CHEMISTRY OF GEOTHERMAL FLUIDS IN DIENBIEN AND SONLA PROVINCES, NW-VIETNAM

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ABSTRACT

North-west Vietnam is a very special area where development of geothermal energy will be significant for socio-economic activities. The data in this project is taken from a previous research in 2004. Thirty-four samples are taken from 119 hot springs for further study, with the purpose of estimating and interpreting the chemical compositions of the water, by using the methods as triangle diagrams, geothermometers, evidence of mixing and log Q/K plot. The 34 samples were divided into 5 groups based on the location and structure of geology. The study results show that Group 1 with samples S1, S2, and S3 give a good estimation of the temperature of the reservoir from 73°C to 150°C with small deviation between methods. Group 2 with samples S8, S18, and S19 give a temperature from 76°C to 111°C. In Group 3 with samples S11 and S12, reservoir temperature is from 59°C to 110°C. Group 4 with S72 and S73 samples, the temperature of reservoir drops between 60-100°C. Group 5 with samples S6, S65, S75, S77, and S78 the reservoir temperatures estimated by silica geothermometers are quite low and they might be from a different reservoir.

1. INTRODUCTION

Geothermal energy is a clean, renewable and enviromentally benign energy source which is based on the heat in the earth. Geothermal energy is number fourth of the renewable energy sources in world electricity production after hydro, biomass and wind.

Vietnam is a country with an area of 331,689 km^2 situated on the Indochina peninsula and more than 300 thermal springs. There have been some geothermal studies done since 1986 that involve basic surveying such as mapping, sampling and analysic of geothermal water and evaluation for the areas in north and central Vietnam, with the aim of supporting socio-economic development. Until now, geothermal utilization in Vietnam is simple, such as swimming pools, spa treatments and vegetable dehydration.

The aim of this study is about working with geothermal fluid as a part of a surface exploration. During this process, sampling locations are selected, water samples are collected and analysed to find out the chemical composition of the thermal water. Geothermometers and chemical programs are applied on

the data from the analytical results. The interpretation of geochemical data aims at estimating the reservoir temperature, the properties of the geothermal fluids, fluids origin and recharge, and if possible, physical processes such as cooling, boiling or condensation, and geothermal potential of area.

2. GEOLOGICAL BACKGROUND

Vietnam is located in southeast Asia and is a part of the South China plate and Indochina plate. The plate boundary is the Red River fault zone that strikes NW-SE and extends over a length of more than 1000 km between the Gulf of Tonkin and Tibet (Tapponnier et al., 1990).

According to the model of Tapponnier et al. (1986), the whole of Indochina extruded to the southest during the collision of India with Asia. The relationship between Indochina and South China movement along the Red River fault zone has been estimated to be from 330 km (Lacassin et al., 1993) to 500-740 km (Tapponnier et al., 1986, 1990) of left lateral motion during the Tertiary (from 65 Ma to 1.8 Ma).

According to Tran (1995) the territory of Vietnam can be divided into five units as structural blocks consisting of the Northeast (NE), Northwest (NW), Truongson (north center of Vietnam), Kontum (south center of Vietnam) and Nambo blocks (South Vietnam). The NE block includes the stratigraphy and igneous rocks ranging from the Late Proterozoic to Quaternary age, 542 Ma to 1.6 Ma. The NW and Truongson blocks involve the thickest Paleozoic strata in Vietnam which are recognized as NW-SE trending Paleozoic folded systems with some differences in tectonic development between them, especially in the late Paleozoic. The Kontum block is an uplifted massif where the oldest stratigraphy of the Archean is found, but Paleozoic rocks are almost absent. The Nambo block is defined as a continental rift filled with thick (6 km) Cenozoic deposits.

The study area is located in a part of Dienbien and Sonla provinces in the NW block which have abundant active tectonic faults (Figure 1). About 34 hot springs have been discovered in this area with temperatures ranging from 35 to 78°C. The geology of this area is quite complicated with presentation of many types of rock that are structured in NW-SE direction. With regard to geology and tectonics, the region is composed of the following zones:

The Dienbien zone is located southwest of study area which lies along the Vietnam-Laos border in southwest and Songma fault at northeast. Dienbien zone was filled up with volcano clastic and coal-bearing sediments in Triassic age, sandstone, siltstone, silicic, tuff basalt, andesite and limestone in Carbon – Permian age and sandstone, clay schist in Silurian – Devon age. Samples marked S1-S5, S7, S8, S14, S15, S16, S17, S18, S19, S20 and S82 are located in this zone.

The Songma zone belonging to the northwest Vietnam folded system (late Caledonian time), which is located in the southwestern study area, is composed of a femic (mostly ferromagnesian minerals) basement complex. This zone was mixed with ophiolite of an old subduction zone. Samples marked S77, S79, S83, S6, S78, S80, S81, S65, S74 and S75 are located in this zone.

The Songda zone was the rift of Mesozoic time which is located in the northeastern part of the study area. A superimposed depression structure overlaps the Songma zone and comprises a terrigenous-carbonate volcanic complex with a prevalence of porphyritic basalt and carbonate-terrigenous formations. Samples marked S11 and S12 are located in this zone.

The Tule zone is a volcano-tectonic depression formed in Jura-Cretacious time. The bedrocks are alkaline-calcareous and volcano-platonic. The Fansipan mountain ridge which is a part of the Tule zone is a granite-granosyenite intrusion. Samples marked S67, S68, S69, S70, S71, S72 and S73 are located in this zone.
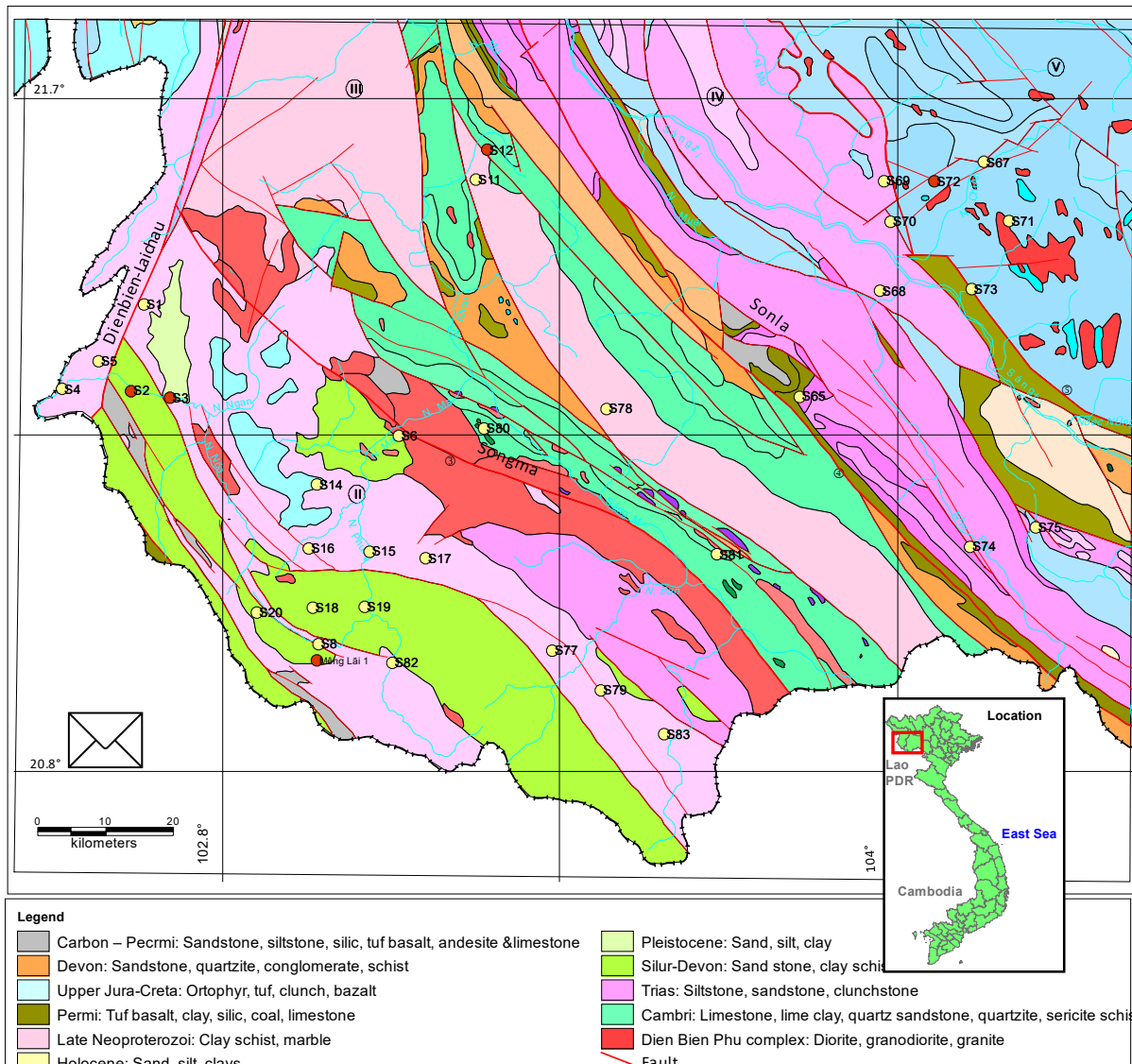
FIGURE 1: Geological map of the study area (modified from VIGMR, 2004), Vietnam map
on the right and samples from S1 to S82 showing on the map

The three main active tectonic faults are the Dienbien-Laichau fault, Songma fault and Sonla fault, where earthquakes are intensively active in this region (Figure 1). The faults and their cataclastic zones are the vents for geothermal heat discharge. Anomalous heat flow is often revealed in the form of thermal springs, which are densely located near the tectonic-zoned faults (Hoang, 1996). The Pomlot (sample S3, Table 1) hot spring which appeared after an earthquake occurred in 1935 is an illustration of this.

TABLE 1: The chemical compositions of the thirty-four thermal springs (mg/l) in the study area (VIGMR, 2004)

"-" = no analysis

No.	Temp. Surf (°C)	pH	TDS	Q (l/s)	Na^+	K^+	Ca^{2+}	Mg^{2+}	SiO_2	Cl^-	B	Li	F	SO_4^{2-}	HCO_3^-	CO_2	NH_4^+	Rb	Mn	del 18O	del D	Charge balance
S1	53,8	7,1	220	1,7	69	4,2	16	6	51,4	4,7	0,02	0,047	0,2	1	238,4	22,5	0,01	0,008	0,11	-9,8	-70,9	4%
S2	78	7,3	410		130,4	15,6	10	1,8	125,8	12,1	0,72	0,244	2,15	81	319,7	-	0,62	0,078	0,04	-9,1	-65,9	-4%
S3	74	6,8	510	0,8	119,3	8,5	46	7,2	66,8	27,6	1,37	0,336	1,3	37,9	518,5	-	1	0,028	0,17	-8,8	-64,8	-9%
S4	57	6,6	260	0,4	104,6	7,1	12	7,2	39,1	6,4	-	-	-	8,9	235,9	2,7	0,01	-	-	-	-	**17%**
S5	37	7,4	220	0,3	111,4	4,6	12	3,6	27,8	6,4	-	-	-	7,4	157,4	27,5	0,01	-	-	-	-	**34%**
S7	37	6,6	870	1	47,4	5,6	208,5	18,3	34,2	6,4	0,12	0,166	0,885	473,8	221,3	22,5	0,01	0,01	0,105	-	-	2%
S8	36,5	6,8	410	0,1	94,7	5,1	67,5	6,3	54,1	11,2	0,215	0,206	0,31	17,2	418,6	25,4	0,01	0,017	0,145	-	-	4%
S14	47	8	900	1	340,6	11,4	18	9,8	-	58,1	-	-	-	23	878,7	-	-	-	-	-	-	1%
S15	43	8	740	0,5	270	8,4	21,9	4	-	30,5	-	-	-	97,5	613,6	-	-	-	-	-	-	2%
S16	38	7,5	210	0,4	29,4	1,4	47,1	4,8	-	33	-	-	-		189,2	-	-	-	-	-	-	0%
S17	30	6	280	2	25	1,2	50,6	22,8	-	11	-	-	-	30,1	277,6	-	-	-	-	-	-	0%
S18	43	6	530	0,2	176,8	12,4	23,1	4,6	60	15,7	-	-	-	9,1	570,5	-	-	-	-	-	-	-2%
S19	46	7,5	430	0,2	135	11,2	23,9	8,6	55	22,7	-	-	-	35,5	389,9	-	-	-	-	-	-	2%
S20	32	6	450	0,5	72	6,2	95,9	7	28	8,1	-	-	-	17,3	482	-	-	-	-	-	-	1%
S82	48,9	8,3	370	0,7	57,1	3,7	55	16,2	18,2	16	-	-	-	25,4	396,5	16,5	0,01	-	-	-	-	-6%
S11	30	7,5	330	0,5	17,4	2,7	54,9	35,6	38	7,6	-	-	-	48	323,3	-	-	-	-	-	-	0%
S12	50,5	7,3	580	0,5	15,3	9,8	124	34,8	58,2	9,2	0,05	0,024	0,4	230	306,6	16,7	0,11	0,024	0,01	-	-	-1%
S67	37	6,8	280	0,2	35,7	6,9	88	30	18,8	8,9	-	-	-	1	219,6	0	0,01	-	-	-	-	**38%**
S68	45,8	7,2	1450	1,6	27,3	4	295	96,6	19	12,8	-	-	-	834	377,7	18,9	0,06	-	-	-	-	0%
S69	41,5	6,9	2000	0,4	32,9	7,1	388	157,2	37,9	11,9	-	-	-	1258	280,6	19,4	0,02	-	-	-8,2	-59,5	4%
S70	44	7,6	1430	0,8	37,4	6,2	380	150	32,6	11	-	-	-	719,4	253,2	8,4	0,02	-	-	-	-	**26%**
S71	36	6,6	590	0,2	72,5	6,8	89	28,2	34,3		-	-	-	244,2	277,8	59	0,02	-	-	-	-	1%
S72	55,5	7,5	740	0,8	100,2	20,8	159	31,8	47,9	17,8	0,36	0,294	1,9	173	470,2	18,5	0,02	0,109	0,015	-8,4	-60,9	13%
S73	55	7,1	4790	1,5	1032	21,3	540	201	44,9	930,2	0,155	0,218	2,675	1885	350,8	29,9	0,01	0,072	0,043	-9,6	-68,3	11%
S77	37	6,8	410	0,2	79,4	5,6	52	14,4	13,4	15,6	-	-	-	107	269,5	24,2	0,01	-	-	-	-	2%
S83	30	6	540	0,3	77,8	2,3	85,5	24	-	15,3	-	-	-	146,1	375,3	-	-	-	-	-	-	0%
S79	38	8,2	350	0,6	25,9	2,2	6	6,6	16,1	55	-	-	-	173,8	158,6	2,2	0,01	-	-	-	-	**-59%**
S6	61,5	7	500	0,1	106,4	9,1	74	15,6	32,7	54	-	-	-	15,2	439,2	6,2	0,01	-	-	-	-	4%
S78	42	7,1	280	0,4	8	0,8	86,5	6,9	19,5	8,3	-	-	-	4,1	332,5	16,3	0,01	-	-	-	-	-5%
S80	34	7,5	910	0,2	278,6	12,4	24	9,4	-	56,7	-	-	-	403,2	244,1	-	-	-	-	-	-	1%
S81	43	6,5	210	0,2	62,5	2,1	9	9,2	-	10,6	-	-	-	25	189,2	-	-	-	-	-	-	1%
S65	40,2	6,5	60	3	4,7	2,5	4,5	6,1	25,9	6	-	-	-	14,3	35,7	2,2	0,1	-	-	-8,7	-61,8	-3%
S74	33	7	670	1,5	92,3	5,6	115,9	23,4	-	21,3	-	-	-	207,8	416,1	-	0	-	-	-	-	1%
S75	34,5	6,7	650	3,8	27,4	3	152	28,8	24,4	6,5	-	-	-	249	372,1	-	0,04	-	-	-	-	-1%

3. CHEMICAL PROPERTIES OF THE GEOTHERMAL WATER

3.1 Sampling and analyses of geothermal waters

One hundred and twenty water samples from hot springs from northwest Vietnam (520 km × 125 km) were collected and analysed in the years 2002-2004 by the geothermal group of Vietnam Institute of Geosciences and Mineral Resources (VIGMR, 2004). It was decided to use some data from VIGMR (2004) but to concentrate on smaller areas in this report to study the chemical characters of geothermal fluid in more detail. Due to the purpose of this study 34 samples were chosen which were spread over a 100 x 165 km area in the north-western part of Vietnam. The surface temperature range for these samples were from 30 to 78°C.

According to Ármannsson and Ólafsson (2006) the various subsamples collected are described in detail in Table 2.

TABLE 2: Treatment and sub-samples from hot springs and hot-water wells
(Ármannsson and Ólafsson, 2006)

Treatment	Container	Specification	To determine
None; amber glass bottle with ground glass stopper	250-300 ml Glass	Ru	pH, CO_2 H_2S (if not in field), conductivity
None	200 ml plastic	Ru	Mg, SiO_2 if < 100 ppm
Dilution; 50 ml of sample added to 50 ml of distilled, deionized water	3x100 ml Plastic	Rd (1:10 to 1:1)	SiO_2 if > 100 ppm
Filtration	200 ml Plastic	Fu	Anions
Filtration; 0.8 ml conc. HNO_3 (Suprapur) added to 200 ml sample	200 ml plastic	Fa	Cations
Filtration; 2 ml 0.2 M $ZnAc_2$ added to sample in 100 ml volumetric glass flask and ≥ 10 ml to ≥ 500 ml bottle containing ≥ 25 mg SO_4 to precipitate sulphide	100 ml, >500 ml Plastic	Fp, Fpi	$SO4$, $\delta^{34}S$ and $\delta^{18}O$ in SO_4
Filtration; one 60 ml and two 1000 ml amber glass bottles	60 ml, 1000 ml Glass	Fui, Fuc, Fut	δ^2H, $\delta^{18}O$, ^{13}C, ^3H

The author of this report has no information about the sampling of this data, but assumes that the major ion concentrations were analyzed by colorimetric, AAS and ICP-AES methods, and the trace elements were analyzed by ICP-MS. Oxigen and hydrogen isotopes were analyzed in New Zealand.

The 34 samples were divided to 5 groups according to the location and structure of geology shown in Table 1.

Group 1 consist of samples S1, S2, S3, S4 and S5 taken in about 20 x 20 km area in the Dienbien zone. This area is the boundary between the highland and lowland and is an active fault zone. The S2, S3, S4, S5 samples are located along the Namron river and the S1 sample was taken beside the Peluong lake.

Group 2 including samples S7, S8, S14, S15, S16, S17, S18, S19, S20 and S82 and are distributed in an area of about 20 x 30 km. This sample group lies on the Dienbien zone as well, but the location is mostly highland and between the small faults in NW-SE direction.

Group 3 includes samples S11, S12 which are located in the Songda zone in the north of study area. This is a small area with the distance between S11 and S12 is about 2 x 3 km.

Group 4 involves samples S67, S68, S69, S70, S71, S72 and S73. They are located in the Tule zone which is spread 20 x 25 km. Most of the samples lie on beside the river shelf.

Group 5 consist of samples S77, S79, S83, S6, S78, S80, S81, S65, S74 and S75. They are all disconnected samples and distributed along in NW-SE direction following the structure of rocks and located in the Songda and Songma zones.

3.2 Chemical composition of the fluids

All of the 34 samples considered are collected from hot springs with temperatures ranging from 30 to 78°C (Table 1). The charge balance can be used to evaluate the analysis (Table 1). The charge balance should be as close to zero as possible, but values between ±15% are used here. Some of the samples were therefore excluded because of the large differences in ionic balance. If the charge balance is higer or lower than ±10% it indicates the erroneous analysis of one of the major ionic species or a missing major ionic species. Five samples, S4, S5, S67, S79, and S70, have charge balance greater than 15%.

Cl-SO₄-HCO₃ diagram
Thermal waters have been classified by a ternary diagram based on the major anion concentrations Cl^-, SO_4^{-2} and HCO_3^- (Figure 2) (Giggenbach 1991). Twenty seven hot springs samples from the study area are plotted on the diagram shown in Figure 2.

According to Giggenbanch (1991) the best suited water samples for geothermometers are comprised of neutral, low sulfate, high chloride geothermal waters along the $Cl-HCO_3$ axis, close to the Cl corner.
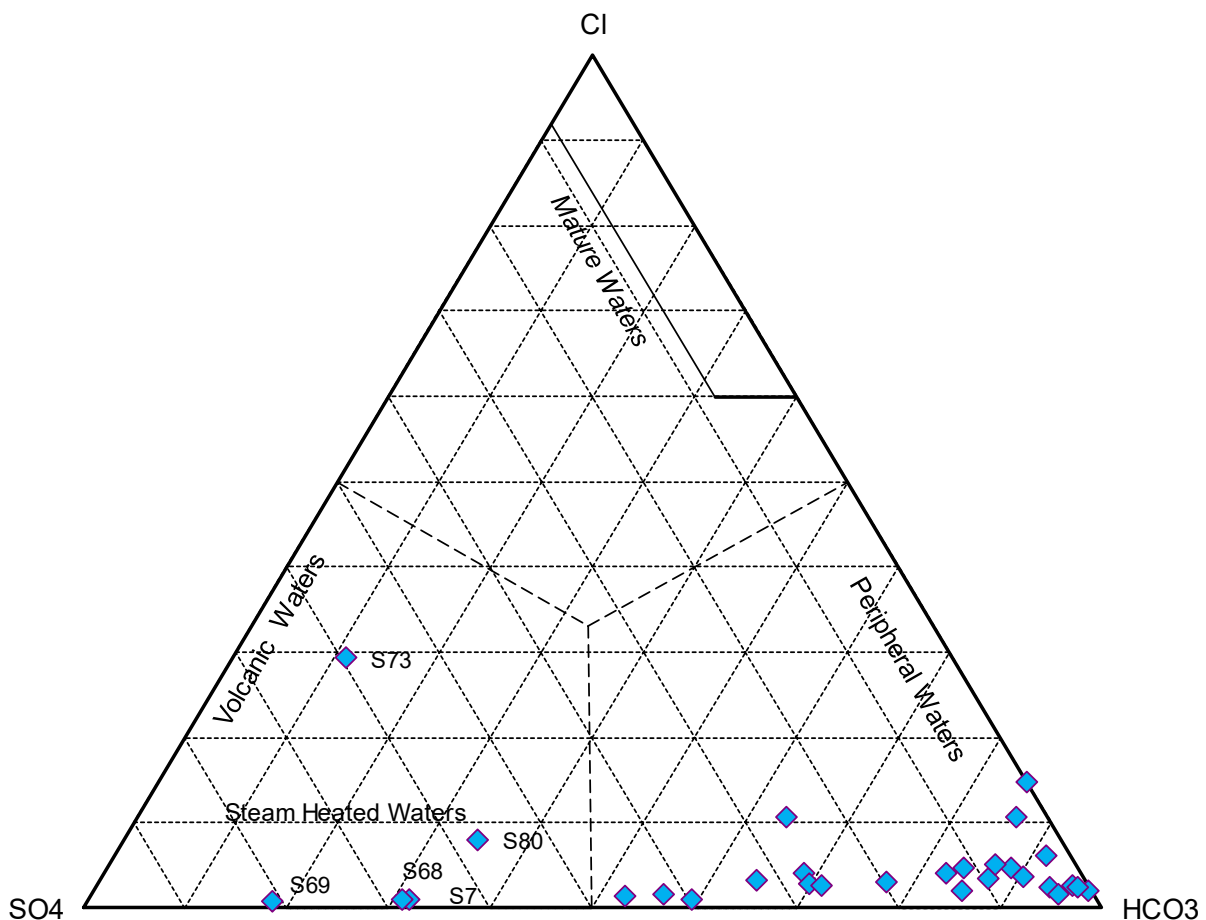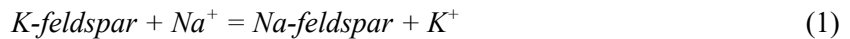

FIGURE 2: The Cl-SO₄-HCO₃ ternary diagram for twenty-seven hot springs samples in study area

The samples from the study area are mainly spread in the HCO_3 corner and a few plot in the steam heated waters part close to the SO_4 corner. This indicates that most of the samples are peripheral waters, where one can use geothermometers. Four samples S7, S69, S68, S73 and S80 which are the steam heated waters, are not suitable for geothermometers according to Giggenbach (1991).

Na-K-Mg diagram
The Na-K-Mg triangular diagram is used to classify water into fully equilibrated, partial equilibrated or immature based on three cations, Na, K and Mg (Figure 3, Giggenbach, 1991). The relationship of the cations are presented in the reactions:

$$K\text{-}feldspar + Na^+ = Na\text{-}feldspar + K^+ \tag{1}$$

and

$$2.8 \, K\text{-}feldspar + 1.6 \, water + Mg^{2+} = 0.8 \, K\text{-}mica + 0.2 \, chlorite + 5.4 \, silica + 2K^+ \tag{2}$$

When we use the geothemometer, most of the problems in their use arise from their application to unsuitable samples. The Na, K and Mg contents of waters in equilibrium with this assemblage are accessible to rigorous evaluation. Tventy seven hot springs samples from the study area are plotted on the Na-K-Mg triangular diagram in Figure 3.
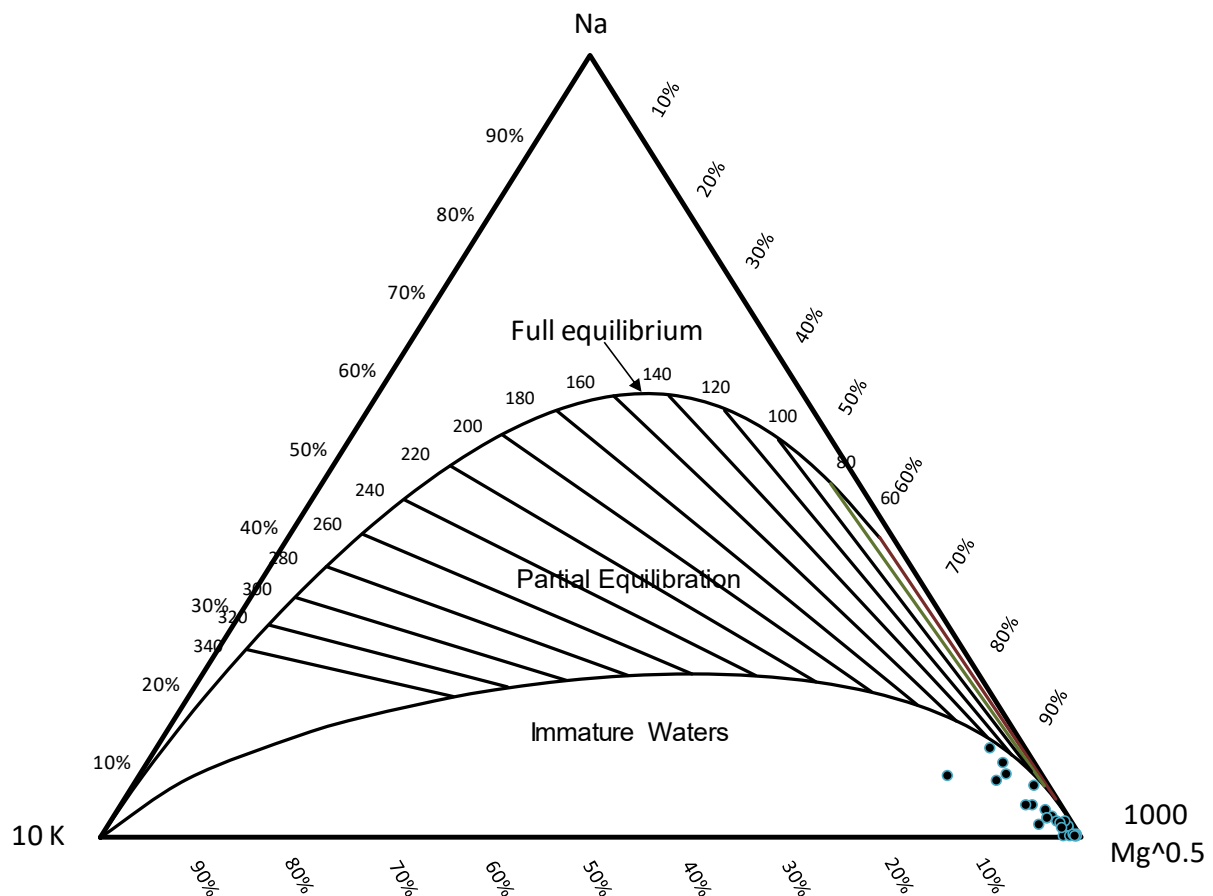
FIGURE 3: The Na-K-Mg triangular diagram for twenty-seven hot springs in study area

Figure 3 shows that most of the samples are placed as immature waters (dissolution of rock with little or no chemical equilibrium) with high Mg content. In this place, samples are frequently quite acid or CO_2 rich waters and therefore according to Giggenbach (1991) the application of both the K-Na and K-Mg geothermometers becomes doubtful.

4. APPLICATION OF GEOTHERMOMETERS

Many water geothermometers have been developed and applied in geothermal fluid study. The water geothermometers can be divided into two main groups. The first group is based on temperature-dependent variations in solubility of individual minerals, and silica minerals are ideal for geothermometry. Second group is based on temperature-dependent exchange reactions which fix ratios of certain dissolved constituents as Na/K geothermometers. The latter ones are complicated and usually calculated by a computer program. In this part the report focuses on the silica geothermometers and cation geothermometers to estimate the reservoir temperatures of study area. Excel spreadsheets by Powell and Cumming (2010) are used to do the calculation and the results are shown in Table 3. The formulas and conditionals are also described in Table 3.

TABLE 3: Reservoir temperatures calculated by various geothermometers

Sample label	Surface temp.	Temperature of reservoir (°C)													
		Amorphous Silica	Alpha Cristobalite	Beta Cristobalite	Chalcedony conductive	Quartz conductive	Quartz adiabatic	Na-K-Ca	Na-K-Ca Mg corr	Na/K Fournier, 1979	Na/K Truesdell, 1976	Na/K Giggenbach, 1988	Na/K Tonani, 1980	Na/K Nieva & Nieva, 1987	Na/K Arnórsson et al., 1983	K/Mg Giggenbach, 1988
S1	53.8	NA	NA	NA	73	103	104	71	61	178	140	196	169	165	149	54
S2	78	NA	100	NA	125	151	144	192	118	233	208	247	246	219	214	100
S3	74	NA	65	18	87	116	115	77	77	190	154	207	185	177	163	67
S8	36.5	NA	55	NA	76	106	106	52	52	169	129	187	158	157	139	58
S14	47	NA	NA	NA	NA	NA	NA	123	NA	138	94	158	118	127	105	71
S15	43	NA	NA	NA	NA	NA	NA	103	85	134	89	154	113	123	100	74
S16	38	NA	NA	NA	NA	NA	NA	NA	16	161	119	179	147	149	130	NA
S17	30	NA	NA	NA	NA	NA	NA	NA	NA	161	120	180	148	149	130	NA
S18	43	NA	60	NA	81	111	110	111	83	188	152	205	183	176	161	82
S19	46	NA	56	NA	77	107	106	103	55	201	168	218	201	189	177	72
S20	32	NA	NA	NA	45	77	81	48	48	204	172	221	205	192	180	61
S82	48.9	NA	NA	NA	NA	60	66	NA	NA	182	145	200	175	170	155	NA
S11	30	NA	39	NA	59	90	92	NA	NA	258	240	270	282	244	245	NA
S12	50.5	NA	59	NA	80	109	109	42	42	453	541	442	634	435	513	53
S71	36	NA	NA	NA	54	86	88	52	52	212	181	227	215	198	189	48
S72	55.5	NA	NA	NA	70	100	101	77	77	289	282	298	330	274	284	71
S77	37	NA	NA	NA	NA	48	56	58	58	189	153	206	184	176	162	51
S83	30	NA	NA	NA	NA	NA	NA	NA	NA	131	85	151	109	120	97	NA
S65	40.2	NA	NA	NA	42	74	78	54	NA	419	483	414	564	402	463	43
S74	33	NA	NA	NA	NA	NA	NA	44	44	178	139	195	169	165	149	46
S75	34.5	NA	NA	NA	39	71	76	NA	NA	225	197	240	234	211	204	NA
S6	61.5	NA	NA	NA	NA	84	86	68	68	204	171	220	205	191	180	NA
S78	42	NA	NA	NA	NA	63	68	NA	NA	217	188	232	223	204	195	NA
S81	43	NA	NA	NA	NA	NA	NA	61	NA	138	94	158	119	127	105	NA

NA - not applicable

4.1 Silica geothermometers

According to Fournier (1991) the solubilities of all silica minerals decrease drastically as temperature decreases below 340°C. The rate of dissolution and precipitation of quartz and amorphous silica change as logarithmic functions of absolute temperature with moderately fast rates at very high temperatures and extremely slow rates at low temperatures (Rimstidt and Barnes, 1980). The silica minerals are formed when the solution becomes saturated.

The formulas for calculating reservoir temperature are based on logarithm of dissolved silica versus the reciprocal of absolute temperature presented below in Equations 3-8, where S refers to the concentration of SiO_2 in mg/l and T is the temperature of reservoir (°C).

Amorphous silica (Fournier, 1977) for 25-250°C

$$T(^oC) = \frac{731}{4.52 - logS} - 273.15 \tag{3}$$

Alpha-Crisobalite (Fournier, 1977):

$$T(^oC) = \frac{1000}{4.78 - logS} - 273.15 \tag{4}$$

Beta-Crisobalite (Fournier, 1991): for 25-250°C

$$T(^oC) = \frac{781}{4.51 - logS} - 273.15 \tag{5}$$

Chalcedony conductive, 0-250°C (Fournier, 1977):

$$T(^oC) = \frac{1032}{4.69 - logS} - 273.15 \tag{6}$$

Quartz conductive (Fournier, 1977) for 25-250°C:

$$T(^oC) = \frac{1309}{5.19 - logS} - 273.15 \tag{7}$$

Quartz, 25-900°C (Fournier and Potter, 1982) adiabatic:

$$T(^oC) = -42.2 + 0.28831S - 3.6686x10^{-4}S^2 + 3.1665x10^{-7}S^3 + 77.034logS \tag{8}$$

Of the 24 sample results obtained from amorphous silica, alpha-crisobalite and beta-crisobalite silica geothermometers give very low temperatures, some of them are lower than surface temperatures, even negative values. In fact, the alpha-crisobalite is a very rare mineral in nature so that the amorphous silica, alpha-crisobalite and beta-crisobalite geothermometers are not suitable in this case.

In the study area, the most of bedrocks are old sedimentary rocks. According to D'Amore and Arnórsson (2000) in mature sedimentary rock, which contain less reactive minerals than volcanic rock, equilibration with quartz may be experienced at temperatures of even less than 100°C. In fact, chalcedony is formed between 0-100°C and quartz is formed at greater than 180°C, but in the old rock where chalcedony tends to becomes quartz after a long time, so it is possible to use both chalcedony and quartz geothermometers.

According to D'Amore and Arnórsson (2000) when calculating temperatures from the silica content of nature water assuming equilibrium with either quartz or chalcedony, the temperatures are termed quartz equilibrium and chalcedony equilibrium temperatures. So in this study case, some geothermal water samples which give temperature of reservoir as less than surface temperature, might not be equilibrium thermal water in silica.

4.2 Cation geothermometers

In the natural systems, there are many different cations of silicates existing in solid solutions, such as Na and Ca in plagioclase and Na, Ca, Mg, K and Li in smectites (clay minerals). The mineral constitution in geothermal solutions depends on the rate of two counteracting processes; dissolution of primary

minerals and precipitation of secondary minerals. Cation geothermometers are based on ion exchange reactions with temperature-dependent equilibrium constants.

The formulas for calculating reservoir temperature by cation geothermometers are described in Equations 9-19 below. Concentrations are in ppm if not otherwise specified.

Na/K/Ca (Fournier and Truesdell, 1973):

$$T(^oC) = \frac{1647}{log\frac{Na}{K} + \beta log\frac{\sqrt{Ca}}{Na} + 2.24} - 273.15 \tag{9}$$

Concentrations are in mol/kg. $\beta = 4/3$ for $t < 100°C$ and $1/3$ for $t > 100°C$ and for $log\frac{\sqrt{Ca}}{Na} < 0$

Na/K/Ca/Mg correction (Fournier and Potter, 1979):
Equation for calculating the Mg correction for the Na-K-Ca geothermometer. Concentrations, C, are in mg/kg.

$$R = \frac{C\ Mg}{C\ Mg + 0.61C\ Ca + 0.31C\ K} \ x\ 100 \tag{10}$$

For R from 5 to 50, the Mg correction (ΔtMg in °C) is:

$$\Delta tMg = 10.66 - 4.7415logR + 325.87(logR)^2 - 1.032x10^5\frac{(logR)^2}{T}$$
$$- 1.968\ x\ 10^7\frac{(logR)^2}{T^2} + 1.605x10^7\frac{(logR)^3}{T^2} \tag{11}$$

The Mg correction is not applied if Δt is negative or $R < 1.5$.

The above Mg correction is applicable only for waters which have a calculated Na-K-Ca temperature of >70°C. If R>50, select the measured spring temperature.

T represents the calculated Na-K-Ca temperature in Kelvin.

For R from 0,5 to 5,

$$\Delta tMg = -1.03 + 59.971logR + 145.05(logR)^2 - 36711\frac{(logR)^2}{T}$$
$$- 1.67\ x\ 10^7\frac{log\ TR}{T^2} \tag{12}$$

Na/K (Fournier, 1979):

$$T(^oC) = \frac{1217}{1.438 + log\frac{Na}{K}} - 273.15 \tag{13}$$

Na/K (Truesdell, 1976) for 100-275°C:

$$T(^oC) = \frac{856}{0.857 + log\frac{Na}{K}} - 273.15 \tag{14}$$

Na/K (Giggenbach, 1988):

$$T(^{O}C) = \frac{1390}{1.75 + log\frac{Na}{K}} - 273.15 \tag{15}$$

Na/K (Tonani, 1980):

$$T(^{O}C) = \frac{833}{0.780 + log\frac{Na}{K}} - 273.15 \tag{16}$$

Na/K (Nieva and Nieva, 1987):

$$T(^{O}C) = \frac{1178}{1.470 + log\frac{Na}{K}} - 273.15 \tag{17}$$

Na/K (Arnórsson et al, 1983) for 25-250°C:

$$T(^{O}C) = \frac{933}{0.993 + log\frac{Na}{K}} - 273.15 \tag{18}$$

K/Mg (Giggenbach, 1988):

$$T(^{O}C) = \frac{4410}{14.0 - log(\frac{K^2}{Mg})} - 273.15 \tag{19}$$

The data from the 24 hot spring samples were calculated using the formulas above and the results are presented in Table 3.

Na-K geothermometers are based on the exchange reaction of albite and K-feldspar and Na and K in aqueous solution. The reaction involved is appropriately expressed as:

$$NaAlSi_3O_8 + K^+ = KalSi_3O_8 + Na^+ \tag{20}$$
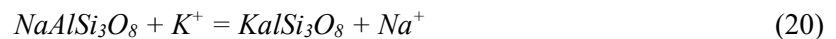
And the equilibrium constant being:

$$K\ alkali\ field = \frac{[Na^+]}{[K^+]} \tag{21}$$

The reservoir temperatures attained from Na/K geothermometers showing in Table 3 indicate that the reservoir temperatures in the study area are quite high. Most of the results give more than 150°C in the reservoir, which will be discussed later.

According to the classification results most of the water samples are immature water and the application of K-Na and K-Mg geothermometers becomes doubtful. Beside that, according to Fournier (1991) the exchange reactions of Na and K between alkali feldspars and solutions proceed very slowly at temperatures below about 300°C. Also, the Na/K geothermometer generally appears to take longer than the silica geothermometer to obtain a new water-rock chemical equilibrium where reservoir temperatures are changing in response to production. There is a tendency to use the Na/K ratio to estimate possible higher temperatures in a deeper part of a system where waters reside for relatively long periods of time. Therefore, K/Na geothermometer might not be suitable to apply in this study case.

The Na-K-Ca geothermometer is based on the exchange reaction of Na^+, K^+, and Ca^{+2} with mineral solid solutions. The geothermometer assumes one type of base exchange reaction at temperatures above about

100°C where exchange involving clay and micas is a major controlling factor in fixing Na-K-Ca concentrations in nature waters.

$$K^+ +\ Na_{2/3}Ca_{1/6}\text{- solid} = (1/6)Ca^{+2} + (2/3)Na^+ + K \text{- solid} \qquad (22)$$
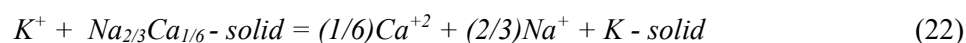
And a different exchange reaction at temperatures below about 100°C,

$$K^+ + (1/3)Na^+ + Ca_{2/3}\text{-solid} = (2/3)Ca^{+2} + KNa_{1/3}\text{-solid} \qquad (23)$$
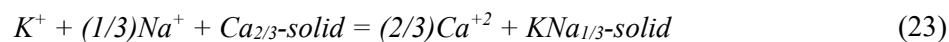
The general form of both of the above reactions is

$$log\ K_{eq} = log\ (Na/K) + \beta log\ (\sqrt{Ca}/Na) \qquad (24)$$

where $\beta = 4/3$ for $t < 100°C$ and $1/3$ for $t > 100°C$ and for $log\frac{\sqrt{Ca}}{Na} < 0$.

According to Fournier (1991) Na-K-Ca geothermometer is entirely empirical and will give excellent results for most water above 200°C but also give erratic results for water at less than 200°C. The erratic results are affected by exchange reactions involving Na^+, K^+, or Ca^{+2} with additional ions as Mg and precipitation of calcium as carbonate where solutions boil on the way from the reservoir to the surface.

Table 3 shows that the reservoir temperatures obtained by Na-K-Ca geothermometer are less than 200°C, most of them even less than 100°C. Besides that, the Mg content in most of sample quite high, therefore the results may be erratic and it should be checked by the Mg correction for the Na-K-Ca geothermometer.

According to the water classification in the Na-K-Mg triangular diagram by Giggenbach (1991) in chapter 3, most of the water samples in study area are high in Mg content and quite acid or CO_2 rich waters. They should be applied with the Mg correction for Na-K-Ca geothermometer.

According to Fournier (1991) Mg correction is applicable only for water which have calculated Na-K-Ca temperatures > 70°C. Therefore, from Table 3 there are samples S1, S2, S3, S14, S15, S18, S19, S72 with Na-K-Ca temperature greater than 70°C and also they have calculated R from 5 to 50, so it is possible to apply the Mg correction geothermometer. The results are shown in Table 4.

TABLE 4: Reservoir temperatures calculated by Na-K-Ca Mg correction

Sample label	S1	S2	S3	S14	S15	S18	S19	S72
Surface temp.	53.8	78	74	47	43	43	46	55.5
R	35	14	19	40	20	20	32	24
Na-K-Ca	71	192	77	123	103	111	103	77
Na-K-Ca Mg corr.	61	118	77	35	85	83	55	77

Calculation of R - see Equation 10

Most of results might be acceptable, except S14 where subsurface temperature is lower than surface temperature.

K/Mg geothermometers (Giggenbach, 1988) are based on the calculation for various temperatures the relative concentrations of K^+ and Mg^{2+} that would be in equilibrium with the mineral assemblage K-feldspar, clinochlore and muscovite. The results of the calculated temperature are shown in Table 3 and will be discussed later.

5. PROCESSES AFFECTING FLUID COMPOSITIONS

The geothermal water ascending from the reservoir to the surface may cool by some processes such as conduction of heat to surrounding rock, mixing with colder water or boiling and therefore losing steam. The chemical and physical characteristics of fluid compositions may support some information about conditions in the reservoir.

5.1 Conductive cooling

The slowly ascending geothermal water with low flows may lose heat by conduction. Calculations show that a flow of 26 kg/min (0.43 l/s) would cool conductively from 200 to 100°C during a vertical ascent from a depth of 1000 m with an initial linear temperature gradient from the reservoir to the surface (Truesdell, 1991). Also flows are no more than 8 kg/min (0.133 l/s) from shallower reservoirs of about 300 m during vertical ascent to the surface. Some chemical components are effected by conductive cooling process such as isotopic content, K and Mg.

Table 5 shows the flow rate (Q) of hot springs in the study area compared with calculations of Truesdell, 1991).

TABLE 5: The flow rate of hot springs in study area comparing with calculations of Truesdell, 1991

Q (l/s)	<0.133	0.133 <Q<0.43	>0.43
Sample	S8, S6	S4, S5, S16, S18, S19, S67, S69, S71, S77, S83, S78, S80, S81	S1, S2, S3, S7, S14, S15, S17, S20, S82, S11, S12, S68, S70, S72, S73, S79, S65, S74, S75

There are 15 samples, with flow rate being less than 0.43 l/s that are effected by conductive cooling. The other 19 samples with a flow rate more than 0.43 l/s may be less effected by conductive cooling process.

5.2 Mixing with colder water

The geothermal water may be mixed with cold water in the upflow zone on the way to discharge at the surface. The geothermal water is characteried by chemical equilibrium conditions in solutions but cold water composition is determined by the kinetics of the leaching process (Truesdell, 1991). These characteristics may be used to quantify the mixing and estimate conditions in the reservoir.

There are some indications of mixing in a solution which is based on the relations between chloride, boron, SO_4^{-2} and $\delta^{18}O$, δD, SiO_2 and so on.

The Cl-SO_4-HCO_3 ternary diagram and the Na-K-Mg triangular diagram by Giggenbach (1991) above show that most of the samples in study area are immature water so they might be mixed with cold water.

The linear relations between chloride and boron or δD and $\delta^{18}O$ constitutes are used as the main evidence for mixing. Chloride and boron concentrations are variable, and as a rule, higher in geothermal water and low in cold water but the Cl/B ratio is stable even in mixing water (Arnórsson, 1985). Only 8 samples in the study area have both Cl and B content (samples S1, S2, S3, S7, S8, S12, S72 and S73). The relationship between Cl and B is shown in Figure 4.

In the study area there are some results of cold water analysis but boron has not been analysed. If mixing of geothermal water with cold water is responsible for variable chloride concentration, it is to be expected that intersection at 0 ppm boron of line through the data points is in the range of 10 ppm
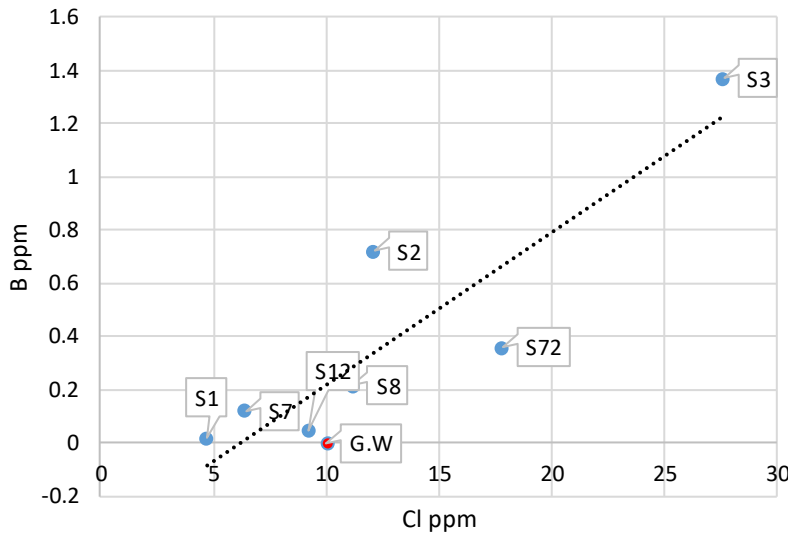
FIGURE 4: The relationship between Cl and B in warm springs
in study area, red dot is groundwater sample

chloride as cold water contains chloride in that range and less than 0.01 ppm boron (Arnórsson, 1985). Figure 4 shows that both chloride and boron concentrations in these samples are very low. Sample 73 is an anomaly compared to the other and cannot been explained right now.

Figure 4 shows that the intersection of the regression line through the data points at 0 ppm boron corresponds with 6 ppm chloride. The mixing evidence showing in Figure 4 is not very clear.

The relationship between δD and δ¹⁸O values for the thermal water and non-thermal water can give some information about mixing processes. Figure 5 shows the relationship between δD and δ¹⁸O. Of 27 samples there are 7 samples which have isotope analysis results, consisting of S1, S2, S3, S69, S72, S65, and S73. Figure 5 above shows that all of them are in the meteoric trend line and none are on the mixing line.
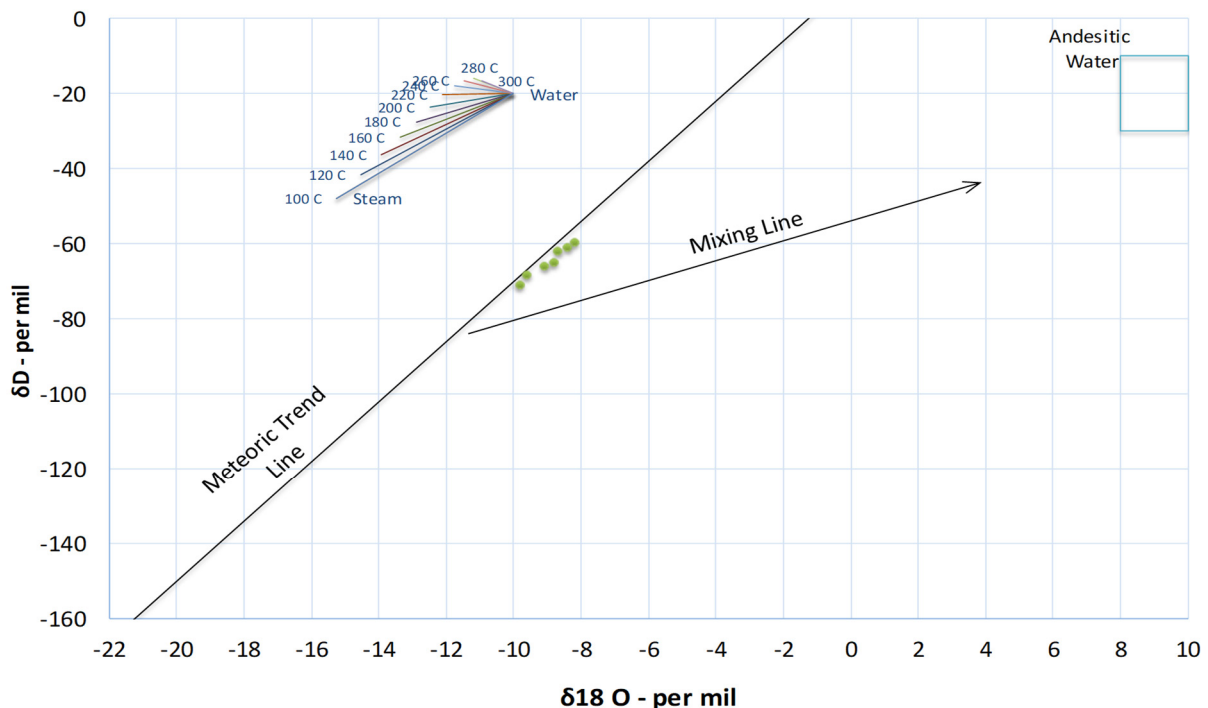
FIGURE 5: The relationship between δD and δ¹⁸O

Magnesium levels are usually very low in high-temperature geothermal fluids, about 0.01-0.1 mg/kg (Nicholson, 1993). In the high-temperature fluid, Mg is readily associated into secondary alteration minerals such as illite, montmorillonite and especially chlorite. Higher Mg concentrations in thermal fluid can either indicate leaching of Mg from the local rock or dilution by ground water which has much higher Mg concentration.

Of the 27 samples, Mg content in warm springs are in a range of 6.1-201 mg/l. According to the result of groundwater analysis in the same area shown in Table 6 it can be seen that Mg content in samples S1, S7, S8, S14, and S20 is quite similar with Mg content in groundwater, some are even higher (S11, S12). Table 6 shows that the thermal fluid of some warm springs in study area might be diluted by groundwater.

TABLE 6: Chemical compositions of groundwater in the study area. Sample location show groundwater located closely with some thermal water (VIGMR, 2009)

Sample	pH	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	Fe^{3+}	Al^{3+}	HCO_3^-	Cl^-	SO_4	Sample location
LK06-DB	7.8	6.3	2.21	23.8	4.89	-	0.35	0.05	109.2	7.1	0.01	S11, S12
LK07-DB	7.65	14.81	12.66	22.09	12.11	-	0.04	0.01	175.7	3.55	0.67	S1
LK08-DB	7.15	39.46	23.47	24	9.6	0.03	8.36	0.297	140.3	11.4	0.63	S1
LK09-DB	7.18	33.29	34.2	16	12	0.018	0.392	0.243	140.3	10.4	1.39	S1
LK10-DB	9.06	63.07	25.38	40	22.8	0.06	3.914	0.297	140	17.7	23.5	S7, S8, S20
LK11-DB	9.19	69.42	27.19	36	18	0.017	0.059	0.297	170.8	7.38	1.25	S7, S8, S20
LK12-DB	9.17	40.83	27.85	14	7.2	0.02	2.078	0.297	146.4	7.09	1.75	S14
LK13-DB	8.1	46.67	27.86	16	25.2	0.017	1.134	0.253	109.8	7.15	1.63	S14

"–" no analysis

6. APPLICATION OF CHEMICAL PROGRAMS

In the geothermal solution, the activity distribution between various aqueous species and minerals is described by the equilibrium constant (K). The formation of minerals is dependent on many factors such as temperature, pressure of reservoir, activity of components or more generally enthalpy and entropy in reservoir. The mineral saturation index is calculated to give the information about dissolving forming or at equilibrium of minerals. The saturation index is defined by

$$SI = log(Q/K) \qquad (25)$$

where *K* is the solubility product and *Q* is the ion activity product.

If the SI value is greater than zero (supersaturation) the mineral may form and if the value is less than zero (undersaturation) the mineral may dissolve. If the value equals to zero the system is stable.

Reed and Spycher (1984) have presented a different approach geothermometer by using the numerical value of log (Q/K) calculated at different temperature. This method evaluates the saturation index of water of a specific composition with a large number of minerals at particular temperature, at which the water has equilibrated. Moreover, the mineral assemblage and temperature of equilibration of hot springs may be determined based on the convergence of log (Q/K) curves for the equilibrium assemblage to zero at temperature of equilibration. The effects of boiling, dilution, temperature variations and lack equilibrium are also described in this method.

The program WATCH version 2.4 (Arnórsson et al., 1982; Bjarnason, 2010) is applied in this case to compute species concentrations, activities and solubility products for minerals when the equilibrated fluids are cooled conductively from the reference temperature to a lower temperature. Nine samples in the study area, which have pretty good estimation of reservoir temperature by quartz geothermometer, are chosen to apply this method consisting of samples No. S1, S2 S3, S8, S18, S19, S11, S12 and S72. In WATCH the samples are cooled conductively from reservoir temperature with reference temperature calculated by quartz geothermometer. The value of log (Q/K) for minerals are obtained from log Q and log K calculation. The diagram of log (Q/K) versus temperature for minerals assemblage of 9 samples is shown in Figure 6.
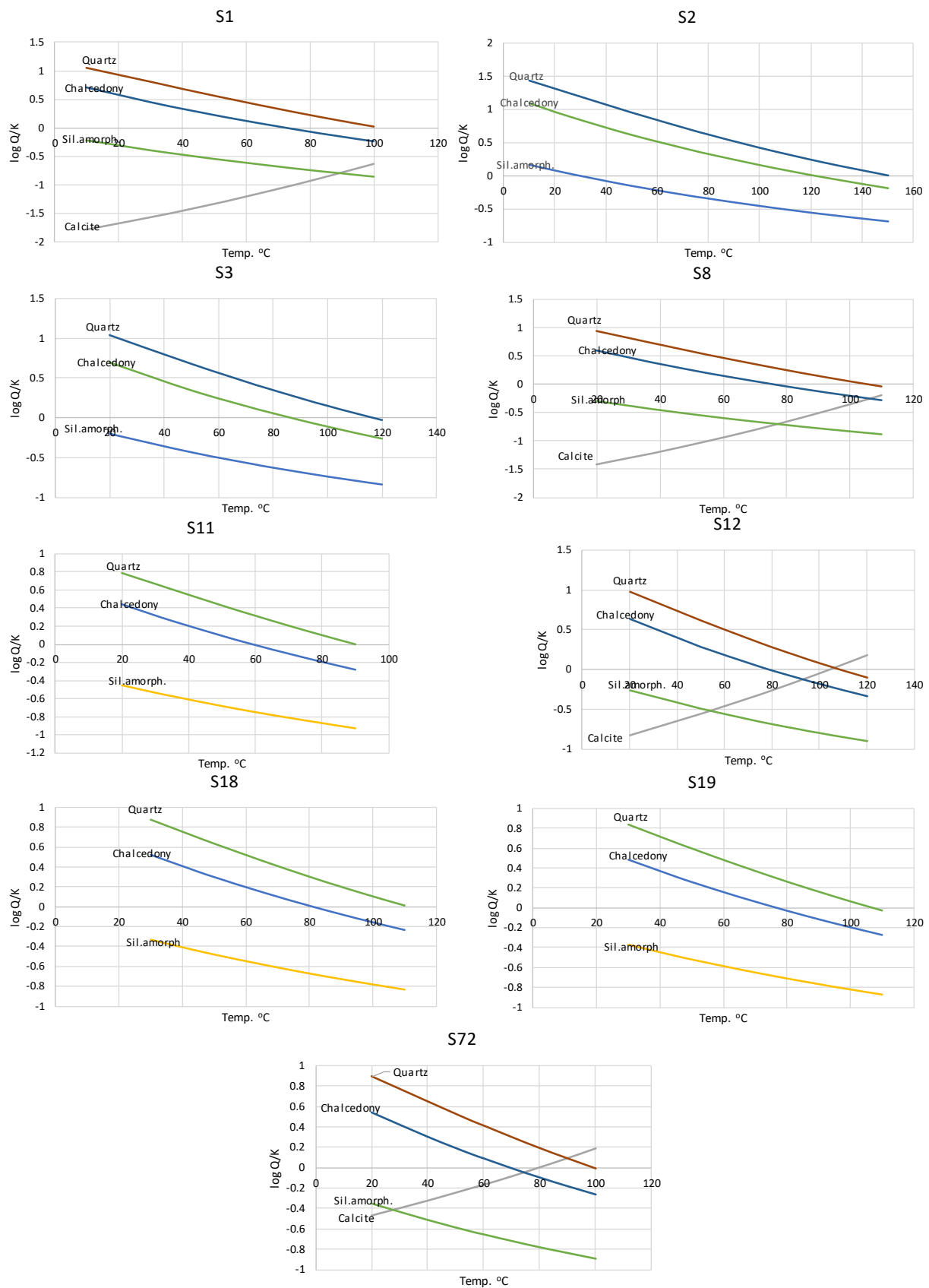
FIGURE 6: The diagram of log (Q/K) versus temperature for minerals assemblage of 9 samples
(S1, S2, S3, S8, S18, S19, S11, S12, S72)

According to Reed and Spycher (1984), it is ideal when the log (Q/K) curve of mineral assemblage converges at zero line, the system is stable and the corresponded temperature will be the reservoir temperature. If the convergence point is above the zero line, the water may be boiling and the water is diluted when the convergence point is below the zero line. There are some other effects such as inaccurate water analyses, and poor thermodynamic data for minerals and aqueous ions and complexes which lead to dispersion on such plots and cloud geologic interpretations.

The calculations illustrate in Figure 6 nine simple diagrams. Figure 6 shows that solutions are in equilibrium in temperature forming chalcedony or quartz minerals. In the S1 diagram shows that the reservoir is in equilibrium with chalcedony at ~75°C and quartz around 100°C. These results are similar to the chalcedony and the quartz geothermometers by Fournier 1977 (formulas 6 and 7 and shown in table 3) which gives 73°C and 103°C respectively. In the S2 diagram, the reservoir temperature is estimated between 120-150°C basing on the equilibrium of chalcedony and quartz and the water is mixed slightly. Similarly, in the S3 plot, the temperature of reservoir is estimated from 85 to 120°C and there is a mixing in this water. The S8 plot shows that the temperature of reservoir ranges from 80 to 110°C and water is diluted slightly. In S18, there are only two curves, quartz and chalcedony are intersection the zero line but the chalcedony curve is closer to the zero line than the quartz curve so the temperature of reservoir will be 80°C. The S19 sample shows that the reservoir temperature is about 100-110°C and water is slightly diluted. In S11 the plot is similar to S18, reservoir temperature is 60°C. The S12 plot shows that temperature of reservoir ranges from 57 to 110°C but at 57°C the water is diluted. In the S72 diagram, the temperature of reservoir is between 60-90°C.

7. DISCUSSION AND CONCLUSIONS

The main aim of this project is to use geothermal fluids as a part of surface exploration. The author chose 34 of 119 samples to study based on location of hot springs which are spread over a 100 x 165 km area in the north-western part of Vietnam. Most of the bedrock in the study area is old sedimentary rock, and some tuff, basalt and granite rocks. There are manifestations of active tectonics and a lot of fractures have been formed which are vents for hot spring discharge.

The thirty four hot springs with temperatures ranging from 35 to 78°C have been divided into five groups based on the location. The silica content in most of the samples is very low, only 7 samples have silica concentration greater than 50 mg/l (samples marked S1, S2, S3, S8, S18, S19, and S12). The Mg content in most of the samples are very high, ranging between 1.6-35.6 mg/l, some samples from 96.6 to 157.2 mg/l. Sample S73 has high Cl content (930 mg/l) and TDS (4790 mg/l) even though this area is far from sea.

Using $Cl-SO_4-HCO_3$ ternary Giggenbach (1991) diagram for classifing water showed that most of the samples are the peripheral waters. Geothermometers can be used for these waters except for the steam heated samples S7, S69, S68, and S80. The Na-K-Mg triangular diagram shows that all of the waters are immature waters, which are dissolution of rock with little or no chemical equilibrium so the application of both the K-Na and K-Mg geothermometers becomes doubtful.

For calculation of reservoir temperature, 15 geothermometers are used including silica and cation geothermometers as presented above. The results of cation geothermometers show that it is really doubtful when most of samples give very high temperature values. Na/K geothermometers are based on the equilibrium constant, so when the water is immature, it is impossible to apply Na/K geothermometers. On the other hand, (22) and (23) reactions usually happen in high temperature conditions and magma rock, so Na/K geothermometers cannot be used in this study area. The Mg-K geothermometer is responding extremely fast to temperature changes and normally reflects a very recent temperature, pretty often the surface temperature of the spring and this is illustrated in Table 3, where the results of K/Mg geothermometer of samples S1, S2, S3, S8, S12, S14, S15, S18, S19, S20, S65, S71,

S72, S74, and S77 give similar temperatures to surface temperatures. As explained above, chalcedony and quartz geothermometers, and some of the results in Na-K-Ca-Mg correction (S1, S2, S3, S15, S18, S19, S72), can be used for estimation of reservoir temperature. The results are shown in Table 3.

According to Figures 4 and 5 and Table 6 there is no evidence of mixing with groundwater in the samples. Maybe there were some mistakes in the sampling process or the water was diluted without re-equilibrium, but using log Q/K diagram, there were some samples that were diluted slightly.

As presented above the temperature of the reservoir can be estimated by plotting the log Q/K value of various minerals in equilibrium of solution in the reservoir and these diagrams can also be used to explain some of the processes affecting fluid compositions. Because the data lacks some information such as isotope elements for most of the samples, and/or maybe there were some mistakes in sampling and analysis process, it is not likely that one can interpret all the samples.

Below are the results of this work and it is summarised in Table 7.

Group 1 (S1, S2, S3, S4, S5) is in the western of part of the study area, spread about 20 km x 20 km. This group consisted of five samples with temperature range 54-78°C, SiO_2 concentration ranging from 28-126 mg/l, Mg concentrations from 1.8 to 7.2 mg/l and Cl concentrations from 4.7 to 28 mg/l. Two of the samples have a charge balance 17% (S4) and 34% (S5) which are too high and therefore these samples have not be used in this study. All the samples are most likely in equilibrium with quartz as indicated by the main rocks in the area, which are siltstone, sandstone and clay schist which are mainly composed of quartz and chalcedony. Therefore, quartz and chalcedony geothermometers by Fournier (1977) are the most suitable.

Group 2 (S7, S8, S14, S16, S15, S17, S18, S19, S20, S82) is south of Group 1, spread over 20 km x 30 km. The charge balances are lower but in five of the samples (S14, S15, S16, and S17) silica has not been analysed. Sample 7 is steam heated water and is not included in the study. Temperature of this group ranges between 30-49°C, with Cl contents from 6.4 to 58.1 mg/l and Mg concentrations are from 4 to 22.8 mg/l. The bedrocks in this group include clay schist, siltstone, and sandstone which are mainly formed of chalcedony and quartz so chalcedony and quartz geothermometers are the most suitable.

Group 3 includes only two samples, S11 and S12, in the northern part of the study area and they are located in a small square about 2 km x 3 km. Temperature measured 30 and 50.5°C, SiO_2 concentrations are 38 and 58.2 mg/l, Cl concentrations are 7.6 and 9.2 mg/l and Mg concentrations are 34.8 and 35.6 mg/l, which is quite high. The bedrock in this area is clay schist, limestone, lime clay, quartz sandstone, quartzite, sericite schist which are mainly composed of quartz, chalcedony, chlorite, and calcite, and as in other groups quartz and chalcedony geothermometers are most suitable.

Group 4 (S67, S68, S69, S70, S71, S72, S73) in the east of part of the study area, spread in 20 km x 25 km. This group includes 7 samples but two of them (S67 and S70) have too high charge balance (38% and 26%), charge balance of S72 and S73 are 13% and 11% but will be used. The SiO_2 concentration is ranging from 18.8 to 47.9 mg/l and Cl concentration range between 7.1-54 mg/l with the exception of sample S73 where the concentration is 930 mg/l. The bedrock in this area is siltstone, sandstone, diorite, granodiorite, granite, tuff, basalt, trachyte, silica, coal and limestone which are mainly composed of quartz, chalcedony, and K-feldspar. Therefore, quartz and chalcedony geothermometer are the most suitable.

Group 5 consist of (S77, S79, S83, S6, S78, S80, S81, S65, S74, S75) and the samples are scattered and distributed along in northwest-southeast direction of the study area. The charge balance of most of the samples are good except sample S79 which will not be included here. SiO_2 concentration of samples S74, S80, S81, and S83 was not analysed and therefore these samples are not included in this work. Temperature ranges from 30 to 61.5°C with the Cl concentrations ranging from 6 to 56 mg/l and Mg concentration ranges from 6.1 to 28.8 mg/l. The bedrocks in this area are sandstone, clay schist, diorite,

TABLE 7: Summary of samples used in this study showing among other things reservoir temperature calculated by chalcedony and quartz geothermometers, log Q/K, water classification, bedrock composition and main minerals in host rock

Sample	Temp. surf (°C)	Temp. of geothermometers in °C			Classif.	Mixing*	Bedrocks	Minerals
		Chalcedony	Quartz	Log Q/K				
S1	53.8	73	103		Peripheral waters	Diluted slightly	Siltstone, sandstone	Quartz, chalcedony
S2	78	125	151	120-150	Peripheral waters	Diluted slightly	Sandstone, clay schist	Quartz, chalcedony
S3	74	87	116	80-120	Peripheral waters	Diluted slightly	Siltstone, sandstone	Quartz, chalcedony
S7	37	54	85	NA	Steam heated waters	NA	Sandstone, clay schist	Quartz, chalcedony
S8	36.5	76	106	80-110	Peripheral waters	No mixing	Siltstone, sandstone	Quartz, chalcedony
S18	43	81	111	80	Peripheral waters	No mixing	Sandstone, clay schist	Quartz, chalcedony
S19	46	77	107	100-110	Peripheral waters	Diluted slightly	Sandstone, clay schist	Quartz, chalcedony
S20	32	45	77	NA	Peripheral waters	NA	Sandstone, clay schist	Quartz, chalcedony
S82	48.9	NA	60	NA	Peripheral waters	NA	Siltstone, sandstone	Quartz, chalcedony
S11	30	59	90	60	Peripheral waters	No mixing	Clay schist, marble	Quartz, chalcedony
S12	50.5	80	109	57-110	Peripheral waters	Diluted slightly	Limestone, lime clay, quartz sandstone, schist, quartzite, sericite	Quartz, chalcedony, chlorite, calcite
S68	45.8	NA	62	NA	Steam heated waters	NA	Siltstone, sandstone, clunchstone	Quartz, chalcedony
S69	41.5	59	90	NA	Steam heated waters	NA	Siltstone, sandstone	Quartz, chalcedony
S71	36	54	86	NA	Peripheral waters	NA	Diorite, granodiorite, granite	Quartz
S72	55.5	70	100	60-90	Peripheral waters	No mixing	Tuff, basalt, trachyte	Quartz, chalcedony, K-feldspar
S73	55	NA	NA	NA	Steam heated waters	NA	Tuff basalt, clay, silic, coal, limestone	Quartz, chalcedony
S77	37	NA	48	NA	Peripheral waters	NA	Sandstone, clay schist	Quartz, chalcedony
S6	61.5	NA	84	NA	Peripheral waters	NA	Diorite, granodiorite, granite	Quartz, andesine, hornblende, K-feldspar, biotite, plagioclase
S78	42	NA	63	NA	Peripheral waters	NA	Clay schist, marble	Quartz, chalcedony
S65	40.2	42	74	NA	Peripheral waters	NA	Tuff basalt, clay, silica, coal, limestone	Quartz, calcite chalcedony
S75	34.5	39	71	NA	Peripheral waters	NA	Tuff, basalt, trachyte	Quartz, chalcedony, K-feldspar

* Most mixing information based on Reed and Spycher (1984)

granodiorite, granite, basalt tuff, trachyte, coal, limestone which are mainly composed of quartz, chalcedony, andesine, hornblende, plagioclase, K-feldspar, and biotite. The quartz and chalcedony geothermometers might be used in this group but it gives quite low temperature estimate.

Table 7 summarizes samples used in this study and shows among other things reservoir temperature calculated by chalcedony and quartz geothermometers, log Q/K, water classification, bedrock composition and main minerals in host rock.

8. RECOMMENDATIONS

The studying of geothermal fluid is a part of a surface exploration. During this process, sampling and analysis play very important roles and it affects the research result directly. Therefore, the sampling procedures should be standard and the equipment should be sufficient in both of number and quality for collecting samples. Chemical components of hot water should be analysed adequately (major elements as well as metal and trace elements) including special stable isotopes which help to evaluate the origin and age of hot water. It is best to work with samples from boreholes.

The discharge zone of hot springs should be described carefully and photographed to have a prospect view when estimating potential of reservoirs. When drilling, cuttings should be collected, and thin sections from drill cuttings should be sampled to see the mineral assemblage in the subsurface.

It is important that thermal springs are studied in great detail with all the available methods in order to better estimate their potential for energy production.

REFERENCES

Arnórsson, S., 1985: The use of mixing models and chemical geothermometers for estimating underground temperature in geothermal systems. *J. Volc. Geotherm. Res., 23,* 299-335.

Arnórsson, S., Gunnlaugsson, E., and Svavarsson, H., 1983: The chemistry of geothermal waters in Iceland III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta, 47*, 567-577.

Arnórsson, S., Sigurdsson, S., and Svavarsson, H., 1982: The chemistry of geothermal waters in Iceland I. Calculation of aqueous speciation from 0°C to 370°C. *Geochim. Cosmochim. Acta, 46,* 1513-1532.

Ármannsson, H., and Ólafsson, M., 2006: *Collection of geothermal fluids for chemical analysis*. ÍSOR – Iceland GeoSurvey, report, ÍSOR-2006/016, 17 pp.

Bjarnason, J.Ö., 2010: *The speciation program WATCH, version 2.4.* Orkustofnun, Reykjavik, 9 pp.

D'Amore, F., and Arnórsson, S., 2000: Geothermometry. In: Arnórsson, S.(ed.), *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 152-198.

Fournier, R.O., 1977: Chemical geothermometers and mixing models for geothermal systems. *Geothermics,* 5, 41-50.

Fournier, R.O., 1979: A revised equation for the Na/K geothermometer. *Geothermal Resources Council, Transactions*, *3,* 221-224.

Fournier, R.O., 1991: Water geothermometers applied to geothermal energy. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 37-69.

Fournier, R.O., and Potter, R.W. II, 1979: Magnesium correction to the Na-K-Ca geothermometer. *Geochim. Cosmochim. Acta, 43,* 1543-1550.

Fournier, R.O., and Potter, R.W. II, 1982: A revised and expanded silica (quartz) geothermometer. *Geoth. Res. Council, Bull., 11-10*, 3-12.

Fournier, R.O., and Truesdell, A.H., 1973: An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta*, *37,* 1255-1275.

Giggenbach, W.F., 1988: Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta, 52*, 2749-2765.

Giggenbach, W.F., 1991: Chemical techniques in geothermal exploration. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 119-144.

Hoang, H.Q., 1996: General evaluation of geothermal potential in the tectonic setting of Vietnam. *Geothermal Resources Council, Bulletin*, 63-76.

Lacassin, R., Leloup, P.H., and Tapponnier, P., 1993: Bounds on strain in large Tertiary shear zones of SE Asia from boudinage restoration. *J. Structural Geology, 15,* 677-692.

Nicholson, K., 1993: *Geothermal fluids: chemistry and exploration techniques.* Springer-Verlag, Berlin, 268 pp.

Nieva, D., and Nieva, R., 1987: Developments in geothermal energy in Mexico, part 12-A: Cationic composition geothermometer for prospection of geothermal resources. *Heat Recovery Systems and CHP, 7,* 243-258.

Powell, T., and Cumming, W., 2010: Spreadsheets for geothermal water and gas geochemistry. *Proceedings of the 35th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA,* 10 pp.

Reed, M.H., and Spycher, N.F., 1984: Calculation of pH and mineral equilibria in hydrothermal water with application to geothermometry and studies of boiling and dilution. *Geochim. Cosmochim. Acta, 48*, 1479-1490.

Rimstidt, J.D., and Barnes, H.L., 1980: The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta, 44*, 1683-1699.

Tapponnier, P., Lacassin, R., Leloup, P.H., Sharer, U., Zhong, D., Wu, J., Liu, X., Ji, S., Zhang, L., and Zhong, J., 1990: The Ailao Shan Red River metamorphic belt: Tertiary left-lateral shear between Sundaland and South China. *Nature, 343*, 431 - 437.

Tapponnier, P., Peltzer, G., and Armijo, R., 1986: On the mechanics of the collision between India and Asia. In: Coward, M.P., and Ries, A.C., (eds.), *Collision Tectonics*. Geological Society, London, Special Publications, 19, 115-157.

Tonani, F., 1980: Some remarks on the application of geochemical techniques in geothermal exploration. *Proceedings, Adv. Eur. Geoth. Res., 2nd Symposium, Strasbourg*, 428-443.

Tran, N.N., 1995: The geology of Vietnam: A brief summary and problems. *Geosci. Repts. Shizuoka Univ., 22,* 1-10.

Truesdell, A.H., 1976: Summary of section III - geochemical techniques in exploration. *Proceedings of the 2nd U.N. Symposium on the Development and Use of Geothermal Resources, San Francisco, 1,* liii-lxxix.

Truesdell, A.H., 1991: Effects of physical processes on geothermal fluids. In: D'Amore, F. (coordinator), *Application of geochemistry in geothermal reservoir development.* UNITAR/UNDP publication, Rome, 71-92.

VIGMR, 2004: *Research and evaluation of geothermal potential in the North-west of Northern Plain, Vietnam with the aim to support for the socio-economic development*. Vietnam Institute of Geosciences and Mineral Resources (VIGMR), Hanoi, Vietnam, Geothermal Resource Assessment Project, internal report, 179 pp.

VIGMR, 2009: *Analysis data, research and evaluation of groundwater resources in the Northwest and Central, Vietnam.* Vietnam Institute of Geosciences and Mineral Resources (VIGMR), Hanoi, Vietnam, internal report.