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Chemical Characteristics of Thermal Fluids from Stykkishólmur, Iceland

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ABSTRACT

The low-temperature geothermal waters that feed the district heating system in Stykkishólmur, W-Iceland, are found in volcanic rocks. The main production aquifer is related to a fracture in a gabbroic intrusion. The high degree of alteration of the reservoir rocks indicates much higher temperatures than presently observed (87°C). Geological investigations reveal that the well is situated within an extinct central volcano. The chemical and isotopic composition of the hot water from the production well in Stykkishólmur differs significantly from that of other low-temperature areas in Iceland. The geothermal water is brackish, calcium is the dominant cation, and the water type is Cl-Ca-Na. The isotopic composition of the thermal water indicates that it is not strictly a mixture of seawater and present-day freshwater. The results from geothermometry equations indicate that chalcedony controls the silica concentration in the reservoir. Chemical equilibrium calculations for geothermal water in Stykkishólmur were performed with the speciation programs SOLVEQ, WATCH, and PHREEQCI. They show the distribution of aqueous species in the water, as well as saturation indices for minerals occurring in the reservoir. Graphs of log (Q/K) vs. temperature indicate that some alteration minerals found in the well are close to equilibrium with the water at the measured temperature. Chalcedony and anhydrite, in particular, seem to be in full equilibrium.

1. INTRODUCTION

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

Temperature logging in shallow wells showed a geothermal gradient anomaly of up to 400°C/km (Figure 1). Based on this, it was decided to drill a production well. Well HO-01 has a depth of 855 m.

The main production aquifers are located at depths of 819 m (90% of the flowrate) and from 171 to 175 m (7% of the flowrate). Minor aquifers are also found, at depths of 262, 451, 778, 785, and 830 m. The aquifer at 171-175 m is a fracture within a basaltic layer, whereas the main aquifer is related to a fracture in a gabbroic intrusion (Figure 2). The temperature log shows the reservoir temperature of 86.4°C (Figure 1).

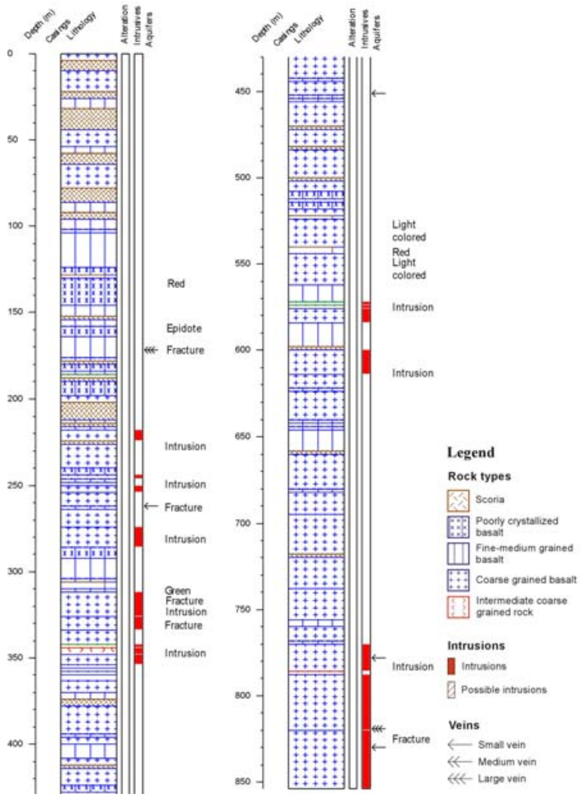

Figure 2: Lithological profile of well HO-01 (from Björnsson and Fridleifsson, 1996).

The reservoir rock consists primarily of coarse-grained basaltic units with thin layers of sediments, two of which could be acidic, and a number of mostly basaltic intrusions. From 780 to 855 m depth, i.e. to the bottom of the well, the rock consists of a gabbroic intrusion (Björnsson and Fridleifsson, 1996). Pyrite, mixed layer clays of smectite and chlorite, with chalcedony, quartz, and calcite are found from the surface to 150 m depth. At depths below 150 m, the high-temperature alteration minerals chlorite and epidote are found. Laumontite is found at all depths, and stilbite (with calcite) near the aquifers. The reservoir rock is altered to a high degree with epidote below 150 m depth, indicating an alteration temperature of approximately 250°C, and with amphibole below 300 m depth, which suggests an alteration temperature of ~ 300°C. The high-temperature alteration and intrusions indicate that the well is situated within an extinct central volcano (from Miocene time, >5 MY). It has been suggested (G.Ó. Fridleifsson, personal communication) that anhydrite might have formed minute grains within the aquifers, but more study of the drill-cuttings is needed to confirm this. This could explain the very high calcium content of the hot water produced from the well. The high degree of alteration of the reservoir rocks indicates much higher temperatures than presently observed. The aquifers in well HO-01 are all associated with fractures, and the last mineral to precipitate in all cases is stilbite.

2. CHEMICAL AND ISOTOPE COMPOSITION OF THE FLUIDS

Results of the chemical and isotope analyses of hot water samples from the production well in Stykkishólmur are presented in Table 1. These samples were taken in the years 1997–2002 using the standard procedure employed at Orkustofnun or ÍSOR (Ólafsson, 1988). The chemical and isotopic composition of the hot water from the production well in Stykkishólmur differs from that of other low-temperature areas in Iceland. The low-temperature waters in Iceland, described by Arnórsson (1995), usually are relatively low in dissolved solids (150-500 ppm), and sodium is always the dominant cation. The geothermal water from Stykkishólmur is brackish, with TDS above 5200 ppm, a chloride content of approximately 3000 ppm, and a temperature of 86.4°C. The water is very hard (2942 mg $CaCO_3$/l), and weakly alkaline with a pH of 8.34 at 18.6°C. Calcium is the dominant cation (~1200 ppm), and the water type is Cl-Ca-Na.

The $\delta^{18}O$–δD relationship in low-temperature geothermal waters in Iceland indicates that they are, for the most part, of meteoric origin (Arnórsson, 1995). Typically, they possess lower δD values (more negative) than the local precipitation. It is also considered that geothermal waters often consist of up to three components, local meteoric water, "ice-age" water, and seawater. Geothermal waters with temperatures of less than 50°C show very limited positive oxygen shift, whereas for hotter waters, the shift increases with temperature (Arnórsson et al., 1993).

Figure 3 shows the isotopic composition of hot waters from well HO-01 as well as that of local cold groundwaters. For comparison, the meteoric water line from Craig (1961) is also shown. The $\delta^{18}O$ and δD values for cold waters are close to the World Meteoric Water Line, with a slight shift towards less negative values, while for hot waters from Stykkishólmur the values lie above this line. These values seem to suggest an origin different from the present-day precipitation.

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

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

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

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

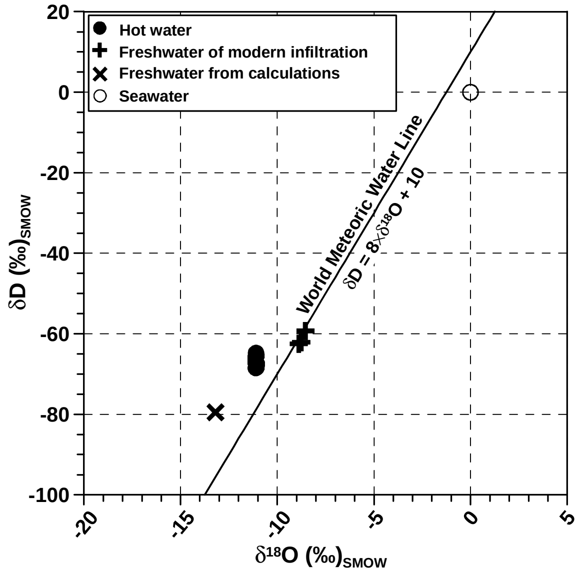

Figure 3: The relationship between $\delta^{18}O$ and δD values in the hot and cold water samples from the study area and in a freshwater from calculation.

In the hot water from Stykkishólmur, the $\delta^{18}O$ and δD mean values are -11.1 and -66.8, respectively, and in the seawater both are approximately 0. Hence, if the hot water is a mixture of seawater and freshwater, the $\delta^{18}O$ and δD values in the freshwater should be -13.21 and -79.5, respectively. The observed mean isotopic composition of the present-day freshwater is quite different, -8.9 and -62.5, respectively (Figure 3). Thus, it appears that water from the production well in Stykkishólmur cannot be strictly a mixture of present-day freshwater and seawater. The freshwater component is evidently a result of cold climate precipitation, with surprisingly large value of deuterium excess.

Balance calculations show that calcium excess in relation to 16% of seawater comes from the cation exchange of Mg^{2+} and Na^{+}.

Chloride and boron in Icelandic natural waters act essentially as incompatible (Arnórsson and Andrésdóttir, 1995). Their distribution in low-temperature geothermal systems in Iceland indicates three sources of supply (Arnórsson, 1995): 1) the atmosphere (seawater spray and aerosols); 2) the rock with which the water interacts; and 3) seawater that has infiltrated the bedrock. The Cl/B mass ratios of the cold water are close to that of seawater (4350), or slightly lower. With rising temperature, B and Cl concentrations increase to 0.05-1 and 10-100 ppm, respectively, and their ratios decrease towards that of the basaltic rock (Figure 4). Arnórsson and Andrésdóttir (1995) explain this relationship by approximately stoichiometric dissolution of Cl and B from the basaltic rock. In case of low-temperature waters containing relatively high concentrations of Cl, they consider mixing of seawater with geothermal meteoric water (Figure 4).

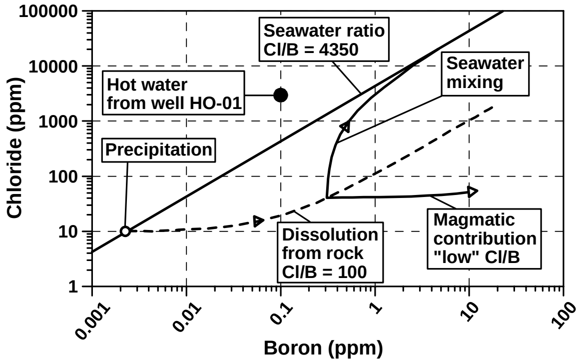

Figure 4: Schematic diagram illustrating Cl/B mass ratios and B and Cl concentrations in natural waters in Iceland affected by different processes (from Arnórsson and Andrésdóttir, 1995).

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

The Cl/Br mass ratio amounts to about 300, and is typical as for seawater.

In the Cl-SO_4-HCO_3 triangular diagram (Figure 5), data points are located near the Cl corner, close to the area marked “mature waters”. This plot is used as an initial classification scheme (anion classification) for geothermal water samples (Giggenbach and Goguel, 1989). It allows one to weed out waters that are not suitable for most ionic solute geothermometers, which “work” only if used with close to neutral waters containing chloride as the major anion (“mature waters”). The compositional area where ionic solute geothermometers may be applied with sufficient confidence is quite small and illustrates the need for this initial classification procedure.

3. ESTIMATION OF SUBSURFACE TEMPERATURE

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

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

Geothermometer	T_M	T_{Q1}	T_{Q2}	T_{Ch1}	T_{Ch2}
Range (°C)		25-250	25-900	0-250	
T (°C)	86.4	119.3	119.5	90.8	90.8

Sources of temperature equations for the silica geothermometers: T_M – measured temperature, T_{Q1} – Fournier (1977), T_{Q2} – Fournier and Potter (1982), T_{Ch1} – Fournier (1977), T_{Ch2} – Arnórsson et al. (1983)

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

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

Geothermometer	T_M	$T_{Na\text{-}K1}$	$T_{Na\text{-}K2}$	$T_{Na\text{-}K3}$	$T_{Na\text{-}K4}$
Range (°C)			25-250		0-350
T (°C)	86.4	110.7	62.9	126.0	95.7

Sources of temperature equations for the cation geothermometers: T_M – measured temperature, $T_{Na\text{-}K1}$ – Fournier (1979), $T_{Na\text{-}K2}$ – Arnórsson et al. (1983), $T_{Na\text{-}K3}$ – Giggenbach (1988), $T_{Na\text{-}K4}$ – Arnórsson (2000)

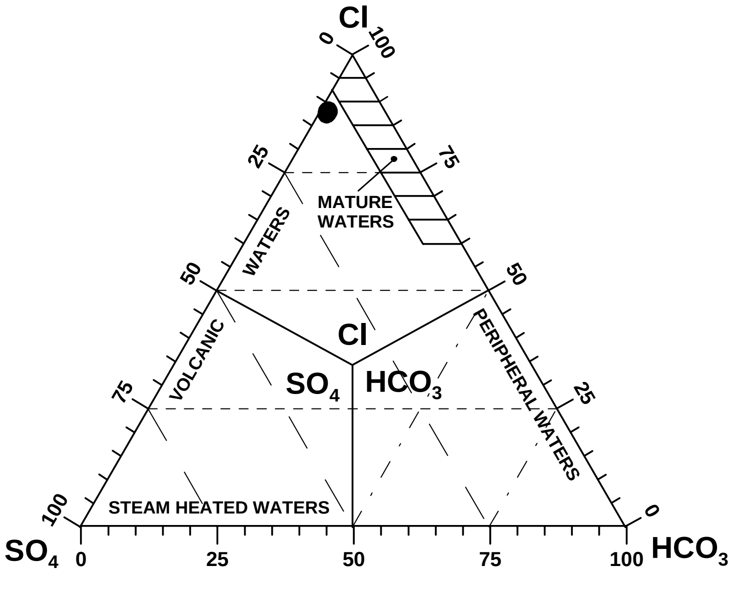

Figure 5: The Cl-SO_4-HCO_3 classification diagram for the hot water from well HO-01 in Stykkishólmur.

The Na-K-Mg diagram (Figure 6) shows the equilibrium state of the water from the production well. The diagram constructed using Giggenbach's Na-K equation (Figure 6A) shows that water is nearly fully equilibrated, but the temperature is too high. The diagram using Arnórsson's Na-K equation (Figure 6B) is more reliable, as it is constructed on the basis of the Na-K equation giving the temperature closer to the measured value (Table 3). Furthermore, it is derived from interpretation of Icelandic data.

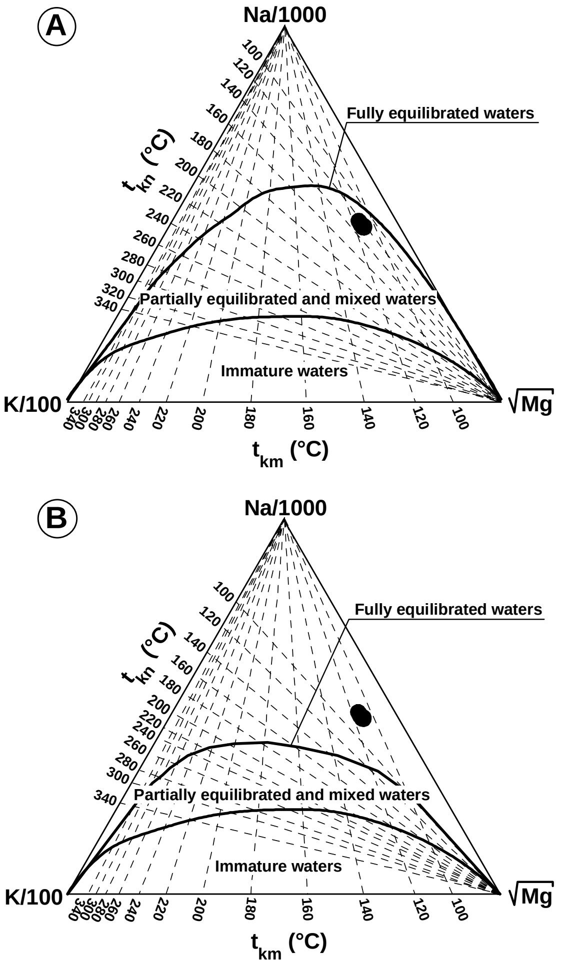

Figure 6: The Na-K-Mg diagrams for the hot water from well HO-01 in Stykkishólmur; Na-K geothermometry equations by: A) Giggenbach (1988); and B) Arnórsson (2000).

4. GEOCHEMICAL MODELLING OF FLUID-MINERAL EQUILIBRIUM

Chemical equilibrium calculations for a water sample from the production well in Stykkishólmur were performed using the speciation programs SOLVEQ (Reed, 1982; Reed and Spycher, 2001), WATCH (Arnórsson et al., 1982; Bjarnason, 1994), and PHREEQCI (Parkhurst and Appelo, 1999). These programs calculate aqueous speciation distribution in the water and saturation indices for minerals occurring in the reservoir. A water sample collected on November 8, 2001 was chosen for the calculations. The ionic balance and the mass balance are both very small for this sample (Table 1), indicating high quality of the sampling and chemical analysis.

The calculated species (Figure 7) show the possibility of forming more complex entities in the water than simple ions, assumed in traditional analysis. Each analysed component is generally formed in more than one species. Chloride species exist in the analysed water mainly as simple ions Cl^-, which constitutes more than 98% of the component molal concentration (Figures 7A). In the case of sulphate, however, a complex ion, $CaSO_4°$, accounts for about 40% of total component concentration (Figure 7B).

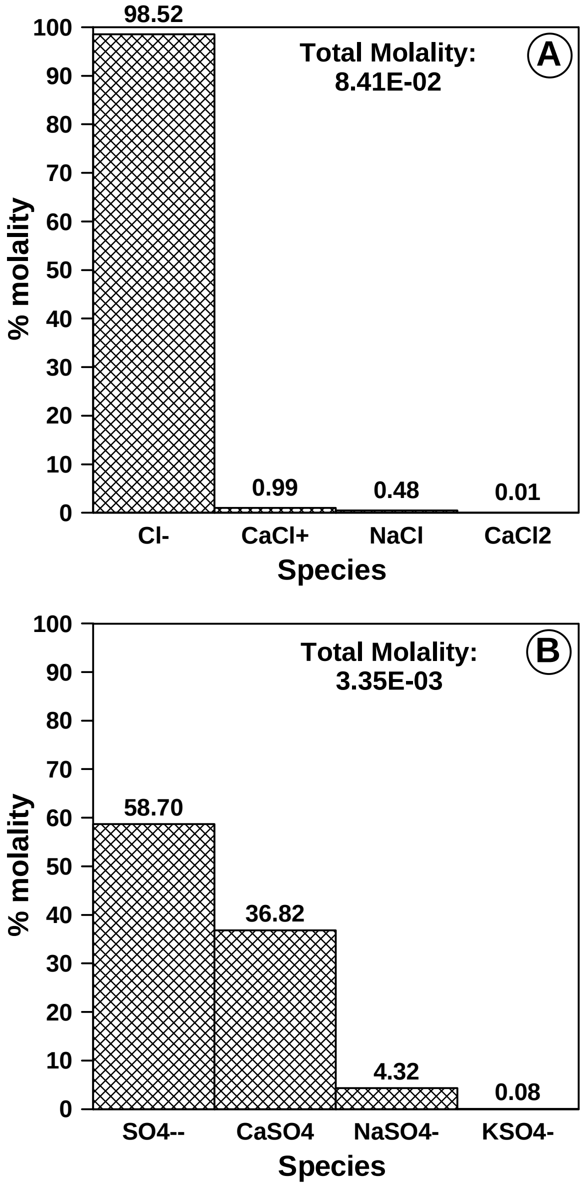

Figure 7: Species in the hot water from well HO-01 in Stykkishólmur, A) chloride; and B) sulphate; the distribution of species was calculated with SOLVEQ.

The log (Q/K) diagrams for the sample from well HO-01 show the state of equilibrium between geothermal water and minerals as a function of temperature (Figure 8). Computations using SOLVEQ, WATCH, and PHREEQCI, indicate that the water attains equilibrium with minerals over a range of temperatures rather than at one specific temperature. The three programs give slightly different results for this sample. This is not surprising, since the three programs use different thermodynamic databases.

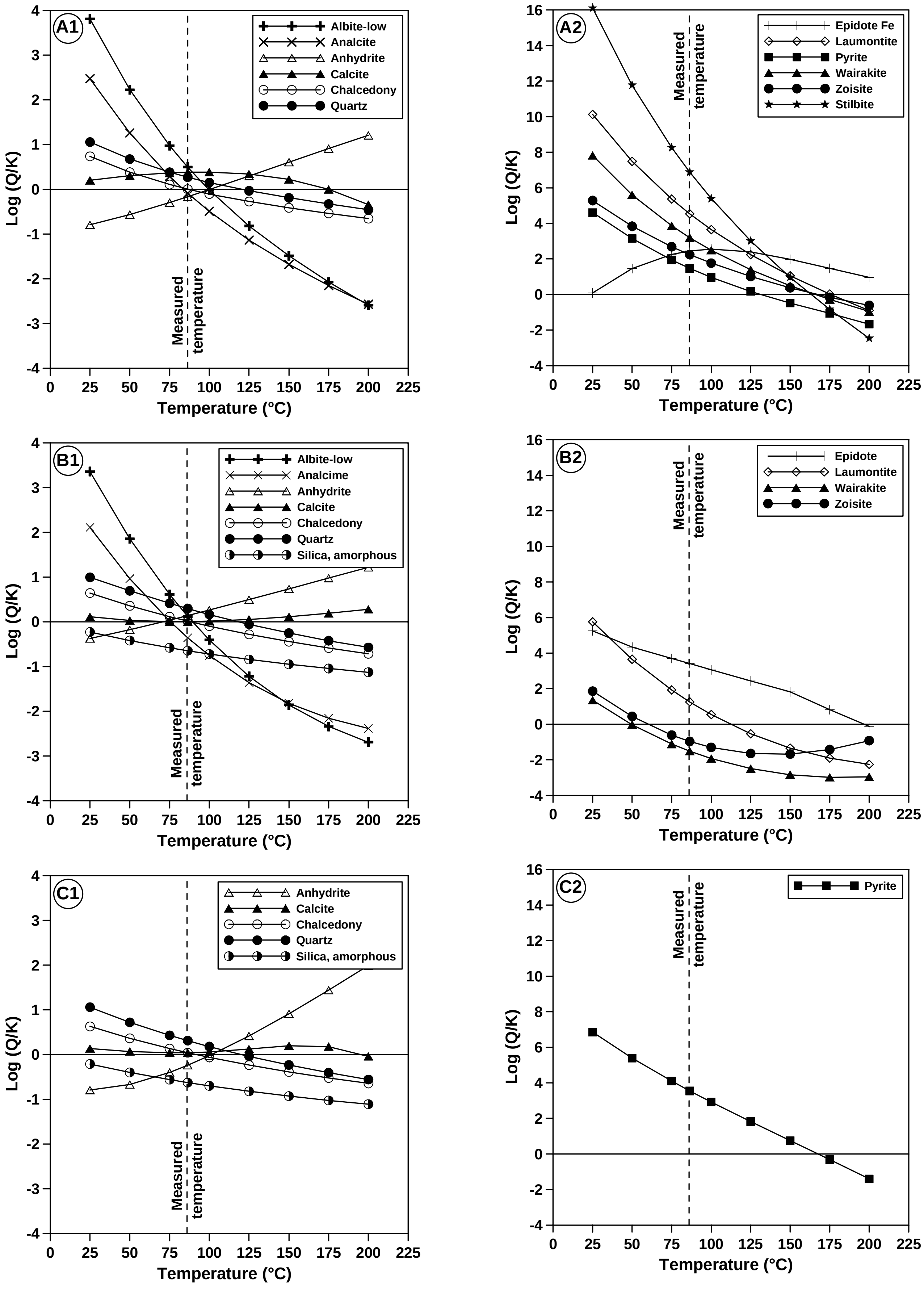

Figure 8: Mineral equilibrium diagrams for the hot water from well HO-01 in Stykkishólmur; the saturation index was calculated with: A) SOLVEQ; B) WATCH; and C) PHREEQCI.

In Figure 8, it can be seen that equilibrium lines for a group of minerals converge in some range close to the measured temperature. Chalcedony and anhydrite intersect the SI = 0 line close to the measured temperature (Figure 8A1, 8B1, and 8C1). The equilibrium temperatures for chalcedony and quartz are almost the same as the estimated temperatures obtained by chalcedony and quartz geothermometers, respectively. Other minerals, found in cuttings, show equilibrium temperatures in the range from 125 to 175°C (Figure 8A2). They are all supersaturated close to the measured temperature.

5. CHEMICAL MONITORING DURING PRODUCTION

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

Seven parameters are continuously monitored in the district heating system in Stykkishólmur. Information about the measured parameters can be found on the following web-site, in Icelandic only:

http://www.isor.is/eftirlit/stykkish1.shtml.

Figure 9 shows variations in conductivity, and chloride concentrations with time in the water discharged from production well HO-01. Changes during the first months of operation are due to breaks in discharge. In the years 1996-2002, conductivity decreased slightly from about 9000 to 8700 µS/cm. A similar variation is noticed for chloride concentrations, though with larger oscillations. It can be explained by the mixing of waters from the two main aquifers in the well, with probably slightly different compositions.

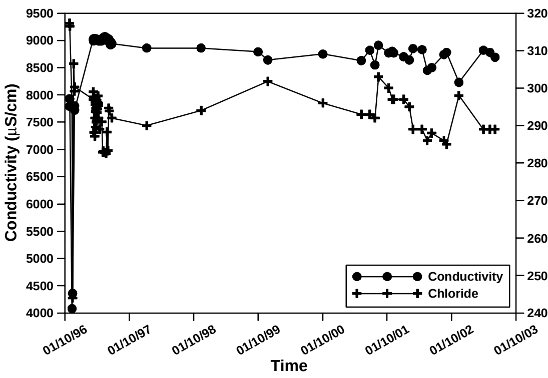

Figure 9: Changes in conductivity and chloride concentration with time in the water from well HO-01 in Stykkishólmur.

5. CONCLUSIONS

Geothermal water from the Stykkishólmur district heating system differs significantly from other low-temperature waters in Iceland. This water contains a high concentration of Cl, which suggests mixing of seawater with geothermal water of meteoric origin. The isotopic composition of the hot water from the production well indicates that this water is not strictly a mixture of seawater and present-day freshwater. The freshwater component is evidently a result of cold climate precipitation, with surprisingly large value of deuterium excess. The Cl/B mass ratio of the hot water is almost 30,000, so it is about seven times higher than that of seawater and a few hundred times higher than that of typical low-temperature waters in Iceland. It may be caused by the uptake of boron by clay minerals which are found in the reservoir.

The results from silica geothermometers for water from Stykkishólmur indicate that chalcedony controls the silica concentration in the reservoir. The temperatures obtained from chalcedony geothermometers are very close to the measured temperatures, 90.8 and 86.4°C, respectively. Temperatures calculated using Na-K equations deviate significantly from the measured temperature, only in one case giving a temperature close to that observed.

Chemical equilibrium calculations for geothermal water from the production well in Stykkishólmur, performed with the speciation programs SOLVEQ, WATCH, and PHREEQCI, give the aqueous speciation distribution in the water, as well as saturation indices for minerals occurring in the reservoir. There are some differences in results of log (Q/K) diagrams depending on which thermodynamic database was used. Some alteration minerals found in the well converge in a range of about 30°C around the measured temperature. In any case, the log (Q/K) diagram for chalcedony intersects the SI = 0 line at the measured temperature.

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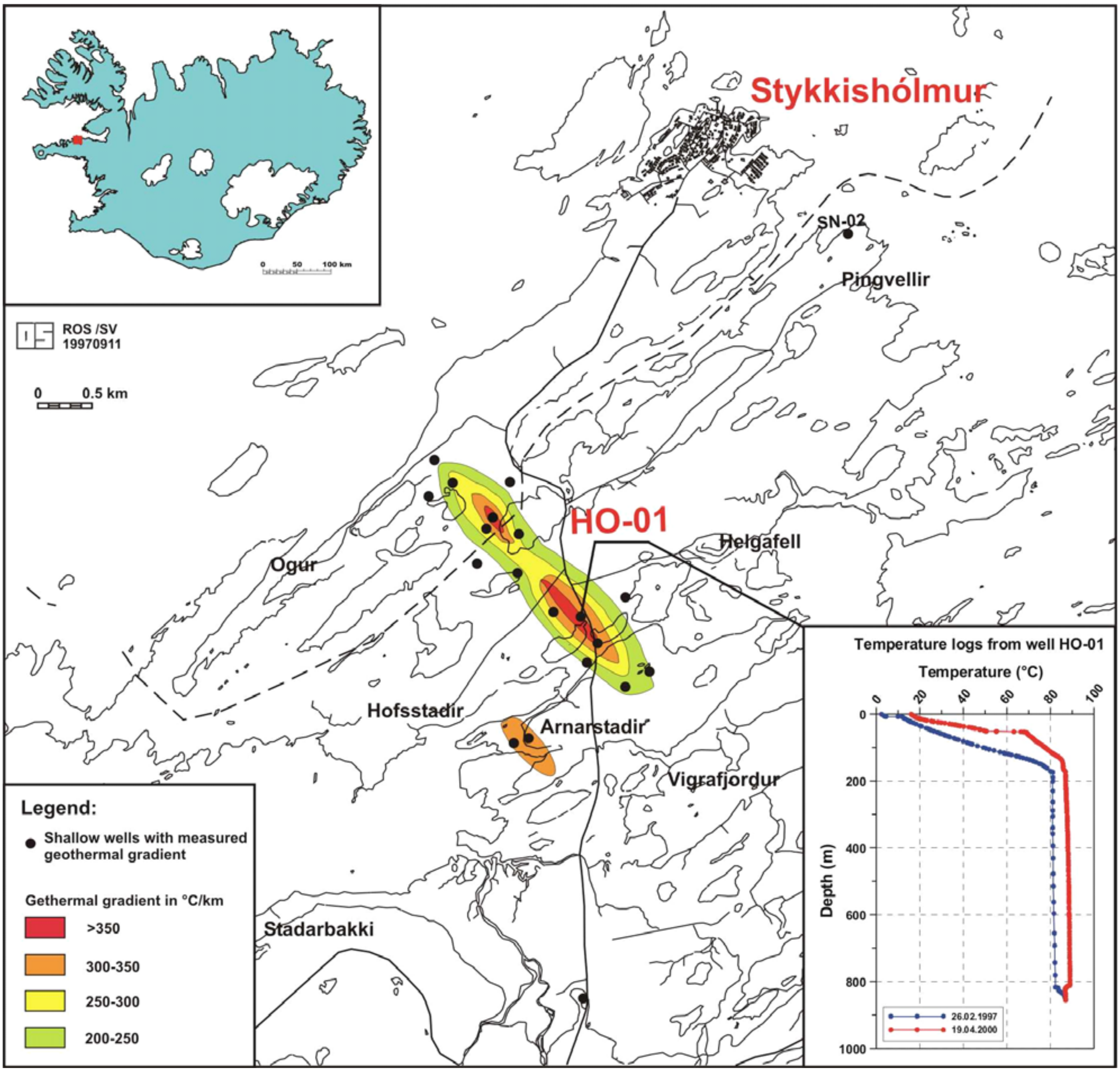

Figure 1: Location of Stykkishólmur, W-Iceland; geothermal gradient anomaly according to measurements in shallow drillholes and temperature logs from production well HO-01.

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

Sample year and number	**1997-0065**	**1997-0179**	**1997-0404**	**1998-0578**	**1999-0521**	**2000-0362**	**2001-0362**	**2002-0354**
Date	97.03.12	97.04.28	97.06.25	98.11.12	99.11.25	00.10.02	01.11.08	02.11.12
Temperature (°C)	86	85.5	87	80.2*	88.2	86.8	86.4	86.2
pH	8.35	8.37	8.45	8.06	8.31	8.4	8.34	8.24
pH temperature (°C)	20.6	21.5	22.7	21.2	23.0	17.0	18.6	22.5
Conductivity (µS/cm)	8990	8960	8940	8860	8640	8750	8770	8230
TDS		5457	4260	5840	6070	5430	5220	5950
CO_2 (total carbonate)	9.42	8.5	9	6.9	3.45	4.43	3.83	3.31
H_2S (total sulfide)	0.05	0.09	0.07	0.06	0.05	0.7	0.07	0.08
SiO_2	72.6	71.95	72.9	72.9	72.7	71.7	71.5	71.6
Na	733	733	731	734	716	740	724	717
K	14	14	13.9	14.1	14.1	14.5	13.4	13.6
Ca	1150	1150	1150	1220	1150	1170	1177	1117
Mg	0.45	0.47	0.51	0.51	0.5	0.5	0.51	0.512
Cl	2990	2960	2920	2940	3018	2960	2970	2980
SO_4	321	318	325	338	327	315	320	326
Sr	6.27	5.92	5.72	5.77				
Mn	0.023	0.022	0.023	0.0164	0.055	0.02	0.0096	
Fe	0.0187	0.0096	0.0099	0.138	0.0076	0.0225	0.0168	
Al	0.0082	0.0072	0.0033	0.006		0.0094	0.014	
Cu	0.0004	0.0003	0.0005					
Zn	0.0031	0.0008	0.0005					
Br	9.87	9.85	9.86	9.61		9.7		10.1
F		1.05	1.07	1.11	1.16	1.23	1.15	1.4
B		0.1	0.11	0.1	0.08	0.11	0.1	0.11
I	0.25	0.25	0.25					
δD (‰ SMOW)		-64.8	-65.9	-68.4	-65.5	-68.5	-67.5	-67.1
δ^{18}O (‰ SMOW)		-11.1	-11.12	-11.08	-11.08	-11.11	-11.06	-11.12
Ionic balance (%)	-1.75	-0.8	0.16	3.3	-3.51	0.66	0	-4.3
Mass balance (%)		-3.52	22.79	-8.62	-12.69	-2.7	1.11	-11.97

* - very little pumping from well