3. Nitrogen and Ar are predominantly originated from the atmosphere with similar ratios as in air and air saturated water. In contrast, the geothermal vapours are progressively enriched in CO_2, H_2S and H_2 suggesting an additional source(s) of these gases, considered to be melt degassing and fluid-rock interaction (Stefánsson, 2017; Stefánsson et al., 2017).

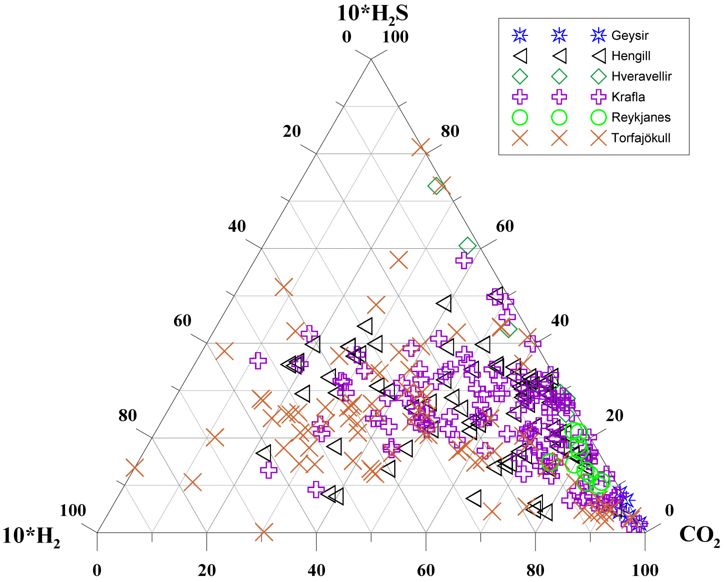

FIGURE 2: The relationship for the major reactive gases (CO_2, H_2S and H_2) in vapour

4.2 Gas geothermometry temperatures

The results of the calculated gas geothermometer temperatures are shown in Figures 4-9 and summarized in Table 3.

4.2.1 Geysir area

Gas geothermometer temperatures for the Geysir area are shown in Figure 4. The calculated temperatures ranges from ~50 to 325°C, i.e. over a considerable range. The temperatures calculated based on CO_2 concentrations show systematically the highest values whereas temperatures calculated based on H_2S and CO_2/H_2 show the lowest values. For comparison, the estimated reservoir temperatures at Geysir area using solute geothermometers is around 260°C (Stefánsson et al., 2017).

TABLE 3: Summary of calculated gas geothermometry temperatures

	Average	**Temp. range (°C)**
Geysir		
tCO_2	284	255 - 335
tH_2S	127	82 - 182
tH_2	159	108 - 192
Hengill		
tCO_2	294	234 - 440
tH_2S	240	82 - 328
tH_2	270	161 - 390
Reykjanes		
tCO_2	303	253 - 448
tH_2S	206	120 - 294
tH_2	250	183 - 290
Hveravellir		
tCO_2	229	143 - 272
tH_2S	166	109 - 226
tH_2	151	82 - 192
Krafla		
tCO_2	394	228 - 832
tH_2S	272	51 - 344
tH_2	288	202 - 507
Torfajökull		
tCO_2	316	128 - 747
tH_2S	244	95 - 340
tH_2	288	136 - 519

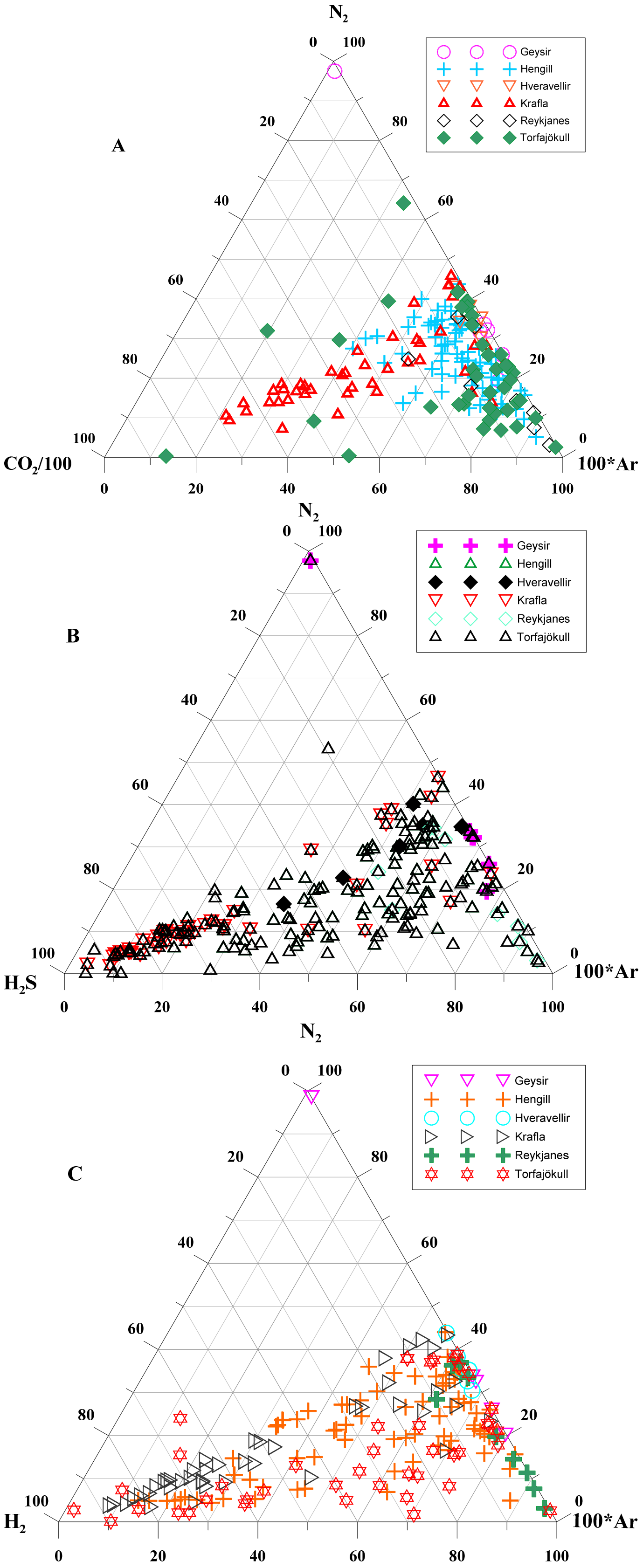

FIGURE 3: The relationship between N_2 and Ar and the reactive gases CO_2, H_2S and H_2

4.2.2 Hveravellir

Gas geothemometer temperatures for the Hveravellir area are shown in Figure 5. Similar trends are observed as for the Geysir area, i.e. the temperatures calculated based on CO_2 concentrations show systematically the highest values whereas temperatures calculated based on H_2S and CO_2/H_2 show the lowest values. For comparison, the estimated reservoir temperatures at Hveravellir area using solute geothermometers is around 280°C (Stefánsson et al., 2017).

4.2.3 Hengill area

Gas geothermometer temperatures for the Hengill area are shown in Figure 6. Very large range in calculated temperature is observed, from ~100°C to ~450°C. The geothermometer temperatures calculated using the CO_2 and H_2 geothermometers show the highest values whereas H_2S geothermometers show the lowest. In addition, large scatter is observed for most of the geothermometers, in the range of 100 to 250°C. In Hengill, there are several geothermal systems including Hellisheidi, Nesjavellir and Hveragerdi. The reservoir temperatures for these areas varies and is 200-380°C (Stefánsson et al., 2017).

4.2.4 Reykjanes area

Gas geothermometer temperatures for the Reykjanes area are shown in Figure 7. At Reykjanes the fluids originate from seawater with Cl concentrations of around 20,000 ppm. For such saline systems, special geothermometers have been developed (Arnórsson and Gunnlaugsson, 1985). The gas geothermometer temperatures at Reykjanes range from around 125 to 450°C with the CO_2 geothermometers being the highest and the H_2S the lowest. The measured reservoir temperatures at Reykjanes are 260-345°C (Stefánsson et al., 2017).

4.2.5 Krafla area

Gas geothermometer temperatures for the Krafla area are shown in Figure 8. A large range of temperatures is observed, around 50-800°C. Again, the highest temperatures were calculated from the CO_2 gas concentrations and the lowest for the H_2S and CO_2/H_2 gas concentrations and gas ratios. Moreover, for many of the gas geothermometer there is a large range of values observed, up to 500°C. The measured reservoir temperatures at Krafla are 200-440°C (Stefánsson et al., 2017).

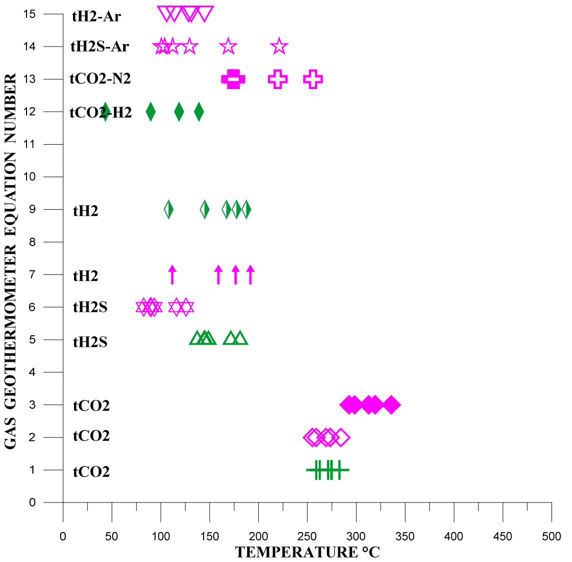

FIGURE 4: Geysir (temp. vs. reaction equation)

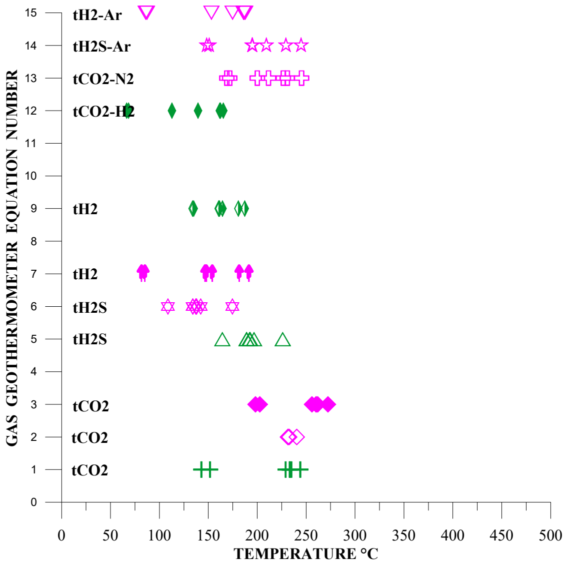

FIGURE 5: Hveravellir (temp. vs. reaction equation)

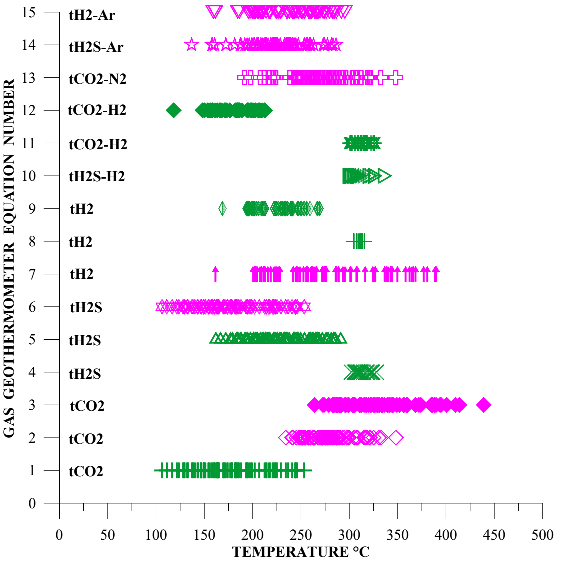

FIGURE 6: Hengill (temp. vs. reaction equation)

4.2.6 Torfajökull area

Gas geothermometer temperatures for the Torfajökull area are shown in Figure 9. A large range of temperatures are observed, 100-750°C. Very similar trends are observed at Torfajökull and Krafla, with the highest temperatures calculated from the CO_2 gas concentrations and the lowest for the H_2S and CO_2/H_2 gas concentrations and gas ratios. The estimated reservoir temperatures at Torfajökull area are 260-300°C (Stefánsson et al., 2017).

4.3 Application of gas geothermometry for estimating subsurface reservoir temperatures

Based on the calculated geothermometery temperatures for various high temperature geothermal systems in Iceland it can be concluded that more than temperature dependent fluid-mineral equilibria must influence fumarole gas composition at surface. Potential processes that may influence the gas composition include:

(i) Gas flux and source(s) of the gases (Stefánsson et al., 2016c)
(ii) Open system boiling and phase segregation (e.g. Scott et al., 2014)
(iii) Vapour condensation, mixing and oxidation at shallow depth (Stefánsson et al., 2016b)

The various gases may be effected by these factors to varying degrees. For example, it has been suggested that CO_2 concentrations in geothermal fluids is influenced by fluid-rock interaction (rock leaching and secondary mineral formation) as well as deep mantle and shallow magma intrusion degassing (Stefánsson et al., 2016c). In fact, the flux of CO_2 from the magma source can overwrite the fluid-rock interaction equilibria, leading to the conclusion that in many cases CO_2 may not be controlled by the temperature dependent fluid-mineral equilibria but rather magma degassing flux. This would result in excessive CO_2 concentrations as observed in many cases, for example at Torfajökull and Krafla. In contrast, H_2S and H_2 are considered to originate upon rock leaching and fluid-rock interaction (Stefánsson, 2017). For these elements, their gas concentrations may therefore reflect the reservoir temperatures, at least in some cases. However, H_2 has very low solubility in water and is degassed upon initial

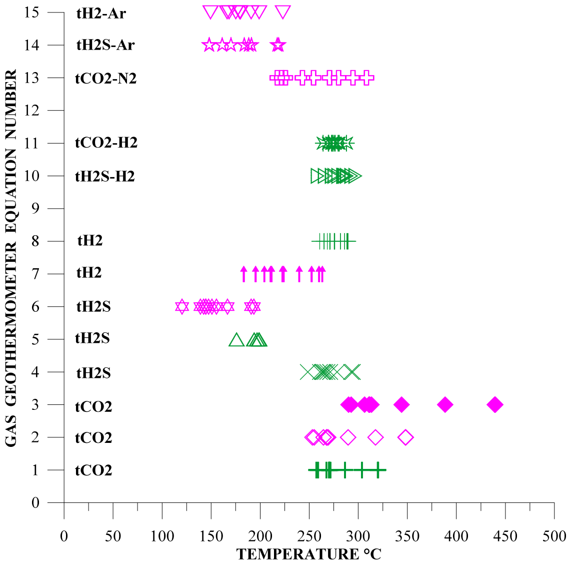

FIGURE 7: Reykjanes (temp. vs. reaction equation)

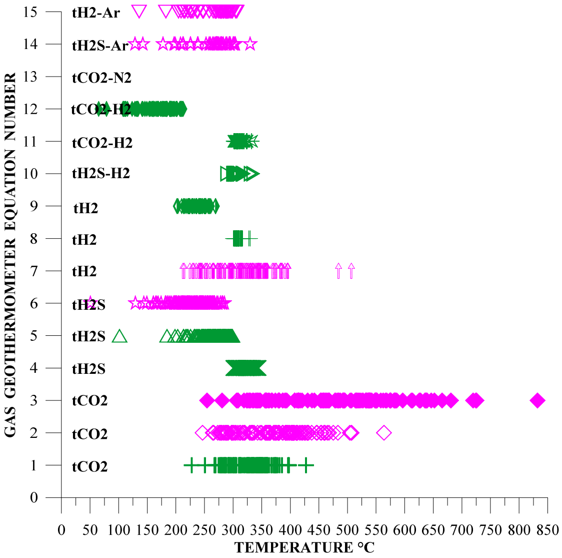

FIGURE 8: Krafla (temp. vs. reaction equation)

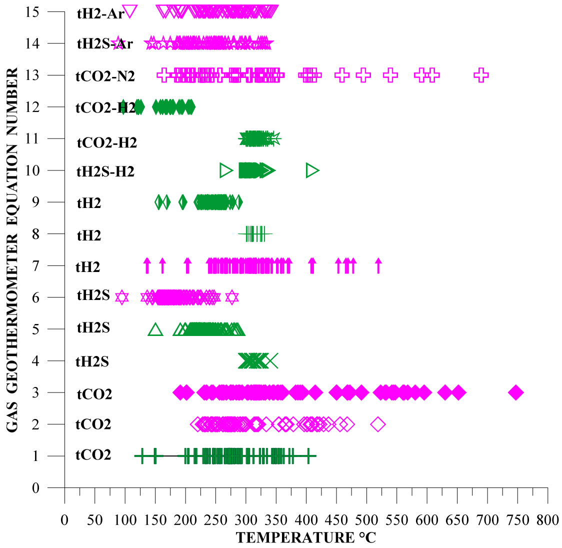

FIGURE 9: Torfajökull (temp. vs. reaction equation)

boiling. Therefore, open system boiling and phase segregation can lead to excess H_2 concentrations in the vapour phase (Scott et al., 2014). In contrast, H_2S is very sensitive to vapour condensation and mixing with oxygenated water as H_2S may oxidise to H_2SO_4 forming steam heated acid water commonly observed at the surface of high temperature geothermal systems. Such a process would result in low H_2S geothermometer temperatures as observed for example at Torfajökull, Krafla, Hengill and Reykjanes.

5. CONCLUSION

The gas geothermometer temperatures were calculated for around 290 fumarole vapour samples from six geothermal areas in Iceland, Geysir, Hveravellir, Hengill, Reykjanes, Krafla and Torfajökull. Large range of temperatures were often observed or from 50 to over 800°C. Based on the calculated temperatures it can be concluded that factors other than temperature dependent fluid-mineral equilibria must also influence fumarole gas composition at surface. Potential processes that may influence the gas composition include: high magma gas flux, for example in the case of CO_2 (Stefánsson et al., 2016), open system boiling and phase segregation, such as in the case of H_2 (Scott et al., 2014) and vapour condensation, mixing and oxidation at shallow depth, such as in the case of H_2S (Stefánsson et al., 2016). Based on the observations made in this study it is summarized that gas geothermometery temperatures may in many cases not reflect subsurface reservoir fluid temperatures of geothermal system.

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