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INTERPRETATION OF CHEMICAL COMPOSITION OF GEOTHERMAL FLUID FROM THE GEOTHERMAL FIELD OF BARANSKY VOLCANO, ITURUP ISLAND, RUSSIA

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ABSTRACT

In this study, the chemistry of representative samples of water from the Baransky volcano geothermal field and hot springs and wells from the low-temperature geothermal area in Snaefellsnes, W-Iceland are compared. The thermal fluids were evaluated chemically using a Cl-SO₄-HCO₃ triangular diagram. The hot spring waters from Baransky volcano are of the steam-heated (SO₄) type with a high SO₄. Ca and Na content, and samples from the wells are mature waters (Cl rich).

The subsurface temperatures of the geothermal reservoirs were estimated by geothermometers and equilibrium calculations using the quartz, Na-K temperatures calculated by WATCH, and the Na-K-Ca temperatures by SOLVEQ. The Na-K and Na-K-Ca geothermometers provided estimated temperatures close to those measured. The quartz and chalcedony temperatures are higher than those measured. The Na-K-Mg triangular diagram was also applied to evaluate the equilibrium of water with reservoir rock. Schoeller diagrams and silica-enthalpy models were used to estimate possible mixing.

1. INTRODUCTION

Russia has large resources of geothermal energy for the production of electric power, the provision of district heating systems and for industrial and agricultural needs. The richest geothermal heat reserves are in East Russia. The Kuril Islands and Kamchatka have reserves of hot water and steam with temperatures up to 280°C at a depth of 700-2500 m, generation power capacity of up to 2000 MW, and heat capacity of no less than 3000 MW utilizing a steam-water mixture and hot water (Kononov and Povarov, 2005; Povarov and Nikolsky, 2005).

In Iturup Island, the geothermal power plant Okeanskaya, with a capacity from 3 to 20 MWt, was put into operation in 1997 at the foot of the Baransky volcano. About 30 wells have been drilled and presently 8 (4×2) MWe are produced there (Povarov, 2000). The Okeanskaya power plant (3.4 MWe) is projected to generate 17 MWe in the future; nine wells are ready for production. The primary

interest here is to study the chemical composition of thermal waters associated with the hydrothermal activity of the Baransky volcano. The hydrothermal system of the Baransky volcano is characterized by high temperatures of the heat source (300-320°C at a depth of 1000-1100 m), a high temperature gradient (up to 50°C/100 m), and a significant heat flow in two localities – the Starosavodskoe field and the Kipyashchaya River (Rychagov, 1993). Many researchers have studied this area (Taran and Znamenskiy, 1995 and 1996; Znamenskiy and Nikitina, 1985; Markhinin and Stratula, 1977; Chudaev et al., 2004). However, information on geochemistry is limited.

The main objective of this study is the interpretation of geochemical data for fluids from the Baransky volcano geothermal field. Some low-temperature geothermal fields in Snaefellsnes peninsula (West Iceland) have been used for comparison. The report consists of several parts:

- Evaluation of chemical classification of thermal fluid;
- Estimation of subsurface temperature by chemical geothermometers and equilibrium calculations;
- Evaluation of mixing processes.

2. STUDY AREAS

2.1 The Baransky volcano geothermal field, general background and geological information

The Kuril Islands stretch for 1,250 km from the southern tip of Russia at the Kamchatka Peninsula southwards to the Japanese island of Hokkaido, thus forming a neat boundary between the Sea of Okhotsk (in the west) and the Pacific Ocean (in the east) (Figure 1). Included are more than 30 large islands, numerous small islands and rocks. The largest islands are Iturup (3,200 km²), Paramushir (2,053 km²), Kunashir (1,490 km²) and Urup (1,450 km²). Kuril Islands are representative of modern volcanic areas.

Iturup Island. Iturup Island is the largest of all Kurils (6725 km²) (Figure 1). Its maximal width is about 40 km, but in the area of most of the volcanic ridges, it is usually 20-30 km. There are more than 20 volcanoes on the island. Much of the island's territory is mountainous with volcanic

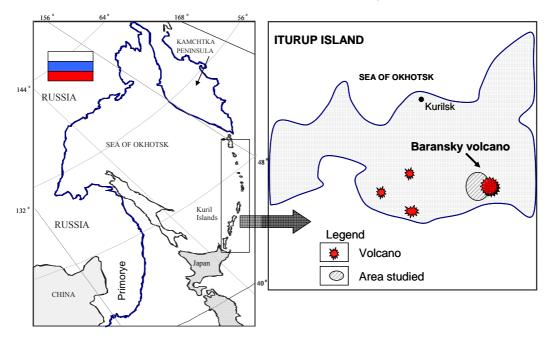


FIGURE 1: Map of the Kuril Islands showing the location of the study area

formations. The basic hydrothermal features on the island are connected with the hydrothermal activity of the Baransky volcano. The most recent historical eruption of the Baransky volcano took place in 1951. The Baransky volcano lies just northeast of Ivan Grozny and is an elliptical truncated cone with its long axis oriented northwest. The height of the volcano is 1126 m. The crater has a diameter of approximately 650 m. Baransky volcano is mainly composed of andesite-basalt lavas and pyroclastics. A lava dome 400-500 m in diameter rises 40-50 m above the floor of the pyroclastic cone's summit crater, grading into a lava flow on the north flank. Faults are associated with the central part of the volcano. The Baransky volcano is characterized by variable and intensive thermal manifestations at the surface (Markhinin and Stratula, 1977). The hydrothermal system of Baransky is located above the active sub-volcanic magma chamber and characterized by high temperatures at the heat source (300-320°C at a depth of 1000-1100 m), steep temperature gradients (up to 50°C /100 m), and a significant heat flow in two localities – Starosavodskoe field and the Kipyashchaya River (Rychagov, 1993).

Kipyashchaya caldera. The caldera overlaps the volcanic domelike uplift of the Grozny ridge that strikes along the general Kuril - Kamchatka direction and includes several volcanic - tectonic structures. The lower part of the geological section is composed of psephite - psammitic and andesitic tuffs and andesibasaltic lavas. The ages and temperature of the solution and some other parameters of the hydrothermal system are controlled by intrusive magmatism.

Starozavodskoye field. This field is located at the upper hypsometric level 300-450 m within the horst structure (Rychagov, 2000).

2.2 Snaefellsnes geothermal area (W-Iceland)

The Snaefellsnes geothermal area is located in W-Iceland (Figure 2). This area is volcanologically active and is characterized by the production of alkaline rock ranging from basaltic to trachytic in composition. The Snaefellsnes volcanic zone represents a flank belt to the main belt of volcanism and rifting in Iceland (Óskarsson and Sigvaldason, 1982). This main belt coincides with the median zone of the Mid-Atlantic Ridge and is characterized by tholeiitic The volcanism. quantity of volcanic material produced in Snaefellsnes in post-glacial times, and apparently also in upper Quaternary times. is very subordinate compared to that produced in the main belt (Jakobsson, 1972). Geological studies by Jóhannesson (1982)

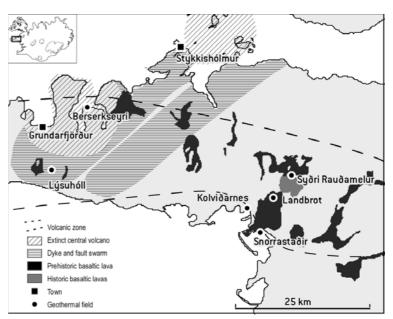


FIGURE 2: Sample locations with geological features of the eastern part of the Snaefellsnes peninsula, West Iceland (adapted from ÍSOR-Orkustofnun: Geological Data Viewer)

indicate that volcanic activity on Snaefellsnes has, since upper Quaternary times, been confined to a narrow zone which coincides with the mountain range running along the middle of the peninsula. This zone apparently represents a structural weakness extending well into the mantle, as witnessed by the magmatic activity. Numerous high-temperature fields occur in the main belt of volcanism and rifting, but no such activity is known in Snaefellsnes.

3. METHODOLOGY

3.1 Classification of thermal waters

3.1.1 Cl-SO₄-HCO₃ ternary diagram

The Cl-SO₄-HCO₃ diagram is used to classify geothermal fluids on the basis of the major anion concentrations (Cl, SO₄ and HCO₃) (Giggenbach, 1988). Using this diagram, several types of thermal water can be distinguished: mature waters, peripheral waters and volcanic and steam-heated waters. The diagram may provide an initial indication of a mixing relationship. The position of data points in such a triangular plot is arrived at by first obtaining the sum S of the concentrations (in ppm) of all three constituents involved. In the present case:

$$S = C_{Cl} + C_{SO_A} + C_{HCO_2} \tag{1}$$

The next step consists of a transformation to percentages %-Cl, %-SO₄ and %-HCO₃, which are used for the construction of the diagram, e.g. %-Cl = $C_{Cl}/S \times 100$, etc.

3.1.2 Na-K-Mg triangular diagram

This triangular diagram is used to classify waters into fully equilibrated, partially equilibrated and immature waters. It can be used to predict the equilibrium temperature and also the suitability of thermal waters for the application of ionic solute geothermometers. It is based on the temperature dependence of the full equilibrium assemblage of potassium and sodium minerals that are expected to form after isochemical recrystallization of average crustal rock under conditions of geothermal interest (Giggenbach, 1988). The use of the triangular diagrams is based on the temperature dependence of the three reactions:

$$K - feldspar + Na^{+} = Na - feldspar + K^{+}$$
⁽²⁾

 $0.8 muscovite + 0.2 clinochlore + 5.4 silica + 2Na^{+} = 2 albite + 0.8K - feldspar + 1.6 water + Mg^{2+} (3)$

$0.8 muscovite + 0.2 clinochlore + 5.4 silica + 2K^{+} = 2 albite + 22.8K - feldspar + 1.6 water + Mg^{2+}$ (4)

The Na-K-Mg triangular diagram shows attainment of water-rock equilibrium if the data point plots on the full equilibrium line, suggesting a field of immature water below the "immature water curve" which indicates initial dissolution of minerals before equilibrium reaction sets in; no geoindicators can be used in this case. The field of partial equilibrium lies between the curves, and suggests either a mineral that has dissolved, equilibrium reactions have set in but equilibrium has not been reached, or a mixture of a water that has reached equilibrium (e.g. a geothermal water) with a dilute unequilibrated water (e.g. cold groundwater). Geothermometer temperatures may often be deduced from such a position. Points close to the \sqrt{Mg} corner usually suggest a high proportion of relatively cold groundwater, not necessarily "immature".

3.2 Geothermometers

Geothermometers are used to predict subsurface temperatures in geothermal systems. These geothermometers are all based on the assumption that specific temperature-dependent mineral-solution equilibria are attained in the geothermal reservoir. Various geothermometers may provide different values. The following processes may interfere and affect different geothermometers differently: lack of equilibration with a particular mineral, different rates of equilibration reaction between minerals and water, mixing with cold groundwater, boiling and condensation during upflow. Geothermometers have been classified into three groups:

- Solute geothermometers;
- Steam or gas geothermometers;
- Isotope geothermometers.

Many solute geothermometers were developed from the mid-1960's to the mid-1980's. The most important ones are the silica (quartz and chalcedony) (Fournier and Rowe, 1966; Fournier, 1977; Fournier and Potter, 1982; Arnórsson et al., 1983), Na/K (Truesdell and Fournier, 1976; Fournier, 1979; Arnórsson et al., 1983; Giggenbach, 1988), and Na-K-Ca (Fournier and Truesdell, 1973). The solute geothermometers used in this report are discussed in the following sections.

3.2.1 Silica (quartz) geothermometer

The silica geothermometer is based on the solubility of quartz and is used to estimate subsurface temperatures in hot spring systems. Solubility of quartz is dependent on pressure, temperature and salinity. The quartz geothermometers work best for well waters in the subsurface temperature range of 120-250°C (Arnórsson, 2000a). The basic reaction for the dissolution of silica minerals is

$$SiO_2(s) + 2H_2O = H_4SiO_4(aq)$$
⁽⁵⁾

When using quartz geothermometers, some factors should be considered (Fournier and Potter, 1982):

- a. The temperature range in which the equations are valid;
- b. Possible polymerization or precipitation of silica before sample collection;
- c. Possible polymerization of silica after sample collection;
- d. Control of aqueous silica by solids other than quartz;
- e. The effect of pH upon quartz solubility;
- f. Possible dilution of hot water with cold water before the thermal waters reach the surface.

Fournier (1977) presented a quartz geothermometer with a maximum steam loss at 100°C as a function of silica concentration (SiO₂ is in mg/kg):

$$t(^{o}C) = \frac{1522}{5.75 - \log(SiO_{2})} - 273.15$$
(6)

The most widely used formula for the quartz geothermometer (Fournier and Potter, 1982) is:

$$t(^{o}C) = -42.198 + 2.883 \times 10^{-1}S - 3.668 \times 10^{-4}S^{2} + 3.1665 \times 10^{-7}S^{3} + 70.34\log S$$
(7)

As suggested, the quartz geothermometer may be applicable down to 100°C in old systems, but in young systems, it may not be applicable below 180°C. The expanded formula by Fournier and Potter (1982) is applicable up to 330°C.

3.2.2 Chalcedony geothermometers

This geothermometer is based on the solubility of chalcedony. Fournier (1991) suggested that there is ambiguity in the use of silica geothermometers at temperatures below 180°C as chalcedony appears to control dissolved silica in some places and quartz in others. Chalcedony is a very fine-grained variety of quartz, which is probably not a separate mineral but a mixture of quartz and moganite and, with time, it probably all changes to quartz (Gíslason et al., 1997). Temperature, time and fluid composition all affect different crystalline forms of silica. Thus, in some places (old systems), where water has been in contact with rock at a given temperature for a relatively long time, quartz may control dissolved silica at temperatures down to 100°C. In other places (young systems), chalcedony

may control dissolved silica at temperatures up to 180°C. The chalcedony geothermometer in a condition of maximum steam loss, presented by Arnórsson et al. (1983), is:

$$t(^{\circ}C) = \frac{1264}{5.31 - \log SiO_2} - 273.15$$
(8)

and without steam loss

$$t(^{o}C) = \frac{1112}{4.91 - \log SiO_2} - 273.15$$
(9)

3.2.3 Cation geothermometers

Cation geothermometers are based on ion exchange reactions, with a temperature – dependent equilibrium constant. An exchange reaction between alkali feldspar and Na^+ and K^+ in aqueous solution has often been given as an example (Fournier and Truesdell, 1973):

$$K^{+} + NaAlSi_{3}O_{8} = KAlSi_{3}O_{8} + Na^{+}$$
⁽¹⁰⁾

The equilibrium constant for the reaction is:

$$K = \frac{(KAlSi_3O_8)(Na^+)}{NaAlSi_3O_8)(K^+)}$$
(11)

Taking the solids to be pure (unit activity), no or equal complexing of Na^+ and K^+ in aqueous solution, and the activity coefficients to be the same for both ions, the equation reduces to:

$$K = \frac{\begin{bmatrix} Na^+ \end{bmatrix}}{\begin{bmatrix} K^+ \end{bmatrix}}$$
(12)

where $[Na^+]$ and $[K^+] =$ The molalities of respective ions.

The Na-K geothermometer suggested by Giggenbach (1988) is expressed by:

$$t(^{o}C) = \frac{1390}{1.75 + \log\frac{Na}{K}} - 273.15$$
(13)

Several workers have suggested empirical Na/K geothermometers based on experiments and obtained different results due to work with different minerals. Basaltic minerals usually give low values (Arnórsson, 1983) but andesitic ones high values (Giggenbach, 1988). At high temperatures they converge and give similar values. The Na/K ratio generally works well for estimating temperatures of water above 200°C.

The Na-K-Ca geothermometer was developed specifically for calcium rich waters that give anomalously high calculated temperatures by the Na-K method. Fournier and Truesdell (1973) developed the equation for the Na-K-Ca geothermometer that has been applied to both low-temperature and high-temperature geothermal reservoirs, expressed by:

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$$t(^{o}C) = \frac{1647}{\log\frac{Na}{K} + \beta(\log\frac{\sqrt{Ca}}{Na} + 2.06) + 2.47} - 273.15$$
(14)

where $\beta = 4/3$ when calculated temperature is >100°C; $\beta = 1/3$ when calculated temperature is < 100°C.

The Na-K-Ca geothermometer may give erroneous calculated temperatures, as a result of boiling and mixing with cold water. The result of boiling is a loss of CO_2 , which can cause $CaCO_3$ to precipitate. The Na-K-Ca geothermometer gives anomalously high results when applied to waters rich in Mg^{2+} . Application of a Mg^{2+} correction will lead to an anomalously low calculated reservoir temperature. Therefore, chemical geothermometer results should be used with great caution when applied to Mg^{2+} - rich waters (Fournier and Potter, 1979). This problem may also be avoided by the application of the Na-K-Mg diagram (Giggenbach, 1988).

3.3 Solution-mineral equilibrium

Geothermometers have been developed to predict reservoir temperature. However, various geothermometers can give different values for the temperature of a reservoir. This may be due to different reaction rates, or mixing with cold water in the upflow. Reed and Spycher (1984) have suggested that the best estimate of reservoir temperature can be attained by considering simultaneously the state of equilibrium between a specific water and many hydrothermal minerals as a function of temperature. Therefore, if a group of minerals converges to equilibrium at a particular temperature, this temperature corresponds to the most likely reservoir temperature. The rising fluid has reacted chemically with rock. The equilibrium state of minerals can be estimated by the ratio of the reaction quotient (Q) to the equilibrium constant (K). The equilibrium constant and the reaction quotient are related to the Gibbs energy through:

$$\Delta G_r = -RT\ln K + RT\ln Q = RT\ln\left(\frac{Q}{K}\right) \tag{15}$$

where R = Gas constant; T = Temperature (K).

The Saturation index (SI) can be obtained from the solubility product and its reaction quotient:

$$SI = \log Q - \log K = \log \left(\frac{Q}{K}\right)$$
 (16)

All minerals in equilibrium at the same temperature converge to SI = 0; SI < 0 for an undersaturated solution, and SI > 0 for a supersaturated solution. If fluid mixes with dilute water, mineral curves will intersect at SI < 0, but if it has boiled at SI > 0.

Computer programs such as WATCH (Arnórsson et al., 1983) and SOLVEQ (Reed and Spycher, 1989) are generally used to calculate aqueous speciation. These programs are used to calculate the equilibrium constant, the reaction quotient and saturation index for the given reaction at any given temperature. The state of saturation of many minerals as a function of temperature can be shown by $\log Q/K$ diagrams.

3.4 Mixing processes

Ascending hot waters may cool by conduction, by mixing with shallow cold water or by a combination of these processes. Chemical analysis of spring waters may provide information about which of these processes is taking place in hot spring systems. Water that ascends quickly with little conductive cooling will have a chemical composition that reflects rock-water equilibrium at depth. Springs with different temperatures have different chemical compositions (Fournier, 1977) when ascending hot waters cool by mixing with cooler water, There are several methods that can be used to infer the mixing of two waters: variation in ratios of conservative elements such as Cl/B, Schoeller diagrams and mixing models. The relationship of chloride to boron concentration appears to be useful for evaluating mixing processes. The relationship between these parameters indicates whether mixing has taken place. The relation between chloride and silica and sulphate concentration may also be useful to obtain evidence of mixing. A Schoeller diagram compares the log concentrations of fluid components from a number of analyses with constituents of each analysis connected with a line. The effect of mixing with dilute water is to move the line representing an analysis vertically without changing its shape (Truesdell, 1991).

Mixing models have been developed to allow the estimation of the hot water component in mixed waters in springs or discharged from shallow drillholes. Three kinds of mixing models are described by Arnórsson (2000b):

- The silica enthalpy mixing model;
- The chloride enthalpy mixing model;
- The silica- carbonate model.

The silica – enthalpy mixing model. The silica – enthalpy diagram may be used to determine the temperature of a hot water component. The model is based on the assumption that silica has not precipitated before or after mixing and conductive cooling has not occurred. There are some criteria for hot spring waters which may be appropriate for the application of this model: (1) a measured water temperature which is at least 50°C less than calculated silica and Na-K-Ca geothermometer temperatures, (2) a silica geothermometer temperature which is lower than the Na-K-Ca temperature, (3) a mass flowrate which is high enough to allow for only a little conductive cooling. This model cannot be applied to boiling springs because heat is carried away in the steam after mixing.

The chloride - enthalpy mixing model. The chloride - enthalpy diagram can be applied to predict subsurface temperature. It accounts for both mixing and boiling processes. This model works best where the initial temperature of the hot water is above 200°C. In using this model it is necessary to assume: (1) no heat loss before or after mixing; (2) re-equilibration with quartz after mixing; (3) that silica is not precipitated during the ascent of the mixed water to the surface (Fournier, 1977).

The silica - carbonate model. This mixing model is based on the relationship between silica and total carbonate. It is based on the assumption that practically all silica in geothermal water occurs as H_4SiO_4 and all carbonate as HCO_3^- . This model can be used to estimate the temperature of the hot water component in mixed waters and also to distinguish boiled and non-boiled waters.

4. CHEMICAL PROPERTIES OF THE GEOTHERMAL WATER

4.1 Sampling

The geochemical study is based on 9 samples collected from hot springs and well 65 (associated with the hydrothermal activity of the Baransky volcano) by the geothermal group of the Far East Geological Institute in 2003 (Figure 3). A sample from well 51, the results for which are also used,

was collected in 1991 (Taran and Znamenskiy, 1995). Two samples were collected from the Kipaschaya River, which flows from the Baransky volcano, and other samples from hot springs and well discharges from the Starozavodskoe fumarole field. The water samples were filtered on site through a 0.45 µm pore filter into low density polyethylene bottles using a polypropylene filter holder. Measurements of pH, Eh, conductivity, carbonate carbon and dissolved oxygen were done on site.

Major ion concentrations were analyzed for by colorimetric, AAS and ICP-AES methods. The trace elements were analyzed by ICP-MS. Gas samples were not collected.

4.2 Classification of the thermal fluids

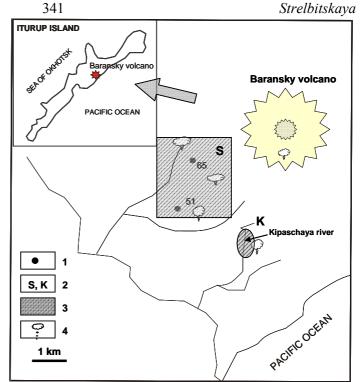


FIGURE 3: Map of the study area showing the geothermal manifestations of Baransky volcano;1- wells; 2- S and K (Starozavodskoe and Kipaschaya fumarole fields); 3-study areas; 4- fumaroles)

Results of chemical analysis of hot spring and well fluids from the Baransky volcano are presented in Tables 1 and 2.

Table 2 also includes the composition of discharges from geothermal wells in Iceland for comparison. The chemical composition of the waters was investigated using the $Cl-SO_4$ -HCO₃ triangular diagram (Giggenbach, 1991) that is used to classify geothermal water on the basis of major anions and a diagram based on the relative Na+K, Ca and Mg concentrations. Concentrations of hot spring and well waters from Baransky volcano are plotted in Figure 4. The samples of cold water and some springs and wells from low-temperature geothermal fields in Snaefellsnes (W-Iceland) have also been plotted for comparison. From the figures, different types of thermal waters can be distinguished, such as mature (Cl) waters and peripheral (HCO₃) waters.

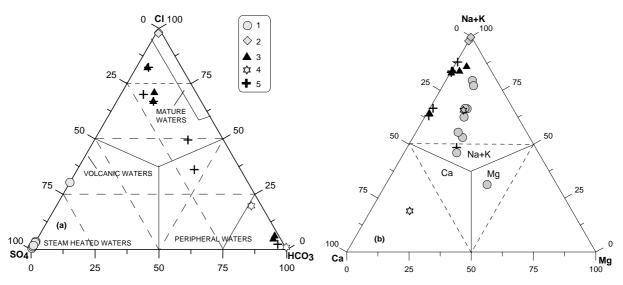


FIGURE 4: Triangular diagrams of relative concentrations of a) Cl, SO₄, and HCO₃; and b) Na+K, Ca and Mg; 1- acid hot spring from the Baransky volcano; 2- wells from the Baransky volcano; 3-wells from Iceland; 4- hot spring samples from Iceland; 5-cold water

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Sample ID	U4	U7	U17	U18	U21	U23	U24	U25	U26
TDS	6370		2190	872	749	576	777	680	592
pН	2.19	1.47	2.56	3.05	3.18	3.46	3.15	3.86	3.74
$T(^{0}C)$	34.6	95.5	58.2	98	65	95.3	69	39.9	44.4
Ca	4.79	30.42	10.63	6.99	11.94	5.34	7.63	7.5	8.1
Mg	3.55	27	8.71	5.15	17.36	6.27	5.57	4.83	4.99
Na	5.34	197.3	30.1	21.2	10.09	25.8	18.9	7.36	10.11
K	4.12	50.7	8.23	3.03	3.26	13.36	3.19	3.16	6.26
HCO ₃	0	0	0	0	0	0	0	0	0
SO_4	3200	5225	1110	443	293.3	242.7	255.3	250	292.4
Cl	17.8	2280	23	17.1	4	7.9	8.5	3.3	5.5
Al	58.88	211.05	40.5	16.71	1.223	1.624	0.6691	0.2084	0.1983
Fe	87.76	86.38	14.87	19.51	46.89	12.12	7.27	24.34	0.42
Cu	0.003	0.008	0.002	0.00091	0.074	0.0016	0.0006	0.0006	0.0009
Br	9.33	1019	13.47	16	51.05	96	23.89	42.75	50.45
Мо	0.00005	0.00012	0.00007	0.00005	0.00041	0.00003	0.00004	0.00006	0.00004
Sb	0.00003	0.0093		0.00004		0	0.00012	0.00014	0.00002
Li	0.0027	0.1988	0.01294	0.01215	0.00837	0.00505	0.00812	0.00624	0.01109
As	0.005	0.468	0.01499		0.034	0.001	0.007	0.018	0.00708
Co	0.0146	0.00057	0.00523	0.00166	0.0176	0.00299	0.0155	0.000099	0.000037
Ni	0.0296	0.0039	0.0067	0.0019	0.0199	0.0023	0.0005	0.0008	0.0004
Zn	0.073	0.073	0.026	0.016	0.922	0.012	0.03	0.009	0.005
Sr	0.093	0.362	0.078	0.073	0.026	0.055	0.074	0.048	0.069
Rb	0.004	0.091	0.015	0.01	0.0059	0.03	0.009	0.01566	0.0197
Cs	0.000015	0.0419	0.00223	0.00214	0.00134	0.00236	0.00116	0.01406	0.00666
Ba	0.00284	0.02588	0.00701			0.02926	0.03688	0.01861	0.0361
Pb	0.0069	0.01889	0.00302	0.00102	0.00238	0.000019	0.000048	0.000012	0.000009

TABLE 1: Results of chemical analysis of hot springs at Baransky volcano, collected in 2003
(concentrations in ppm)

Steam heated (SO₄) waters. The hot springs containing these waters discharged within the fumarole fields of the Baransky volcano. These waters have temperatures ranging from 34 to 98°C and TDS from 680 to 6370 mg/l. The pH values for these waters range from 1.47 to 3.86. The major cation is Na. They are high in SO₄, have a low Cl concentration and high Al and Fe concentrations due to the dissolution of host rock.

Mature (Cl) waters. The chemical composition of the fluids from both wells studied (wells 65 and 51) is classified as that of a Cl-rich geothermal water. The chloride waters are discharged from geothermal wells. The waters are neutral with pH = 7; Cl-ion predominates. In contrast to these Na-Cl waters, hot waters discharged from wells SN-124 (Berserkseyri), KA-1 and KA-2 (Kolvidarnes) are neutral or alkaline (pH 6.6-8) and Cl, Na and K concentrations are lower than those in waters from wells 65 and 51.

Peripheral (HCO₃) waters. The data points for hot springs at Sydri Raudamelur and Lýsuhóll, wells LH-01, LH-07 and cold waters from Snaefellsnes are located in the HCO₃ corner and can be classified as peripheral waters suggesting mixing with cold water, or CO₂ from a magmatic source. The temperature of the waters ranges from 40 to 60°C, with pH values 6.88-8.45. These are CO₂ – rich waters. Their CO₂ content ranges from 102 to 1518 mg/l.

Origin of H_2SO_4 *in thermal waters.* The sulphuric acid type fluid is generally formed by three kinds of mechanism (Matsuda and Kan-ichi Shimada, 2000):

• Oxidation of H ₂ S;	• Hydrolysis of SO ₂ ;	 Hydrolysis of native S.
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Well	W51	W65	SN-124	LH-07	LH-01	KA-1	KA-2	
Place	Iturup	Iturup	Berserkseyri	Lýsuhóll	Lýsuhóll	Kolvidarnes	Kolvidarnes	
Water sample								
T(°C)	150	190	75.9	60	40	66	66	
pH/T(°C)	7.46/20	7.34/40	6.66/22.8	6.88/11	6.5/40.	8	7.2/66.	
Р	2.5	1.2	1	1	1	1	1	
enthalpy	1630	1170	n.d	n.d	n.d	n.d	n.d	
Ca	46	5.67	403	79.9	46	28	29.2	
Mg	0.12	0.02	13.8	20.8	26.6	1.06	0.87	
Na	1750	1481	725	485.8	414	149	144	
Κ	400	271.3	19.6	36.5	31.1	2.9	3	
В	28	34.3	0.26	0.48	1.06	n.d	0.94	
SiO ₂	859	831	156	177.9	187	79	96	
HCO ₃	28.1	29.3	n.d	n.d	n.d	n.d	n.d	
SO_4	40	34.5	281	43.1	27.4	59.9	48.4	
F	0.25	0.25	2	4.8	4	0.5	1.1	
Cl	2961	3550	1720	69.5	101	214	210	
H_2S	2.5	1.5	n.d	0.02	n.d	n.d	n.d	
CO2	n.d	n.d	92.6	1358	1518	45.8	37.7	
Al	0.1	0.09	0.005	0.03	n.d	n.d	n.d	
Fe	0.05	0.076	0.81	0.826	3.24	n.d	0.017	
Rb	1.35	0.37	n.d.	n.d.	n.d.	n.d.	n.d.	
Cs	0.96	0.24	n.d.	n.d.	n.d.	n.d.	n.d.	
source	[2]	[1]	[3]	[3]	[3]	[3]	[3]	
Steam sample %								
CO2	65.3	68.5	n.d.	n.d.	n.d.	n.d.	n.d.	
H2S	23.6	23.4	n.d.	n.d.	n.d.	n.d.	n.d.	
H2	4.4	2.2	n.d.	n.d.	n.d.	n.d.	n.d.	
CH4	0.2	0.46	n.d.	n.d.	n.d.	n.d.	n.d.	
N2	5.6	6.4	n.d.	n.d.	n.d.	n.d.	n.d.	
Ar	0.046	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Y(steam fraction)	0.05	0.045	n.d.	n.d.	n.d.	n.d.	n.d.	
source	[2]	[2]	[3]	[3]	[3]	[3]	[3]	

TABLE 2: Chemical composition of wet-steam well discharges from the Baransky volcano
and from Snaefellsnes, W-Iceland (concentrations in ppm)

[3]: ÍSOR data base;

[1]: Data from Chudaev et al., (2004); [2]: Data from Taran and Znamenskiy (1995) n.d. Not determinated

The oxidation of H₂S is a typical mechanism for the formation of acid sulphate type hot spring water. This mechanism is rarely the cause of acidity of deep geothermal fluids due to the highly reduced conditions in the geothermal reservoir and the prevention of shallow fluid infiltration into the reservoir. Reaction hydrolysis of SO₂ is represented by the following equation:

$$4SO_4 + 4H_2O \rightarrow 3H_2SO_4 + H_2S \tag{17}$$

SO₄-Cl type hot water can be formed in this reaction.

Hydrolysis of native S is represented by the following equation:

$$4S + 4H_2O \rightarrow H_2SO_4 + 3H_2S \tag{18}$$

Ellis and Giggenbach (1971) state that sulphur hydrolysis is believed to be common in active volcanic areas. Native sulphur is usually formed by the oxidation of H_2S near the surface, so the hydrolysis is a surface process, not representative of the deep system.

Origin of HCl. The main factors in HCl formation are pH, temperature and chloride concentration in the fluid. D'Amore et al. (1990) and Truesdell et al. (1989) have suggested that the origin of vapour containing HCl is the product of a high temperature (>325°C) reaction of NaCl, water and silica from Na₂SiO₃ and HCl.

According to the suggestion discussed above, the process of formation of steam-heated acid and Na-Cl water types from the Baransky geothermal field is shown schematically in Figure 5. The meteoric water infiltrates through faults

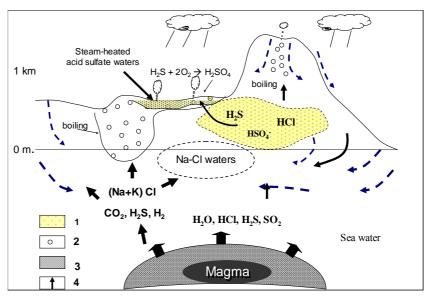


FIGURE 5: Formation model for various types of geothermal waters; 1-steam heated acid waters; 2-zone of boiling; 3-magma; 4- meteoric waters and thermal fluid transport path

at depth. This water has interacted with magmatic gases (CO₂, H_2S , SO₄, H_2); for Na-Cl thermal fluids, the host rock interacts with shallow low-salinity waters and forms sodium – chloride water that rises to the surface due to lowered pressure.

Hydrolysis of SO₂ of magmatic origin at depth causes the formation of the H_2S – rich vapour that rises from depth to the surface forming steam-heated acid - sulphate waters by atmospheric oxidation of H_2S and by mixing with meteoric waters. Hydrogen sulphide in the steam is oxidized to sulphate as:

$$2O_2 + H_2 S \to 2H^+ + SO_4^{2-} \tag{19}$$

Therefore, the hot spring waters from both fumarole fields (Starosavodskoe field and Kipyashchaya) are steam-heated acid waters except for the samples of well discharges, which are of the mature type. Acid waters are formed by the interaction of shallow water with magmatic gases and the atmospheric oxidation of hydrogen sulphide at the surface. Sodium - chloride waters are formed by the interaction of geothermal fluids with the host rock and dilution with low-salinity shallow waters at depth (Taran and Znamenskiy, 1995; White and Muffler, 1971).

The Na-K-Mg triangular diagram of Giggenbach (1988) indicates the equilibrium temperatures of minerals (feldspars, clay) containing these elements, and was used to identify equilibrium between the geothermal fluids and rock and to determinate reservoir temperature (Figure 6). The diagram using Arnórsson's Na-K equation was used for interpretation of the Icelandic data (Figure 6b). Figure 6a shows that samples W 65 and W 51 from the deep geothermal wells fall on the full equilibrium line, suggesting attainment of water-rock equilibrium. The calculated equilibrium temperature is 280-300°C. All the spring samples "U4-26" from the fumarole fields plot in the area of immature waters, close to the \sqrt{Mg} - corner of the diagram which means that these waters have not attained equilibrium and application of solute geothermometers to estimate discharge temperatures is unsuitable for these samples. Samples KA-1, KA-2, KA, S and L from Snaefellsnes (W-Iceland) low-temperature fields plot on the full equilibrium line and correspond to reservoir temperatures from 100 to 120°C, close to measured values (Table 3). Sample SN-124 plots in the partial equilibrium area, and LH-01, LH-07 and SR, B-1 and B-2, plot in the area of immature waters.

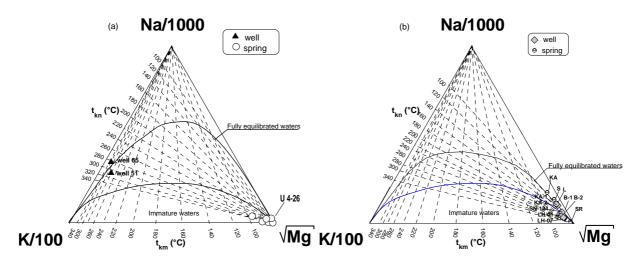


FIGURE 6: Na-K-Mg diagrams for a) The hot springs and wells from the Baransky volcano; and b) Low-temperature fields in Snaefellsnes, W-Iceland; Na-K geothermometry equations by: a) Giggenbach (1988); and b) Arnórsson (2000a)

TABLE 3: The results of solute geothermometry and mineral equilibrium calculations
using the WATCH and SOLVEQ computer programs

Sample no.	Place	T _{mea} (°C)	T _{Na-K-Ca} (°C)	T _{Na-K} (°C)	T _{quartz} (°C)	T _{chalced} (°C)		
Wells								
W65	Iturup	190	284	267	268.8	255.9		
W51	Iturup	150	278	292	280	265		
SN-124	Berserkseyri	75	77	88.6	163.3	139.4		
LH-07	Lýsuhóll	40	n.a.	n.a.	170.9	147		
LH-01	Lýsuhóll	40	n.a.	n.a.	174.9	151.8		
KA-1	Kolvidarnes	66	57	71	121.3	92.7		
KA-2	Kolvidarnes	66	57	71	121	93		
Springs								
B-1	Berserkseyri	50	83	93	167.4	143.9		
B-2	Berserkseyri	41	80	94.4	156.1	131.3		
KA	Kolvidarnes	60	54	71.2	121.7	93.1		
S	Snorrastadir	42	45	57.2	156.3	131.5		
L	Landbrot	54	59	60	156.1	131.2		

Quartz, chalcedony and Na-K geothermometer results are calculated by WATCH, Na-K-Ca temperatures are calculated by SOLVEQ;

n.a. - not applicable

4.3 Subsurface temperature estimation

The silica, Na-K and Na-K-Ca geothermometers were used to estimate subsurface temperature for hot springs and well discharges. The quartz, and Na-K temperatures were calculated with the WATCH program (Arnórsson et al., 1983) and Na-K-Ca temperatures with the SOLVEQ program (Reed and Spycher, 1989). Results for solute geothermometry are reported in Table 3.

The table shows that the deeper temperatures obtained by Na-K and Na-K-Ca geothermometers compare well with the values obtained from the quartz and chalcedony geothermometers for the hot well discharges considered. The calculated quartz geothermometer temperatures for well waters

studied indicate reservoir temperatures of 121-280°C; the chalcedony geothermometer gives reservoir temperatures 92-265°C. The Na-K and Na-K-Ca geothermometers correspond to reservoir temperatures of 77-284°C. Calculated temperatures for the hot springs are quite different. Na-K and Na-K-Ca temperatures give much lower values than the silica geothermometers, most likely as a result of mixing and high concentrations of Ca, Mg and CO₂ in the spring waters. The high concentration of CO_2 may have disturbed the Ca-equilibria so that the cation geothermometers may not be reliable and the chalcedony and quartz temperatures are probably closer to the source temperatures.

4.4 Log (Q/K) diagrams

The range of equilibrium temperatures was arbitrarily defined as the temperature interval over which at least two minerals attain equilibrium within 4°C of each other, the cluster equilibrium temperature as the range over which most minerals appear to reach equilibrium, and the best equilibrium temperature as the temperature at which the greatest number of minerals are in equilibrium with the aqueous solution by Tole et al. (1993). The equilibrium temperature can be obtained from a Log(Q/K)diagram. Mineral saturation indices (SI) are used to describe the extent to which a particular solution is supersaturated or undersaturated with respect to a particular mineral phase. The saturation index (SI) for hydrothermal minerals in aqueous solutions at different temperatures was estimated by SOLVEQ (Reed and Spycher, 1984). As is clear from the triangular diagrams in Figures 4 and 6 these are steam-heated waters that are dissolving minerals with no equilibrium attained and are, therefore, not suitable for methods employing log Q/K which assumes equilibrium. The two wells (65 and 51) and a few wells (SN-124 (Berserkseyri) and LH-07 (Lýsuhóll)) from Snaefellsnes (Iceland) were chosen and the equilibrium state of their water calculated for major hydrothermal minerals. Albit-hi, albit-lo, anhydrit, ankerite, sanid-hi, brucite, dolo-ord and dolo-dis minerals were selected to calculate the equilibrium state for hot water from wells 65 and 51 (Iturup, Russia); albit-hi, albit-lo, analcite, clinozoisite, diaspor, illite, microcline, montm-Ca, montm-Mg, montm-Na, muskovite, sanidine-hi and zoisite for discharges from wells SN-124 and LH-07 (Iceland). The Log (Q/K) temperature diagrams for selected samples at the different temperatures are shown in Figure 7. These diagrams show that solute - mineral equilibria for selected minerals seem to be attained at the equilibrium temperature 275°C for wells 51 and 65, and for samples SN-124 and LH-07 at 150°C.

4.5 Mixing processes

Ascending waters may cool by boiling (adiabatically), by conduction, by mixing with shallow cold water or by combinations of these processes. The recognition of where mixing took place underground is difficult where water-rock re-equilibration has taken place after mixing. Fournier (1991) suggested some indications of mixing:

- A measured water temperature which is at least 50°C lower than the calculated silica and Na-K-Ca geothermal temperatures;
- Silica (quarts and chalcedony) geothermometer temperatures which are significantly lower than the Na-K-Ca temperature:
- A mass flowrate which is high enough to allow for only little conductive cooling during upflow;
- Variation in chloride concentrations of springwater is too large to be explained by steam loss;
- Variation in ratios of relatively conservative elements that do not precipitate from solution during movement of water through rock, such as Cl/B;
- Variation in oxygen and hydrogen isotopes;
- Systematic variations in spring composition and measured temperatures.

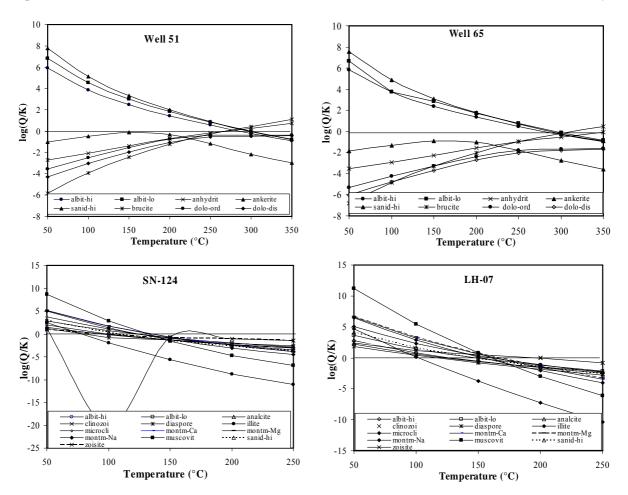
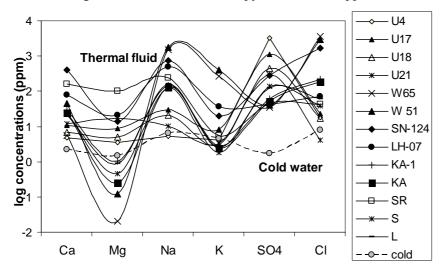


FIGURE 7: Mineral equilibrium diagrams at 150°C for samples from wells 51 and 65, Iturup Island, and wells SN-124 and LH-07, Snaefellsnes

Schoeller diagrams and the silica-enthalpy model were applied to estimate mixing processes. Major



components of thermal, cold and mixed waters from the areas studied are shown in Figure 8. The figure shows that the thermal waters have higher concentrations of Na, K, SO₄ and Cl than the cold waters, which have а higher Mg concentration. A relatively high concentration of Mg shows that cold water mixed with the is geothermal water.

FIGURE 8: Schoeller diagram of selected samples for hot springs and cold groundwaters

The Si-enthalpy model was applied to the Icelandic hot springs (B-1, and L). It assumes that conductive cooling does not take place and silica has not precipitated. Results for this model are shown in Figure 9. The straight line is drawn from the cold water sample point through the mixed water hot spring points (B, L) to the intersection with quartz solubility curve. Point C gives the initial enthalpy and temperature of the deep hot water component. The calculated initial enthalpy is 782 kJ/kg and the original temperature of mixed hot water components obtained from steam tables is about 184°C.

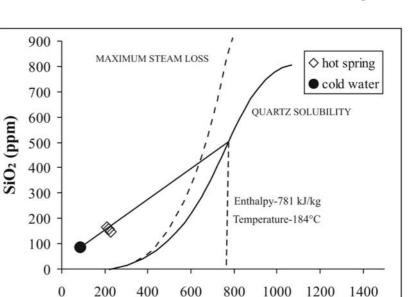


FIGURE 9: Silica enthalpy diagram for determining the temperature of thermal water mixed with cold groundwater for selected hot springs

Enthalpy (kJ/kg)

5. CONCLUSIONS

The main objective of this study was to evaluate chemical classification of thermal fluids with reference to the estimation of subsurface temperature using chemical geothermometers and to carry out equilibrium calculations, and the evaluation of mixing processes for fluids from the geothermal field of the Baransky volcano and the low-temperature geothermal fields Berserkseyri, Lýsuhóll and Kolvidarnes in Snaefellsnes, Iceland for comparison. The major conclusions of the study are as follows:

- The geothermal fluids from the fumarole fields of Baransky volcano are of two types: steamheated (SO₄) waters and mature (Cl) waters. Based on data obtained and information from Matsuda and Kan–ichi Shimada (2000), a model for the formation of various types of thermal fluids from Baransky volcano was described. According to the Na-K-Mg triangular diagram, water from the deep wells 51 and 65 is in equilibrium with the host rock and the corresponding reservoir temperature is in the range 280-300°C. Water samples U7-U26 do not equilibrate with the minerals and do not give information on the deep system. Samples KA-1, KA-2, KA (Kolvidarnes), S (Snorrastadir) and L (Landbrot) from the Icelandic low-temperature fields plot near the full equilibrium line with a corresponding reservoir temperature of 100°C. Samples SR (Sydri Raudamelur), LH-07, LH-01 (Lýsuhóll), B-2, B-1 (Berserkseyri) are carbon-dioxide rich and plot near the HCO₃ corner.
- Geothermometers are used to predict subsurface temperatures. The calculated quartz geothermometer temperatures for the wells studied indicate reservoir temperatures of 121-280°C; the chalcedony geothermometer gives reservoir temperatures 92-265°C; the Na-K and Na-K-Ca geothermometers correspond to reservoir temperatures of 77-284°C. The temperatures obtained by Na-K and Na-K-Ca geothermometers compare well with the values obtained by the quartz geothermometer for the hot well discharges and the temperatures were close to those measured. Calculated temperatures for all hot springs are quite different due to

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the high CO₂, which may have disturbed the Ca-equilibrium by calcium lost through calcite precipitation. In this case, the cation geothermometers may not be reliable and the chalcedony and quartz temperatures may be closer to the source temperatures. Calculation of mineral saturation indices shows that the best equilibrium temperatures for wells 51 and 65 are attained at a temperature of 275°C, but for wells SN-124 and LH-07 at 150°C.

• The results for the Si-enthalpy mixing model applied to the Icelandic hot springs (B-1 and L) suggest a reservoir temperature close to 184°C.

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