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APPLICATION OF CHEMICAL GEOTHERMOMETERS TO LOW TEMPERATURE FIELDS IN SOUTHERN BULGARIA

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ABSTRACT

Bulgaria is quite rich in thermal waters with temperatures between 20 and 100°C. In Southern Bulgaria there are more than 600 hot springs and wells in about 120 localities. This report made use of 203 chemical analyses from different hot springs and wells. The chemical composition of the thermal waters from 18 fields were interpreted by chemical geothermometers. Four fields, Burgas, Kazanlak, Razlog and Sofia, were selected as suitable areas for interpretation of all samples.

The main results of this report are predicted temperatures for about 200 samples using various quantitative chemical geothermometers (chalcedony, Na-K, Na-Li, Na-K-Ca and K-Mg). Chemical equilibrium calculations were made using the computer programme WATCH and plotting the log(Q/K) diagram. It was found that water with temperatures 10-20°C higher than are now found, could be obtained by drilling in several areas in Southern Bulgaria. It is likely that about 10% of the geothermal occurrences could be used directly for heating because they have temperatures above 70°C. This might mean expanded utilization of hot water in Southern Bulgaria, which at present is used directly and indirectly in spas, swimming pools, greenhouses but only in a few cases for heating.

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1. INTRODUCTION

Bulgaria is situated within the Balkan peninsula. It is a country with an area of 111,000 km^2, approximately the same size as Iceland. Its territory forms part of two main tectonic structures, namely, the Moesian platform and the Alpidic-Himalayan belt. All the natural geothermal springs that are found in the country are in Southern Bulgaria. There are more than 600 hot springs and wells with temperatures between 20-100°C found.

The author was awarded a Fellowship to participate in the Geothermal Training Programme of the United Nations University held at Orkustofnun, Iceland. This report presents the work during the last 10-12 weeks. After a short review of the geological environment, it focuses on the interpretation of chemical data on water from hot springs and wells from geothermal waters of Southern Bulgaria with emphasis on four fields within the area. Burgas field is located within the volcanic rocks (andesites); Kazanlak field - within the intrusive complex (granites); Razlog field - within metamorphic and intrusive rocks (gneiss and granites); and Sofia field - within sedimentary rocks (limestones, sandstones and terrigenous-clastic materials) and volcanic rocks (andesites). Various chemical geothermometers are used such as chalcedony, Na-K, Na-Li, Na-K-Ca, K-Mg. It is rare for these geothermometers to give approximately the same result, and this is the case when applied to low-temperature geothermal water in Southern Bulgaria. Of the geothermometers the chalcedony geothermometer proved to be the most appropriate for application. The maximum predicted temperatures are between 100°C and 110°C for Southern Bulgaria, thus the geothermal water in this region should be used for the same purposes it serves now such as balneology, bathing, recreation etc.

2. GEOLOGICAL BACKGROUND AND GEOTHERMAL REGIONS

Tectonically, Bulgaria is divided into four units (Iaranov, 1959): The Moesian platform; the Balkan orogenic belt; the Srednogorie zone; and the Rodopian massif. The northern half of the country consists of the Moesian platform with its deformed southern margin (the Balkan Foreland). The other three regions constitute Southern Bulgaria (Figure 1).

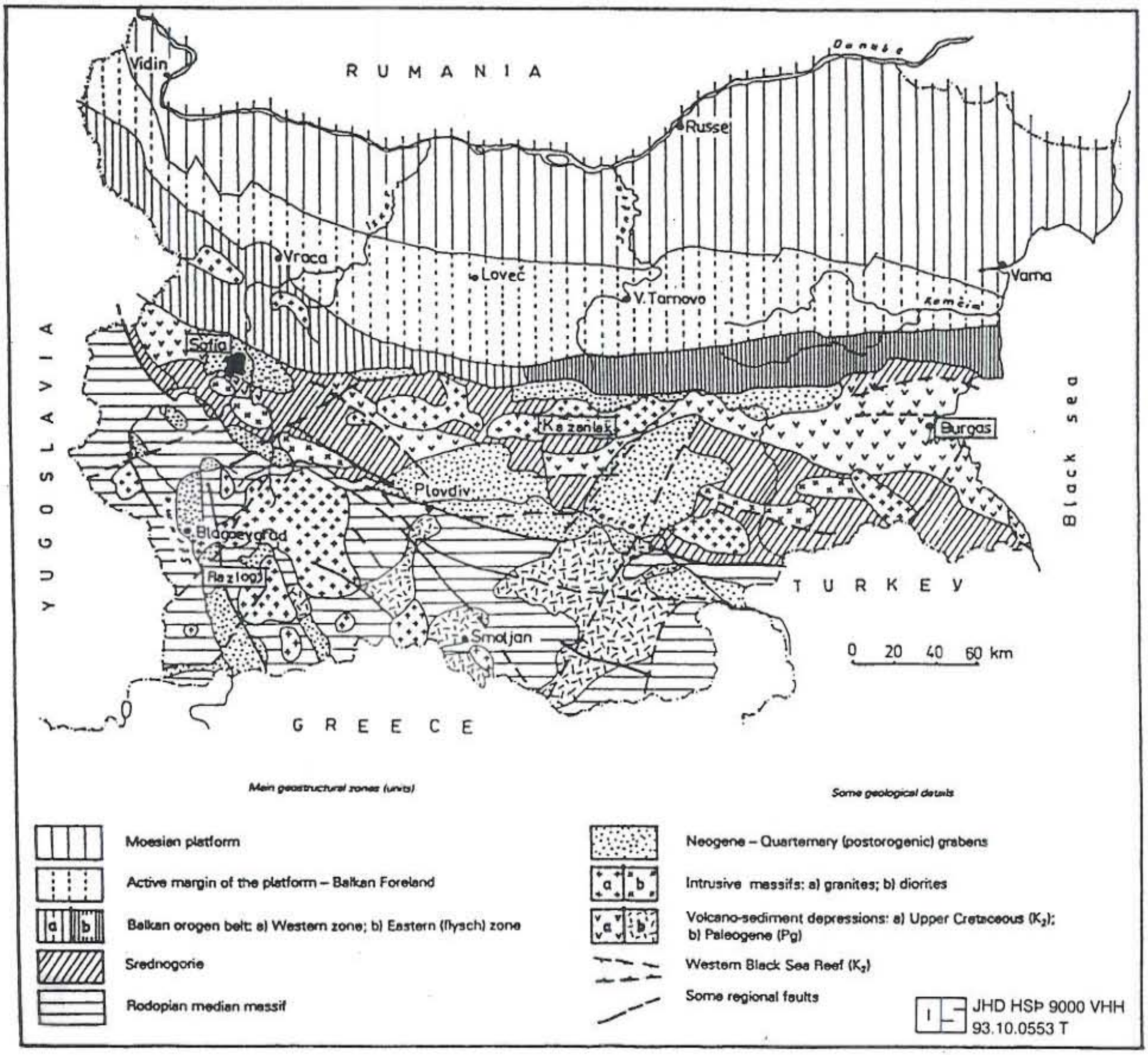

FIGURE 1: Geostructural scheme of Bulgaria (Shterev and Penev, 1991)

The Moesian platform has a Caledonian-Hercynian basement and a cover of Upper Palaeozoic and Mesozoic sediments. Its eastern part has a thin sedimentary cover. The western part consists of a depression with deposits up to 6000-7000 m thick. The main geothermal reservoirs in the platform area are situated in the carbonate strata of Malm-Valanginian, Middle Triassic and Upper Devonian ages. These strata consist of up to 100 m thick artesian aquifers of limestone and dolomite, very fractured and with high permeability caused by karstification or secondary dolomitization. The Balkan orogenic belt is to the south of the Moesian platform. It has no geothermal prospects, except for the lineament of granitoid bodies in the western part.

The Srednogorie zone is a rich and heterogeneous hydrothermal region, where unstratified (fault-fractured), stratified, and mixed hydrothermal systems are present. It is broken by postorogenic (Neogene-Quaternary) grabens, filled with terrigenous clastic deposits. Stratified hydrothermal systems occur in all the deeper bodies of Mesozoic carbonate rocks and in the Neogene conglomerates and sandstones. Unstratified hydrothermal circulation takes place in the massifs of granitic and metamorphic rock. Thermal aquifers are present in the Upper Cretaceous volcano-sedimentary depressions.

The main part of the Rodopian massif is made up of metamorphic and granitic rocks, broken by a dense system of seismically active faults. Unstratified hydrothermal systems are found in this geological area with thermal waters of low mineralization, of meteoric origin, and with temperatures up to 101°C (Sapareva bania). Some Palaeogene volcano-tectonic depressions occur in the eastern part of the Rodopian massif. Deep circulation of meteoric thermal water also takes place in old caldera and dyke structures. In the middle and southern parts of the massif, the metamorphic basement contains large bodies of marble that are hydrothermal reservoirs as well as in permeable terrigenous-clastic materials in the deep Neogene and Palaeogene grabens.

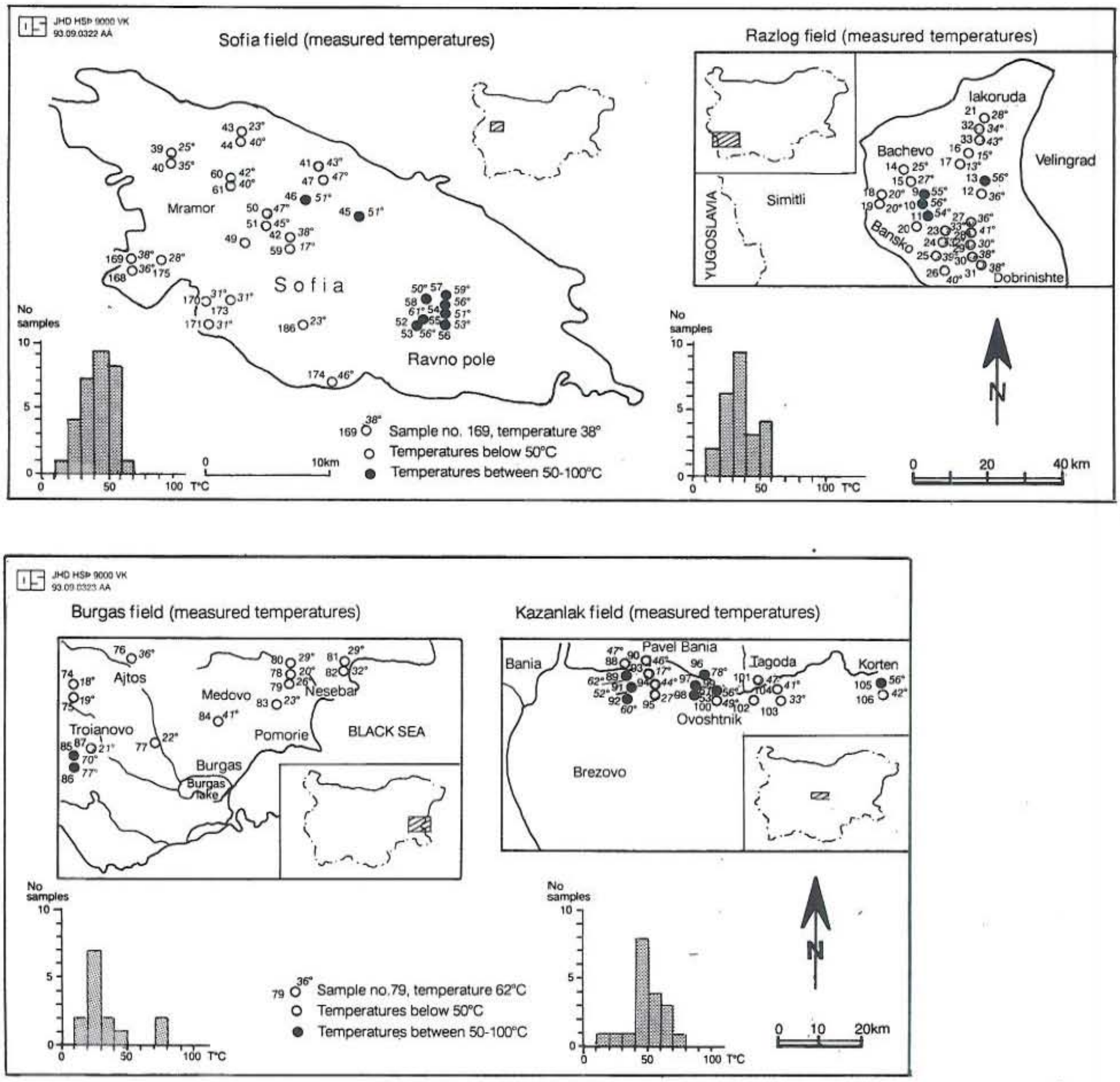

FIGURE 2: The Sofia, Razlog, Burgas and Kazanlak geothermal fields and measured temperatures for samples from hot springs and wells

The Srednogorie zone and the Rodopian massif, whose geothermal waters are the subject of this report, are divided into four hydrothermal regions (Shterev and Penev 1990):

1. Granitic rocks and siliceous metamorphic rocks (unstratified systems);
2. Volcano-tectonic depressions (Upper Cretaceous and Palaeogene);
3. Carbonate bodies and massifs (karst aquifers);
4. Terrigenous-clastic reservoirs.

The four selected fields, Burgas, Kazanlak, Razlog and Sofia, described in the report, represent all four hydrothermal regions in the Srednogorie zone and Rodopian massif (Figure 1). These are low-temperature fields with measured temperatures below 100°C. They are located within different geological areas; volcanic, intrusive, metamorphic and sedimentary zones, respectively. There are several types of rocks in each area but one always predominates over the others.

Figure 2 shows the four selected fields, location and number of samples and measured temperatures at the site. Also shown are histograms with the temperature range for each field.

3. SAMPLING METHODS FOR GEOTHERMAL FLUIDS

Sampling and analysis of geothermal fluids are very important parts of geochemical studies because they control the accuracy of estimating the temperature of subsurface fluids whose chemical composition is the result of water-rock interactions.

It is important to obtain reliable samples of the geothermal fluids for chemical analyses and to make field measurements of several parameters because they may change during transport of the samples from the field to the laboratory. Deep geothermal systems are often accompanied by certain surface manifestations. Hydrothermal alteration depends on rock types, temperature of the water-rock interaction and the composition of geothermal fluids involved in this complex process. Any preliminary knowledge of geology, mineralogy, petrology and geophysics of the geothermal region is very important for meaningful geochemical sampling, analysis and interpretation (D'Amore et al., 1991).

Some practice in the sampling of geothermal water and steam, from low and high temperature wells, springs and fumaroles was obtained during this training course. The samples were analyzed in the chemical laboratory of Orkustofnun (National Energy Authority of Iceland). Below is a brief description of the field methods used for collecting water from natural thermal manifestations and geothermal wells.

First of all, the samples should be collected where the spring naturally emerges at the surface and not downstream of any installations for tapping and transporting the water. The most important measurements that should be done in the field are of the temperature of the water and the flow-rate. If possible the pH and the pH-temperature of the water should be measured as well as its conductivity. For the main sampling the water has to be cooled to approximately room temperature (20°C). Prior to any sampling it is necessary to rinse the sampling equipment and containers thoroughly. It is best to use the water to be sampled for rinsing. When sampling begins, one first fills a gas-sampling bulb with water for pH, pH-temperature, CO_2 and H_2S measurements. Next, an untreated sample is collected for SiO_2 analysis into a 100 ml bottle and labelled Ru f. SiO_2. If the SiO_2 concentration is expected to be more than 100 mg/l, it is necessary to dilute the sample with distilled water. Ideally, the concentration of silica in the diluted sample should be in the range 30 to 100 mg/l. If dilution is necessary, three such samples are collected into 100 ml polyethylene bottles and labelled Rd f. SiO_2 and the dilution factor is marked on the bottle. The next step is to collect samples into four 500 ml polyethylene bottles by the following procedure: First a filtered and untreated sample is collected into one bottle and labelled Fu. Next 1 ml 6 N HCl is added to 500 ml filtered sample in a sampling bottle. Two such bottles may be needed for a whole chemical analysis. The samples are labelled Fa. In order to precipitate sulphide 2 ml of 0.2 M $Zn(CH_3COO)_2$ solution is added to a 100 ml volumetric flask and filled to the mark with the filtered sample. The sample is transferred to a 500 ml sampling bottle and labelled Fp. The collection of cold water is basically done in the same way as the collection of hot water except no cooling is needed (Olafsson, 1988).

4. CHEMICAL GEOTHERMOMETERS

Various chemical geothermometers have been developed to predict reservoir temperatures in geothermal systems (Fournier, 1989). Both qualitative and quantitative chemical geothermometers are used in geothermal investigations. The quantitative techniques currently available require chemical analyses of thermal waters from springs or wells. On the other hand, qualitative techniques may be used to look for anomalous concentrations of various "indicator" elements in the water.

Most qualitative geothermometers are based on the distribution and relative concentration of volatile elements in the geothermal fluids. White (1970) reviewed the qualitative geothermometers that had been suggested up to 1970. Tonani (1970) suggests that enrichment of B, NH_4, HCO_3, Hg, and H_2S (which oxidizes to sulphate and lowers the pH of the water) in near-surface waters may result from high temperature at depth. Mahon (1970) noted that high Cl/F and Cl/SO_4 ratios in fluids from a geothermal area generally indicate a high temperature in the system. He also noted that variations in CO_2/NH_3, CO_2/H_2 and CO_2/H_2S may indicate zones likely to be close to deep hot water. Sigvaldason and Cuellar (1970) considered hydrogen in thermal gases generally to be a qualitative indicator of high temperature. Fournier and Truesdell (1970) noted that the mole ratio $Cl/(HCO_3+CO_3)$ was very useful in distinguishing waters from different aquifers in the Yellowstone National Park: Higher ratios indicated waters coming from hotter aquifers. Anomalously high concentrations of nonvolatile trace elements may also be indicative of high subsurface temperatures. Brondi et al., (1973) report that high concentrations of Li in springs give a good indication of high temperature at relatively shallow depths. A method using variations in the helium contents has been widely used as an indicator of high subsurface temperatures (Friedman and Denton, 1976).

The quantitative geothermometers are widely used to estimate subsurface temperatures in geothermal reservoirs, based on the concentrations of selected chemical constituents in samples from springs and shallow wells. The attendant assumptions may be summarized as follows (Fournier, 1977):

1. Temperature-dependent reactions involving rock and water interactions fix the amount or amounts of dissolved "indicator" constituents in the water;
2. There is an adequate supply of all the reactants;
3. There is equilibrium in the reservoir or aquifer in respect to the specific indicator reaction;
4. No re-equilibration of the "indicator" constituents occurs after the water leaves the reservoir;
5. Either no mixing of different waters occurs during movement to the surface or no evaluation of such mixing is possible.

Different reactions may occur in ascending water at different rates. Therefore, the apparent last temperature of equilibration may be different for different chemical geothermometers. The two main types of temperature dependent reactions that may be useful as quantitative geothermometers are solubility and exchange reactions. Solubilities of minerals generally vary as functions of temperature and pressure. The silica geothermometer of Fournier and Rowe (1966) is based on the solubility of quartz and is widely used to estimate subsurface temperatures in hot spring systems. At lower temperatures other silica species such as chalcedony, cristobalite, or amorphous silica may control the amount of dissolved silica in the water (Fournier and Truesdell, 1970; Arnorsson, 1975).

Equilibrium constants for exchange and alteration reactions are temperature dependent. In such reactions, the ratios of dissolved constituents change with changing temperature of equilibration.

There are many possible constituents and reactions that may be useful. Examples are Na/K ratios of alkali chloride solutions equilibrated with alkali feldspars (Orville, 1963), Na/K ratios in natural waters (White, 1970), and Na-K-Ca relations in natural waters (Fournier and Truesdell, 1973).

The Na-K-Ca geothermometer has proved to be more reliable than the Na-K geothermometer for low temperature waters. The K-Mg (Giggenbach, 1988) and Na-Li geothermometers were proposed for temperature estimations. The Na-Li geothermometer (Fouillac and Michard, 1981) is very sensitive to slight changes in the Li content that result from exchange reactions involving other ions than Na. It is therefore recommended to use this geothermometer in combination with other geothermometers.

Ascending hot water may cool by boiling (adiabatically), by conduction, by mixing with shallow colder water, and by a combination of these processes. Chemical analyses of spring waters may provide information on which of these processes are occurring in a given geothermal system. Waters that ascend quickly and directly from aquifers with little conductive cooling are likely to have chemical compositions that reflect rock-water equilibrium at the aquifer temperature. Where the aquifer is at a temperature below atmospheric boiling, the water can emerge at about the temperature of the aquifer. Where waters ascend either slowly or indirectly to the surface, conductive cooling is likely to occur. Even water from a spring with a large flow rate may cool considerably by conduction if it moves horizontally for a long distance at a shallow level. In this case, different springs along the flow path or springs with different rates of discharge could have different temperatures but similar chemical compositions. Where hot ascending waters cool by mixing with cooler groundwater, springs with different temperatures are likely to have different chemical compositions.

The waters in many hot springs consist of mixtures of deep hot water and shallow cold water. The chemical composition of the mixed water may be used for temperature estimation applying mixing models (Fournier and Truesdell, 1973). Mixing models should not be applied unless there is an independent evidence for mixing because if used for unmixed water, the predicted temperature could be too high. Some independent indications of mixing are: large discrepancy between the temperatures indicated by the silica and the other geothermometers; systematic variation in temperature and composition of water in springs from the same area; a relatively cool spring with a large mass flow, in which much higher temperatures are indicated by the geothermometers; variation in oxygen and hydrogen isotopes; variation in chloride concentrations. The silica mixing model is the most appropriate for high temperature waters. In order for the silica mixing model to give accurate results, it is vital that no conductive cooling has taken place after mixing. If the mixed water has cooled conductively after mixing, the calculated temperature of the hot-water component will be too high. It is also a necessary condition that no silica deposition has taken place before or after mixing and that the solubility of silica in the high-temperature water is quartz controlled (Fournier, 1989).

In this report, several geothermometers (chalcedony, Na-K-Ca, K-Mg, Na-K, and Na-Li) have been used to predict subsurface temperatures in Southern Bulgaria. The Na-K and chalcedony geothermometer temperatures were computed by the programme WATCH; the Na-K-Ca and K-Mg temperatures by the computer programme CAT_TEMP; and the Na-Li geothermometer temperatures were calculated using an empirical thermometric relationship ($\log Na/Li = 1000/T - 0.38$), which was suggested by Fouillac and Michard (1981). It was found that the chalcedony, K-Mg and Na-K-Ca geothermometers give the most reliable results for geothermal waters in Southern Bulgaria.

5. COMPUTER PROGRAMMES FOR CALCULATIONS

5.1 The computer programme "WATCH"

The computer programme WATCH (Arnorsson et al., 1982; Bjarnason, 1993) is intended to serve as a tool for interpreting the chemical composition of geothermal fluids, for computing different geothermometer temperatures and it is also applicable to other geochemical problems. The input to the programme is from a component analysis of each phase (liquid, gas, steam) of the geothermal waters at the surface, including the water pH and the temperature at which it was measured, and a reference temperature at which the composition is to be calculated. The concentrations of all the species (67 and H^+ and OH^-, which are treated separately) considered in the programme are expressed in terms of the component concentrations by mass balance equations. The chemical equilibria between the species are expressed as mass action equations. The two sets of equations are solved simultaneously by an iterative procedure. This procedure is carried out a few times during each run of the programme. An initial estimate of the ionic strength of the water is obtained using only the concentrations of the major cations. This value of the ionic strength is used to compute activity coefficients, at the temperature of the pH measurement, using the extended Debye-Huckel formula. The chemical equilibria and mass balance equations are now solved simultaneously at this temperature to yield a distribution of the species. From the new distribution of species, a proper ionic strength is computed. This ionic strength is used to recompute the activity coefficients and species concentrations still at the temperature of the pH measurement.

The pH-calculation, the calculation of the activity coefficients, the mass balance iteration, and the ionic strength calculation are all, in turn, carried out a couple of times. The equilibrium gas pressures are then computed from the final equilibrium species concentrations. The reference temperature can be chosen in several ways. It can be chosen as the measured temperature of the well or spring, or as a chalcedony, quartz, or sodium-potassium chemical geothermometer value. The geothermometer temperatures are calculated from the concentrations of chemical species. This means that the pH and speciation calculations must be repeated each time the geothermometer temperature is updated. This is iterated until the temperature is consistent to within 0.01°. Also, the reference temperature can also be chosen arbitrarily.

The output from the programme lists the component and species concentrations at the reference temperature, as well as the activity coefficients. Ionic balance, geothermometer temperatures, partial pressures of gases, and redox potentials are also calculated. Finally, the ion activity products (log Q) and solubility products (log K) of selected minerals (29 geothermal minerals) are computed. From these, the corresponding saturation index (log Q/K) can be obtained.

The WATCH programme can also be used to compute the resulting species concentrations, activity coefficients, and activity and solubility products when the equilibrated water is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature (Bjarnason, 1993).

In this report, the results of about 200 chemical analyses of geothermal waters from Southern Bulgaria were subjected to calculations employing the programme WATCH. They are divided into 18 files representing the data for the 18 geothermal fields in this part of Bulgaria. The files contain from four up to nineteen chemical analyses. The result of each analysis was considered at three different temperatures: the measured, the chalcedony and the Na-K geothermometer temperature. An example of the output for such a calculation is shown in Appendix I. Table 1 shows the results for the chalcedony geothermometer for all the samples studied. The WATCH programme was also used to estimate chemical equilibrium states of the thermal waters. The results for the four selected fields are presented in Chapter 7.

5.2 The computer programme "CAT_TEMP"

The computer programme CAT_TEMP (Olafsson, 1993) is a tool for calculating Na-K, K-Mg, and Na-K-Ca temperatures. It computes Na-K temperature using six different methods (Arnorsson, 1983; Fournier, 1979; Truesdell, 1976; Tonani, 1980; Nieva and Nieva, 1987; Giggenbach, 1988). The K-Mg temperature is calculated according to Giggenbach (1988) and the Na-K-Ca temperature according to Fournier and Truesdell (1973). All available data (approximately 200 analyses) were treated using CAT_TEMP programme. However, this report focuses only on K-Mg and Na-K-Ca temperatures because they have been found to yield reliable results for geothermal waters in Southern Bulgaria. An example of the output data is shown in Appendix II. The results of the calculated temperatures for the K-Mg and Na-K-Ca geothermometers are presented in Table 1.

TABLE 1: Geothermometer temperatures for chemical samples from Southern Bulgaria

No.	Sample No.	T_{meas} (°C)	T_{chal} (°C)	$T_{K\text{-}Mg}$ (°C)	$T_{Na\text{-}K\text{-}Ca}$ (°C)	No.	Sample No.	T_{meas} (°C)	T_{chal} (°C)	$T_{K\text{-}Mg}$ (°C)	$T_{Na\text{-}K\text{-}Ca}$ (°C)
1	39	25	28	64	86	41	98	53	65	105	144
2	40	35	24	35	18	42	99	56	47	93	134
3	41	43	50	67	100	43	100	49	43	96	133
4	42	38	57	66	102	44	101	47	61		
5	43	23	33	59	105	45	102	45			
6	44	40	70	67	108	46	103	33			
7	45	51	60	46	61	47	104	41			
8	46	51	52	79	133	48	105	56	83	100	112
9	47	47	41	66	101	49	106	42	87	100	112
10	49	48	48			50	9	55	46		
11	50	47	58	87	143	51	10	56	46	50	66
12	51	45	53	87	143	52	11	54	61	53	69
13	52	61	66	64	77	53	12	36	41		
14	53	56	68	66	76	54	13	56	47		
15	54	56	66	67	77	55	14	25	47	50	54
16	55	51	66	67	78	56	15	27	40	61	78
17	56	53	65	74	91	57	16	15	24		
18	57	59	66	67	75	58	17	13	14		
19	58	50	60	76	113	59	18	20	43		
20	59	17	65	48	92	60	19	20	40		
21	60	42	85	68	129	61	20	21			
22	61	40	91	69	123	62	21	28	71		
23	168	36	36			63	23	33	70	83	82
24	169	38	36			64	24	32	74	117	89
25	170	31	37			65	25	39	79	72	90
26	171	31	40			66	26	40	62	75	87
27	173	31	29	57	62	67	27	36	79	79	92
28	174	46	31	32	23	68	28	41	65	73	84
29	175	28	37			69	29	30	78	65	89
30	186	23	28			70	30	38	68	60	77
31	88	47	56	100	127	71	31	38	65	77	89
32	89	62	54	91	122	72	32	34	77		
33	90	46	87	101	120	73	33	43	75		
34	91	52	91	110	132	74	74	18	46		
35	92	60	90	116	128	75	75	19	16	20	34
36	93	27	51	111	144	76	76	36	53	37	50
37	94	44	59	106	139	77	77	22	49		
38	95	17	59	113	138	78	78	20	64		
39	96	78	74			79	79	26	62	44	88
40	97	61	55	70	112	80	80	29	56		

TABLE 1: Continued

No.	Sample No.	T_{meas} (°C)	T_{chal} (°C)	T_{K-Mg} (°C)	$T_{Na-K-Ca}$ (°C)	No.	Sample No.	T_{meas} (°C)	T_{chal} (°C)	T_{K-Mg} (°C)	$T_{Na-K-Ca}$ (°C)
81	81	29	28	65	91	131	125	22	44	46	37
82	82	32	37	72	86	132	126	44	46	54	56
83	83	23	46			133	127	46			
84	84	41	42			134	128	52	71	65	77
85	85	70		99	104	135	129	52	70	57	59
86	86	77	66	116	106	136	130	43	77	57	78
87	87	21	56	28	62	137	131	43	64	61	69
88	1	39	46			138	132	46	82	71	96
89	2	38	50			139	133	48	85	75	96
90	3	27	49			140	134	19	36		
91	4	32	66			141	135	36	74	38	36
92	5	19	51			142	136	32	47	48	60
93	6	32	49	47	40	143	137	29	62	42	35
94	7	19	52			144	144	41	63		
95	8	26	87			145	145	55	59		
96	22	72	53	107		146	156			68	
97	34	46	49	53	57	147	157			57	85
98	35	73	100	104	101	148	158			36	67
99	36	65	88	90	95	149	159	41	59	55	28
100	37	58	66	71	81	150	160	41			45
101	38	45	35	44	58	151	161	28			
102	62	63	88	71	102	152	162	48	54		
103	63	45	39	50	64	153	163	39	46	31	44
104	64	82	97	93	127	154	164	47	47	45	50
105	65	83	108			155	165	61	44	68	84
106	67	26	22	30	34	156	167	45	47		
107	68	40	29	35	35	157	176	25	103		
108	69	17	58	22		158	177	22	100		
109	70	20	48	39	18	159	178	28	56	48	65
110	71	36	43	55	88	160	179	20	46	19	
111	72	32	54	78	143	161	180	26	38	53	88
112	73	55				162	181	21	44	54	82
113	107	56	73	84	108	163	182	26			
114	108	56	70	112		164	183	33	44	30	20
115	109	98	20			165	184	43	60	96	136
116	110	56	64	90	129	166	185			54	84
117	111	57	101			167	187	29	109	91	131
118	112			79	126	168	188	26	95	80	109
119	113	16	29	55	58	169	189			46	48
120	114	54	57	82	103	170	190	76	94	97	
121	115	28	24	37	51	171	191	71	85	99	
122	116	47	76			172	192	73	90	99	
123	117	14	31	69	83	173	193	26	98	81	109
124	118					174	194	70		101	141
125	119	62	79	84	127	175	199	47	36	48	69
126	120	48	74	77	104	176	200	24	44	27	33
127	121	23	48	67	85	177	201	41	46		
128	122			29	41	178	202	42	45		
129	123	15	29	39	39	179	203	40	45		
130	124			17	27						

NOTE: Samples No. 1-30 are from the Sofia field, 31-49 from the Kazanlak field, 50-73 from the Razlog field, 74-87 from the Burgas field and 88-179 from other fields in Southern Bulgaria.

6. MINERAL EQUILIBRIA IN HYDROTHERMAL WATERS

The so-called saturation index which is the value of log(Q/K) for each mineral, where Q is the activity product and K is the equilibrium constant, provides a measure of the proximity of the aqueous solution to equilibrium with the mineral. By plotting log(Q/K) versus temperature for natural waters, it is possible to determine whether the water has been in equilibrium with a host rock mineral assemblage, probable minerals in the equilibrium assemblage, and the equilibrium temperature. Most geothermal waters approach equilibrium with a subsurface mineral assemblage at a temperature close to the measured temperatures.

Using the activities of aqueous component species calculated for homogeneous equilibrium at a series of temperatures, it is possible to compute the value of super- or undersaturation of the aqueous phase with respect to a number of minerals at each temperature. This is expressed for mineral k in terms of $\log(Q/K)_k$:

$$\log(Q/K)_k = \log(\Pi a_{i,k}^{\nu_{i,k}}) - \log K_k \qquad (1)$$

in which K is the equilibrium constant for mineral k, $a_{i,k}$ is the activity and $\upsilon_{i,k}$ is the stoichiometric coefficient of the component species i in the equilibrium mass action expression for mineral k. The numerical value of $\log(Q/K)_k$ is greater than zero for supersaturated minerals and less than zero for undersaturated minerals.

The plotting of log(Q/K) for minerals is similar to plotting points on activity diagrams (e.g., a_{Na}/a_H) to ascertain the approach of natural water to equilibrium with respect to certain minerals. Activity diagrams are limited because they display only two compositional variables simultaneously at a fixed temperature whereas a log(Q/K) diagram applies to a range of temperatures and takes into consideration the activities of all components in each mineral and simultaneously displays minerals of various compositions. The log(Q/K) plots work well for low-temperature springs as well as high temperature geothermal waters, both of a widely variable composition.

Geothermal fluids, which are formed by mixing of two or more different fluids, will show either a) a shift in the positions at which the minerals are apparently in equilibrium to lower log(Q/K) values if the solutions that mix with the geothermal fluid are very dilute or b) a complete lack of any identifiable equilibrium temperature if the solution mixing with the geothermal fluid is not dilute (Reed and Spycher, 1984).

7. GEOTHERMOMETER TEMPERATURES IN SELECTED FIELDS

This chapter focuses on the interpretation of chemical data for hot springs and well waters from the Burgas, Kazanlak, Razlog and Sofia geothermal fields in Southern Bulgaria (Figures 1 and 2). Various chemical geothermometer temperatures (chalcedony, Na-K-Ca, K-Mg, Na-K and Na-Li) are compared. Figure 3 shows the chalcedony temperatures for the different sites of the four selected geothermal fields. The histograms show the temperature range within each field.

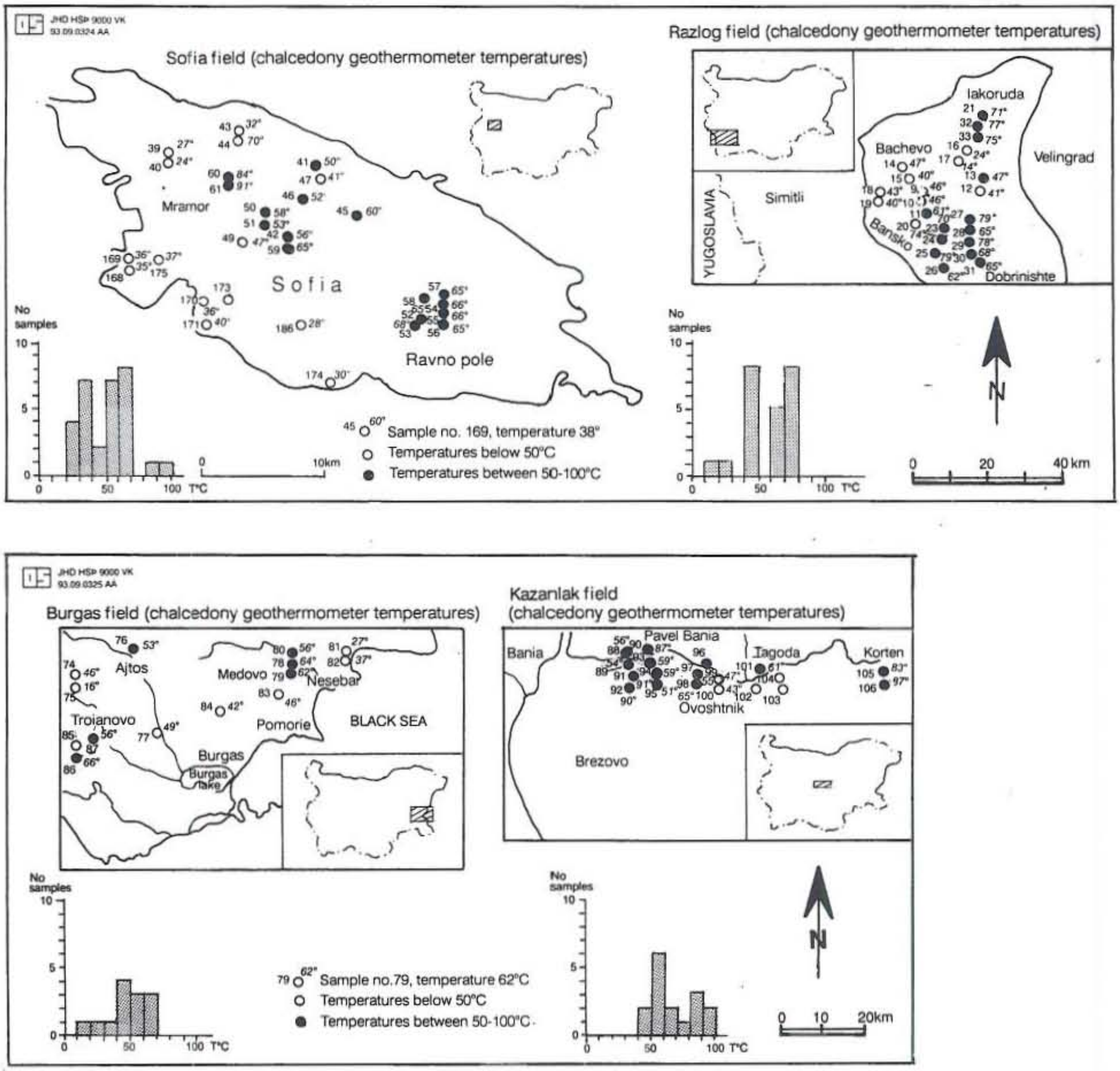

FIGURE 3: The chalcedony temperatures for the samples from the Sofia, Razlog, Burgas and Kazanlak geothermal fields in Southern Bulgaria

7.1 The Sofia field

Initially, the geothermal water exploitation of the Sofia field was limited to natural discharge from hot springs (e.g. Ovcha kupel, Sofia-centre, Pancharevo and Gorna bania) or free flow from several shallow wells. The water was used for public baths and balneological purposes. The bedrock of the field is composed of different rocks. The major reservoir rock types are Triassic limestone and sandstone, Jurassic limestone, Cretaceous sandstone and andesite. As secondary reservoirs, Pliocene sands accumulate the hot water where they directly cover the bedrock. However, geothermal water is mainly stored in the bedrock of the field. Most aquifers started as artesian aquifers with a piezometric level of up to 30 m above the surface, but after installing downhole pumps in several wells with the hope of increasing the fluid production, surface activity has diminished or even disappeared altogether.

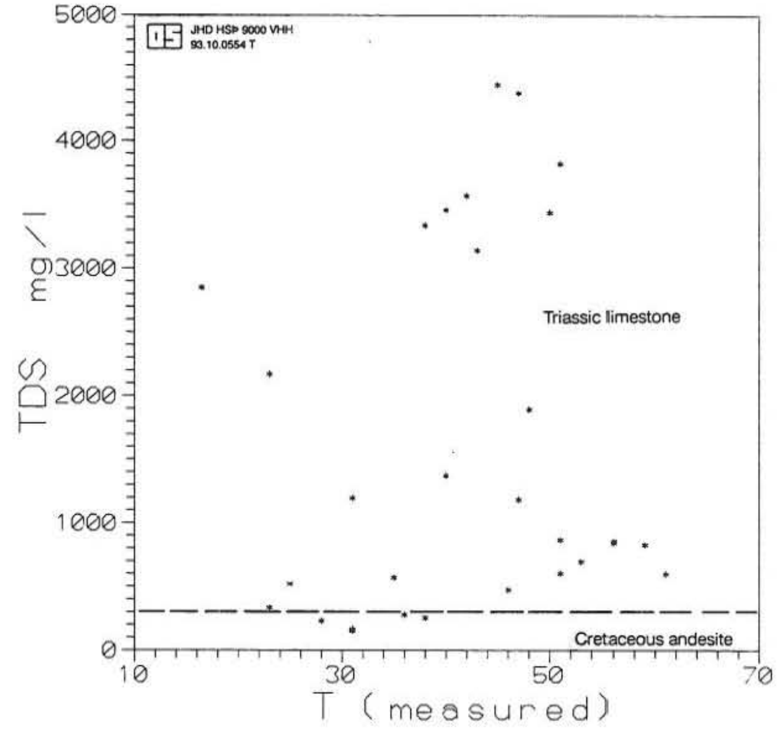

FIGURE 4: The Sofia field, total dissolved solids vs. measured temperature (°C)

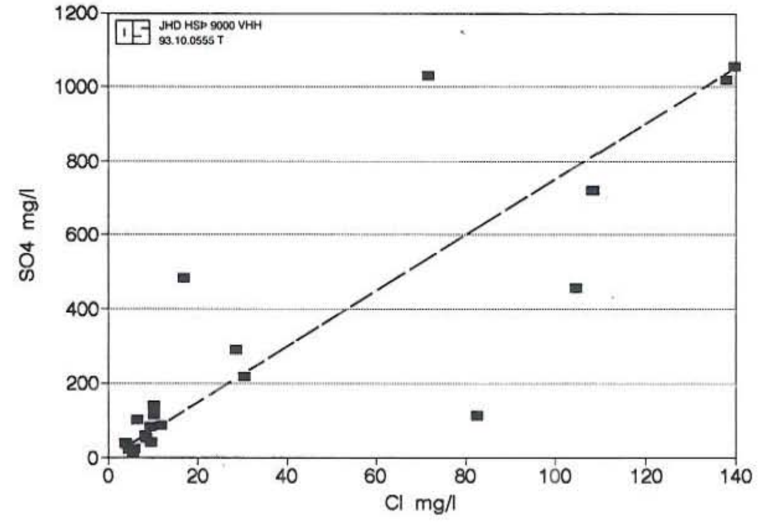

FIGURE 5: The Sofia field, SO_4 vs. Cl

Drilling for hot water and other purposes began in the Sofia field in the early 1960s. Some of the deeper boreholes passed through Pliocene-Quaternary clays, sands and reached the bedrock of the field. The bedrock was found at different depths - from 52 m (Sofia-centre, well 3) to 1140 m (Elin Pelin, well 1). Today, a total of 139 deep wells have reached the bedrock which is the main reservoir of thermal water in the field. The deepest well reaches down to 1607 m depth. More than 40 are producing wells. The production from the field increased steadily during the 1960s. Flowrate from springs and wells generally lies in the range of 1-15 l/s. The maximum temperature of the natural hot water is 81°C (Kazichene, well 1).

The chemical composition of 30 natural spring and geothermal well waters in this field were taken into consideration (Table 2). Most are located within Triassic limestone while others are within Cretaceous andesite. The water samples can be divided into two groups accordingly.

Figure 4 shows the total dissolved solids (TDS) versus the measured temperature. The water chemistry from the andesite area is quite stable with TDS between 150 mg/l (Kniajevo) and 300 mg/l (Bankia). However, the waters from the limestone aquifers have a very variable composition, TDS ranging from 500 mg/l to 4500 mg/l. Figures 5 and 6 show the sulphate concentration of the water plotted against chloride and potassium concentration, respectively. As demonstrated by the broken lines on the figures, there is a slight correlation between these elements, indicating a SO_4:Cl ratio (mg/l) of 7:1 and SO_4:K ratio (mg/l) of 30:1.

TABLE 2: Chemical composition of geothermal waters in the Sofia field (mg/l) (the location of samples is shown in Figure 2)

No.	pH	TDS	Cl	SO_4	CO_2	Na	K	Ca	Mg	SiO_2
39	8.30	518	20.5		237.6	116.9	2.76	5.6	1.0	18.5
40	7.15	570	4.1	37.9	268.4	19.7	2.63	84.2	15.8	16.4
41	7.86	3143	28.6	291.3	1372	848.5	7.0	7.8	5.2	32.5
42	7.62	3341	30.5	218.1	1531	891.6	8.2	12.1	7.3	36.9
43	7.28	2170	5.9	23	1131	345.8	12.1	39.9	31.9	20.5
44	7.93	1372	6.5	101.2	602.7	348.8	4.2	3.4	1.8	50.2
45	7.55	604	5.5	13.2	281.6	93.5	3.8	27.0	10.7	39.6
46	7.39	3823	108.2	720.9	1337	977.6	23.1	40.1	20.3	32.9
47	8.23	1184	11.8	88.1	523.5	302.5	2.2	3.1		26.7
49	7.78	1896	104.7	455.9	527.9	526.7	5.63	11.7	3.7	30.2
50	6.70	4382	137.9	1017	1373	1128	35.3	73.9	24.1	37.5
51	6.80	4448	139.8	1055	1381	1127	35.1	78.6	24.8	33.4
52	6.70	870	10.1	139.5	325.5	123.8	10.7	67.7	15.3	43.8
53	6.70	857	10.1	117.7	325.5	121.4	10.8	70.1	12.8	46.2
54	6.80	843	10.1	121	316.7	115.9	11.2	70.1	12.8	44.5
55	6.80	867	10.1	131.7	321.1	124.2	11.2	68.5	13.2	44.4
56	7.50	696	9.4	83.9	263.9	140.1	6.8	19.1	2.7	44.1
57	6.80	828	10.1	114.4	316.7	101.0	10.8	68.1	11.8	43.8
58	7.60	3442	71.5	1029	919.6	974.3	11.3	10.1	6.1	40.0
59	7.30	2850	82.6	114	1357	723.0	5.65	31.1	19.4	43.8
60	6.85	3573	23.3		1826	821.0	20.24	54.5	39.0	63.9
61	6.98	3462	23.1		1768	692.0	19.2	56.1	33.1	72.2
168	9.59	281	8.3	60.7	52.8	75.2	0.81	1.9		41.0
169	9.58	256	8.3	61.7	35.2	72.2	0.72	2.0		42.4
170	9.55	167	4.5	22.6	30.8	42.0	0.22	2.0		36.8
171	9.50	152	5.5	17.7	26.4	36.0	0.35	2.6		37.8
173	7.05	1195	16.9	483.9	287.0	125.8	11.4	154.3	32.1	18.8
174	7.03	474	3.9	39.9	220.0	8.9	3.3	58.1	32.8	19.6
175	9.24	230	8.4	53.5	44.0	62.0	0.46	3.6		29.4
186	9.20	335	9.6	42.0	114.4	92.2	0.11	2.1		22.0

The highest values are found in the water from the two boreholes of Ilientzi. For the other constituents that have been investigated, e.g. SiO_2, Ca, Mg and CO_2, no direct correlation has been observed. Most of them are in higher concentrations in the water from the limestone aquifers compared to that from the andesite aquifers. Due to lack of isotope data, little can be said about the origin of the water.

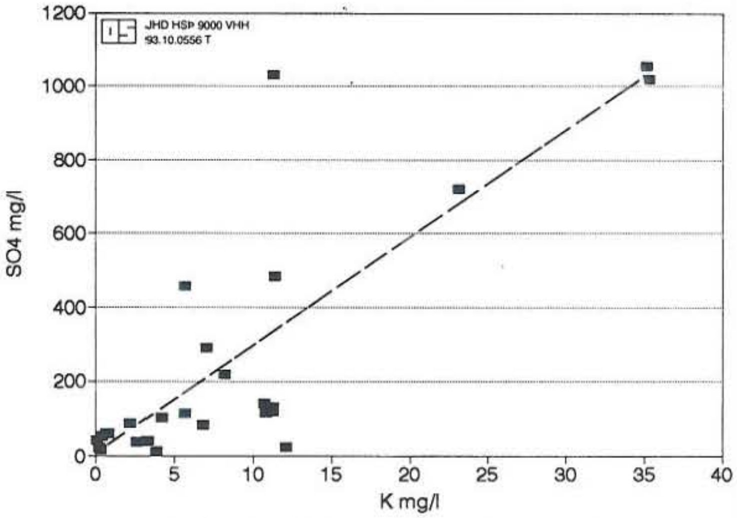

FIGURE 6: The Sofia field, SO_4 vs. K

Using the activities of aqueous components calculated for a series of temperatures, it is possible to compute the degree of saturation of the aqueous phase with respect to several minerals at each temperature.

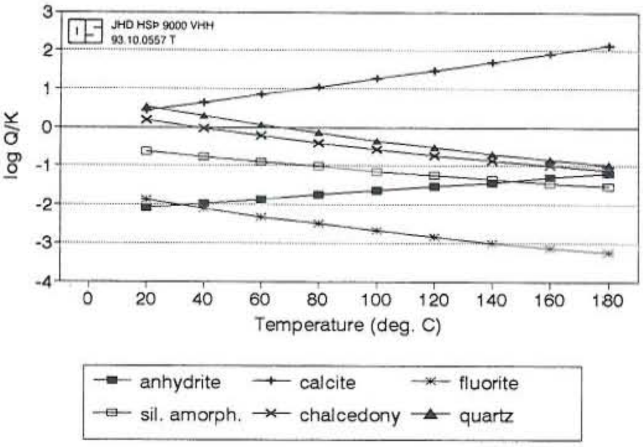

FIGURE 7: The Sofia field, equilibrium temperature graph for one sample (Al Voykov)

Figure 7 demonstrates such equilibrium calculations for one of the samples using a plot of log(Q/K) versus temperature for geothermal water in the Sofia field. Six geothermal minerals were used; namely, anhydride, calcite, fluorite, silica amorphous, chalcedony and quartz. At least four of them (calcite, silica amorphous, chalcedony and quartz) are found in the reservoir rock. The curves for chalcedony and quartz intersect the log(Q/K)=0 at 40°C and 70°C. The water is undersaturated with respect to amorphous silica, anhydrite and fluorite but supersaturated with respect to calcite. Thus, a calcite scaling problem could occur in this case. The equilibrium curves for most of the other samples are similar to the ones shown in Figure 7. The equilibrium temperature was not defined but is likely to be in the range of 40°C to 90°C for the Sofia geothermal field.

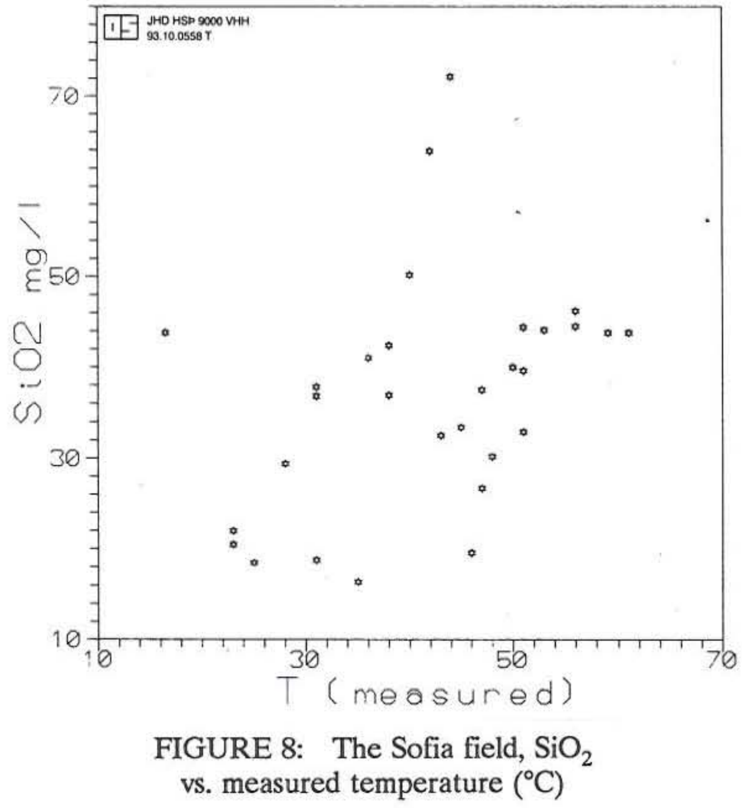

FIGURE 8: The Sofia field, SiO_2 vs. measured temperature (°C)

Figure 8 shows, that there is a slight correlation between the silica concentration of the water and the measured temperature, indicating increased solubility of silica with increased temperature of the geothermal field.

The chalcedony and Na-K geothermometer temperatures were computed using the computer programme WATCH. The chalcedony temperature has been plotted versus the measured temperatures (Figure 9) as well as against CO_2 concentrations (Figure 10). It can be seen that there is a relatively good correlation between the chalcedony temperatures and the measured temperatures. An exception is the water from the quarter of Birimirtzi, whose measured temperature (17°C) is exceptionally low compared to the calculated chalcedony temperature (65°C). This discrepancy can best be explained by cooling of the geothermal water due to accumulation in a secondary reservoir (Pliocene sand). It is likely that water with a higher temperature can be found at a greater depth in the area. A drillhole has to reach the bedrock, which is the main reservoir for the geothermal water. The data for Na-K geothermometer temperatures versus measured temperatures did not show any correlation except for a few samples from the first group, but the data for the second group revealed unrealistically high Na-K temperatures.

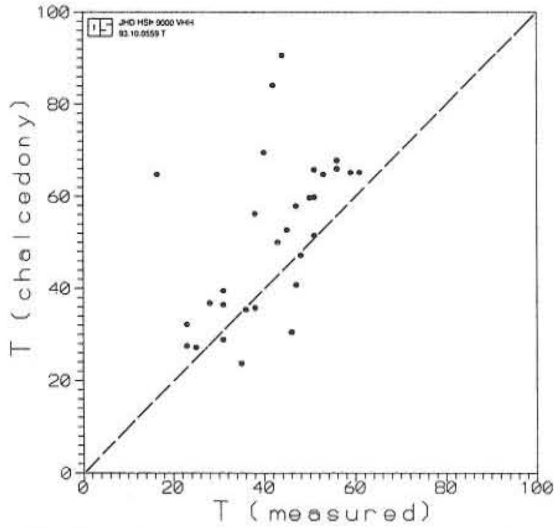

FIGURE 9: The Sofia field, chalcedony temperature vs. measured temperature (°C)

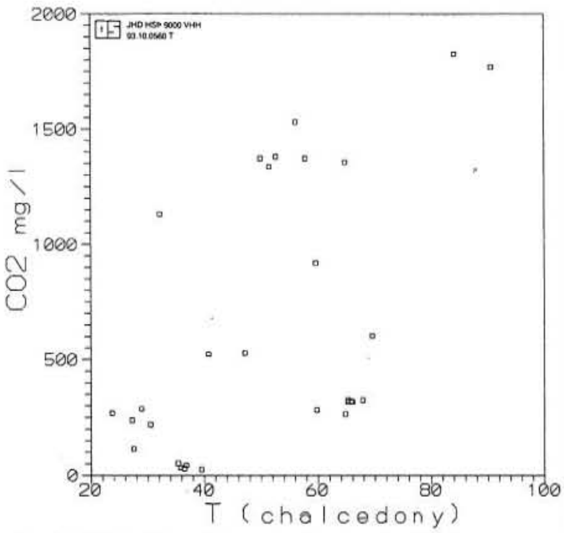

FIGURE 10: The Sofia field, CO_2 vs. chalcedony temperature (°C)

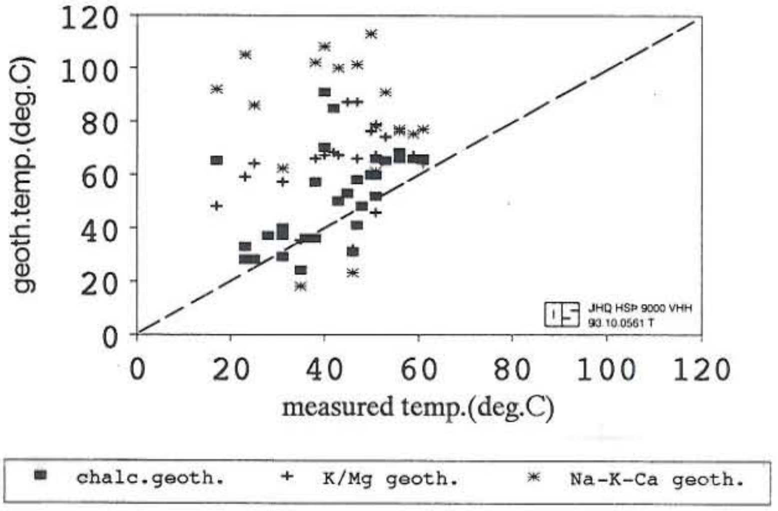

FIGURE 11: The Sofia field, geothermometer temperature vs. measured temperature

The Na-Li geothermometer temperatures were calculated but most of the results indicated temperatures higher than 200°C. These are obviously not reliable results and therefore they are not not discussed in this report.

The K-Mg and Na-K-Ca geothermometer temperatures were calculated using the CAT_TEMP computer programme. The results of the K-Mg and Na-K-Ca along with the chalcedony geothermometer are plotted versus measured temperatures in Figure 11. The results show poor correlation between the K-Mg and Na-K-Ca geothermometers and the real surface temperatures but the chalcedony geothermometer shows relatively good correlation as discussed above.

It can be concluded, that for the Sofia field, the chalcedony geothermometer is found to be the most reliable one of the geothermometers that were studied. The data for measured temperatures and calculated chalcedony temperatures are shown in Figures 2 and 3. As is demonstrated in the histograms (Figure 2) the maximum measured temperature is about 60°C. According to chalcedony geothermometer the highest predicted temperatures in the geothermal reservoir are above 90°C (Figure 3).

Based on all geothermometer data it is possible that waters with a relatively high temperature can be found in the northern part of the city of Sofia and in the towns of Mramor, Dobroslavtzi, Gniliane, Trebich; and within an area east of Sofia, between the towns of Kazichene and Ravno pole where 81°C geothermal water has already been found (the data for this water is not included in the report). All these prospect areas are in the sedimentary rocks of the field. The maximum temperature for the water that has accumulated in the volcanic rocks, of the southern and western parts of the Sofia field, is not expected to be higher than 40°C. These results are in agreement with those obtained by the helium method and other methods of geothermal exploration that have been used in this field. Apparently, no geothermal water with significantly higher temperature than the measured temperature of existing waters are likely to be found. However, the best area for drilling is around the town of Mramor where the highest temperature for this field was predicted by the chalcedony geothermometer. The water might prove to have total dissolved solids in excess of than 2000 mg/l and could be used directly for heating but a calcite scaling problem is predicted by model calculations.

7.2 The Kazanlak field

The four geothermal areas in the Kazanlak field along the Tundja river are from west to east as follows: Pavel bania, Ovoshtnik, Iagoda, and Korten. All of them are located in intrusive rocks (Palaeozoic granites). The size of each area is within the range of 2-4 km^2. Geothermal water is accumulated in the granite rock. The granite rock is covered by Pliocene-Quaternary sediments which are of different thickness in each area. Na-HCO_3 type waters were observed in the Pavel bania and Ovoshtnik areas while Na-SO_4 type waters were found in the Iagoda and Korten areas.

There are 7 natural springs in Pavel bania which have been known for a long time. The springs were connected to pipes during the 1930s. In the late 1950s, 15 shallow wells (30 m) and 3 deeper wells (more than 100 m) were drilled. During 1968-69, the deepest wells, 7 and 8, were drilled (approximately 700 m). The granite basement rock was found at a depth of 50 to 90 m. The total flow before drilling was 6 l/s but increased three times (to about 18 l/s) after drilling, and a maximum temperature of 58°C was observed.

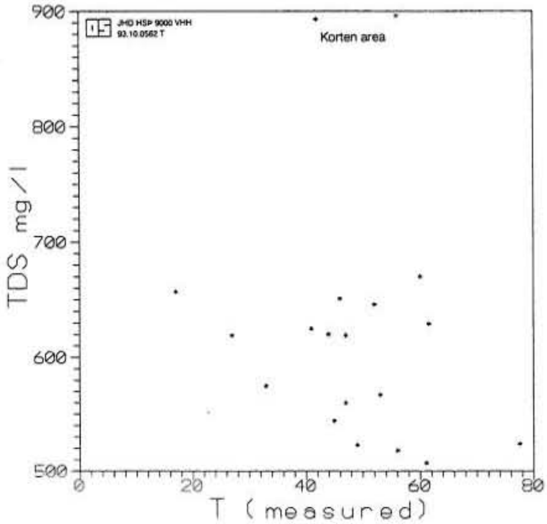

FIGURE 12: The Kazanlak field, total dissolved solids vs. temperature (°C)

There was only one hot spring in the Ovoshtnik area but after an earthquake (in 1920s), a new one appeared. Then, 5 wells (450-900 m deep) were drilled which reached the main reservoir (granite rock) at 300-350 m depth. The total flow is more than 30 l/s with a maximum temperature of 78°C. Drilling for hot water in the Iagoda area began in 1961 when 5 wells were drilled. They produce more than 20 l/s geothermal water with a temperature of 47°C. Two wells were drilled in Korten area and the hot water flow is more than 10 l/s at 56°C. Today, a total of 19 geothermal wells and springs produce hot water in the Kazanlak field. The flow rate is about 70 l/s and the maximum temperature 78°C.

The chemical composition of all natural springs and geothermal wells in the Kazanlak field was taken into consideration including 8 samples from Pavel bania; 5 samples from Ovoshtnik; 4 samples from Iagoda; and 2 samples from Korten (Table 3). As shown in Figure 12, the total dissolved solids (TDS) concentration is not related to the measured temperature in this field. It

TABLE 3: Chemical composition of geothermal waters in the Kazanlak field (mg/l) (the location of the samples is shown in Figure 2)

No.	pH	TDS	Cl	SO_4	CO_2	Na	K	Ca	Mg	SiO_2
88	7.60	619	12.3	22.2	250.8	154.6	9.0	7.4	0.6	35.9
89	7.60	629	12.3	27.2	255.2	155.9	8.7	8.6	1.1	34.3
90	7.40	651	10.7	20.2	250.8	149.8	8.6	8.8	0.5	67.8
91	7.70	646	10.6	18.5	244.1	148.6	9.1	6.3	0.3	75.1
92	7.80	670	11.9	23.0	253.0	154.6	9.2	7.4	0.2	74.6
93	7.60	619	13.4	20.4	255.2	150.5	14.4	8.3	0.7	32.2
94	7.60	620	12.3	19.3	255.2	148.2	12.8	8.1	0.8	38.5
95	7.50	657	14.1	23.0	264.0	156.5	13.1	8.9	0.5	38.5
96	8.60	524	19.8	53.9	138.6	135.1	6.4	3.5		68.2
97	8.60	507	19.8	63.4	143.0	137.6	4.2	3.9	1.4	41.3
98	8.50	567	21.4	66.5	162.8	149.6	8.6	3.9	0.4	49.8
99	8.62	518	22.3	63.4	149.6	145.5	6.3	3.3	0.5	34.3
100	8.45	523	20.7	63.6	158.4	146.8	6.3	3.5	0.4	28.6
101	8.30	560	24.7	119.7	129.8	152.8	6.2	4.7		42.9
102	8.30	544	24.4	116.4	81.0	149.0		7.0	2.0	63.8
103	8.75	575	24.9	120.6	118.7	156.6		5.1	1.0	62.0
104	8.60	625	26.1	120.6	139.2	157.2		5.0	0.2	83.4
105	8.15	896	38.2	321.7	139.2	241.4	7.4	12.2	0.4	66.8
106	7.82	893	38.2	309.0	139.2	239.4	7.5	12.4	0.4	68.8

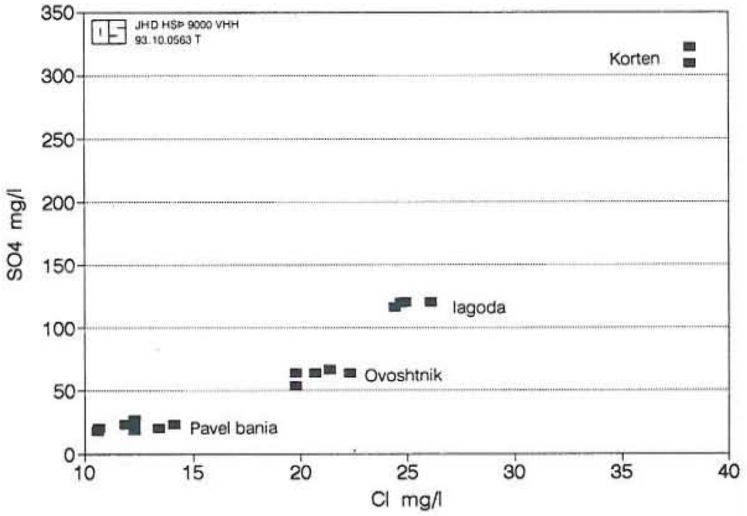

FIGURE 13: The Kazanlak field, SO_4 vs. Cl

is low, 500-700 mg/l, except for the geothermal water from Korten where it is slightly higher, 900 mg/l. All the waters can be classified as fresh waters. There is a very good correlation between SO_4 and Cl (Figure 13). The samples clearly fall into four groups. In Figure 13 it can be seen that these four groups represent the four areas mentioned above. This means that there is clearly a chemical zonation from west to east in this geothermal field. A similar situation can be seen in Figure 14 where Cl was plotted versus Na. In this case, there are three groups because the samples for Ovoshtnik and Iagoda group together. No correlation was found for other chemical species such as SO_4 and K or SiO_2 and Mg.

As an example of geothermal water from the Kazanlak field, Figure 15 shows the results of equilibrium calculations for one sample, using a log(Q/K) versus temperature plot. The six geothermal minerals that were used are: albite, calcite, fluorite, amorphous silica, chalcedony, and quartz. The curves for albite and chalcedony intersect the log(Q/K)=0 at 40°C. The curves for quartz and fluorite intersect the equilibrium line at 70-90°C. The curve for calcite shows that this

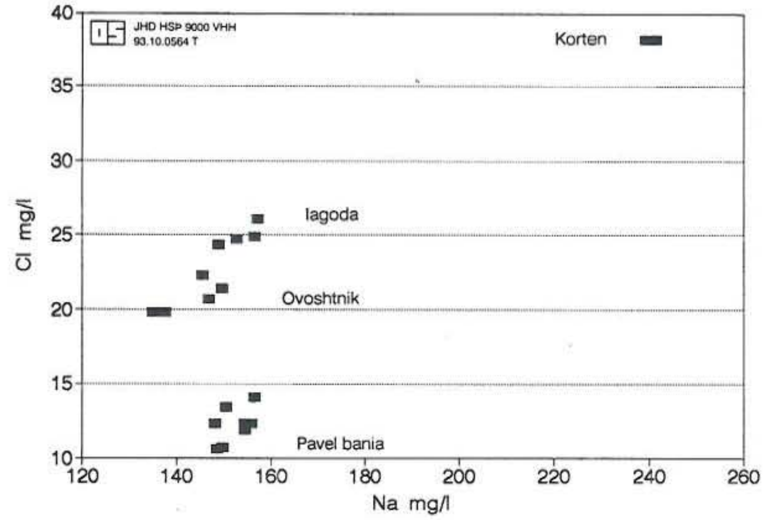

FIGURE 14: The Kazanlak field, Cl vs. Na

water is supersaturated with respect to calcite, except at very low temperatures. Only the curve for amorphous silica shows undersaturation. Based on this data from Kazanlak field it can be concluded that the equilibrium temperature in the geothermal reservoir is between 40°C and 80°C.

Using the computer programme WATCH, the chalcedony and Na-K geothermometer temperatures were computed. The chalcedony temperature was plotted versus CO_2 values (Figure 16). No correlation between them was established but the geothermal waters were divided into two groups according to their CO_2 values. One group includes the geothermal water from Pavel bania area with CO_2 from 240 to 270 mg/l. The other group includes waters from other three areas of the Kazanlak field. They show a lower CO_2 content (between 120 mg/l and 160 mg/l).

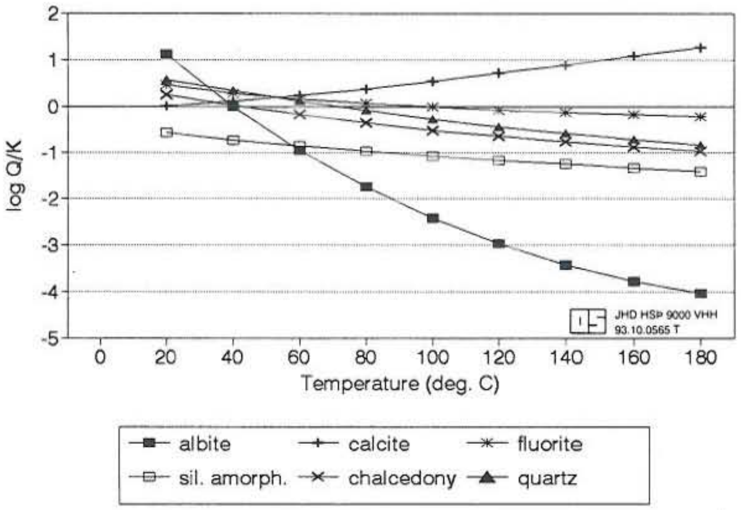

FIGURE 15: The Kazanlak field, equilibrium temperature graph (Iagoda)

Figure 17 shows a correlation between chalcedony and measured temperatures. There are two exceptions. The first one is for several springs in the Pavel bania with low measured temperatures. However, the existence of a hot water in that area has already been demonstrated. The second exception is for several boreholes in the Pavel bania and Korten areas which have predicted temperatures higher than 80°C. These can only be proven or refuted after drilling a new well in the area.

The data for Na-K geothermometer temperatures versus measured and chalcedony temperatures were plotted but no correlation was established in either case because of unrealistically high predicted temperatures. The data for Na-Li geothermometer temperatures, calculated according to an empirical thermometric relationship (Fouillac and Michard, 1981), are likewise unrealistic and also excluded from the report. The K-Mg and Na-K-Ca geothermometer temperatures were calculated using the CAT_TEMP computer programme. As shown in Figure 18, these two geothermometers are not suitable for application in this geothermal field.

It was found that the chalcedony temperatures are the most appropriate for application in comparison with the other four geothermometers for the Kazanlak field. The data for measured temperatures and chalcedony temperatures are shown in Figures 2 and 3, respectively. The

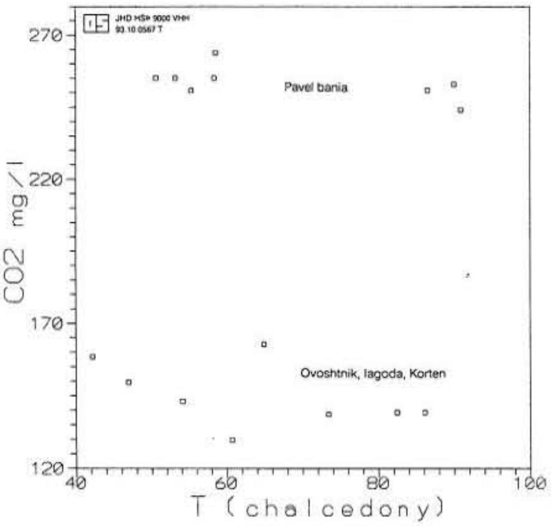

FIGURE 16: The Kazanlak field, CO_2 vs. chalcedony temperature (°C)

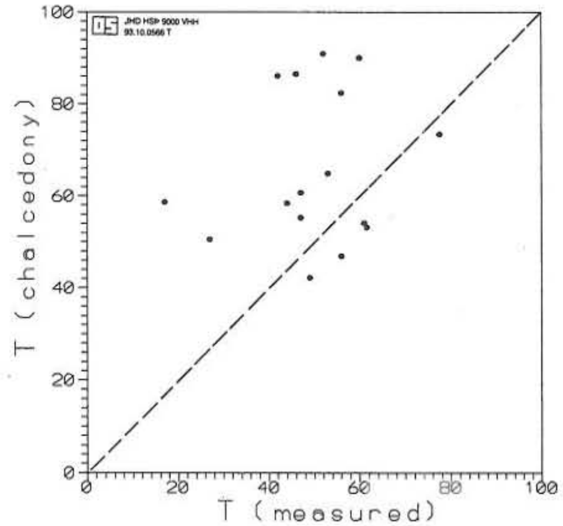

FIGURE 17: The Kazanlak field, chalcedony temperature vs. measured temperatures (°C)

measured temperatures for most of the geothermal waters are between 40 and 70°C (Figure 2). Using the chalcedony geothermometer, it was observed, that the highest predicted temperature (more than 90°C) is found in the Pavel bania area (Figure 3). It is not likely that a natural water with a significantly higher temperature than is found now, can be found in the other three areas in the Kazanlak field.

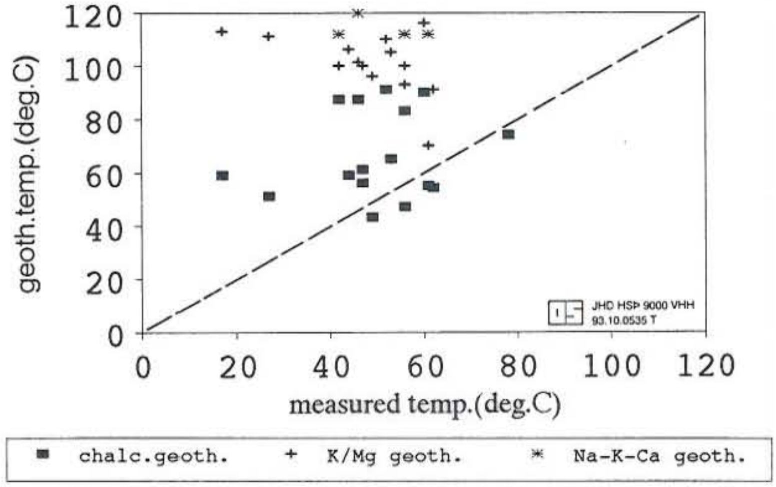

FIGURE 18: The Kazanlak field, chalcedony, K-Mg and Na-K-Ca temperatures vs. measured temperature

7.3 The Burgas field

The Burgas field is located on the Black-Sea coast in the eastern part of Bulgaria. Geothermal activity is widespread all over the field and the main geothermal manifestations are a number of warm springs (Karnobat, Aytos, Troianovo, Medovo, Kableshkovo, Rudnik, Burgaski bania). The biggest spring is located in Burgaski bania (about 7 km from the town of Burgas). The flowrate of this spring is 48 l/s at a temperature of 41°C. The first deep well (1250 m) was drilled in 1966 in Slanchev briag sea-side resort and it produces geothermal water of 32°C. The deepest borehole (3000 m) was drilled near the town of Pomorie for oil exploration. The rocks of the area within which the Burgas field are located belong to Srednogorie zone. They consist mainly of andesites of Upper Cretaceous age.

The results of chemical analyses of 14 springs and wells in this field are shown in Table 4. It can be seen in Figure 19 that most of them have total dissolved solids below 1000 mg/l. Only two samples from the deep boreholes in Slanchev briag have very high TDS values of more than 14000 mg/l. The reason is that both of these wells are situated on the seashore where the sea water influence on the geothermal water is significant.

TABLE 4: Chemical composition of geothermal waters in the Burgas field (mg/l) (the location of the samples is shown in Figure 2)

No.	pH	TDS	Cl	SO_4	CO_2	Na	K	Ca	Mg	SiO_2
74	9.45	440	25.8	32.9	136.4	183.8	0.2	0.8		40.6
75	8.90	440	11.6	35.4	176.0	124.2	0.2	1.9	0.6	13.9
76	9.00	470	25.4	59.7	145.2	122.0	0.6	3.7	0.7	41.6
77	9.50	408	17.7	22.2	134.2	113.0	0.2	1.0		45.8
78	9.60	495	25.0	20.6	149.6	135.4	1.2	1.4		71.5
79	9.50	405	22.8	14.8	112.2	117.4	0.6	0.6	0.4	64.4
80	9.50	438	22.1	17.7	136.4	121.2	0.7	0.6		60.1
81	7.70	14901	9149		37.4	4393	32.4	1112	132.0	18.3
82	7.60	14725	9028	2.7	30.8	4197	31.9	1315	70.4	23.5
83	7.85	468	15.9	39.5	184.8	82.9	0.4	23.4	9.5	29.0
84	9.70	570	141.9	68.3	50.6	168.1	0.5	1.9		62.8
85	8.80	1054	327.1	225.5	28.6	320.1	8.7	24.7	0.6	0.5
86	8.85	1045	327.1	214.8	35.2	315.6	9.0	23.8	0.2	73.4
87	9.55	511	26.0	40.7	154.0	142.8	0.5	1.4	1.1	58.4

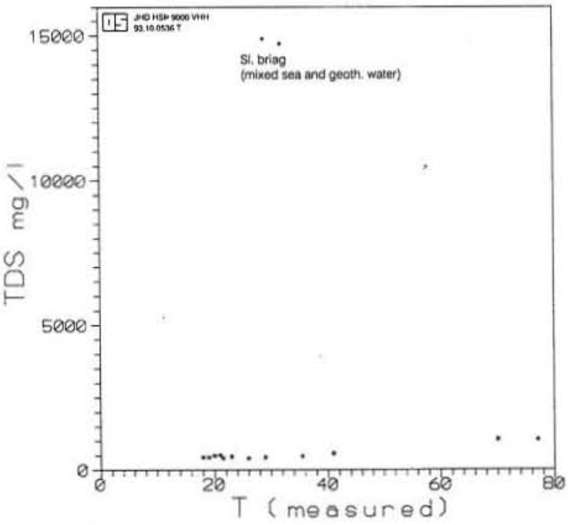

FIGURE 19: The Burgas field, total disolved solids vs. temperature (°C)

Figure 20 clearly shows the influence of the sea water and an approximately linear relation between sodium and chloride. No correlation was found for other chemical species.

The log(Q/K) values were plotted versus temperature to find the equilibrium temperature. An example is shown in Figure 21. The geothermal minerals that were used are: albite, calcite, fluorite, silica amorphous, chalcedony and quartz. The fluid is supersaturated with respect to calcite at all temperatures but it is undersaturated with respect to amorphous silica. On the other hand the other four curves intersect the log(Q/K)=0 at different temperatures. The equilibrium temperature can not be determined accurately in this case, but it could be in the range 50 to 80°C. As demonstrated in Figure 22, no correlation was observed between measured temperature and the silica concentration of the waters. The chalcedony and Na-K geothermometer temperatures were computed using the computer programme WATCH.

The results for the chalcedony geothermometer are plotted against measured temperatures and CO_2 values (Figures 21 and 22). The correlation between the

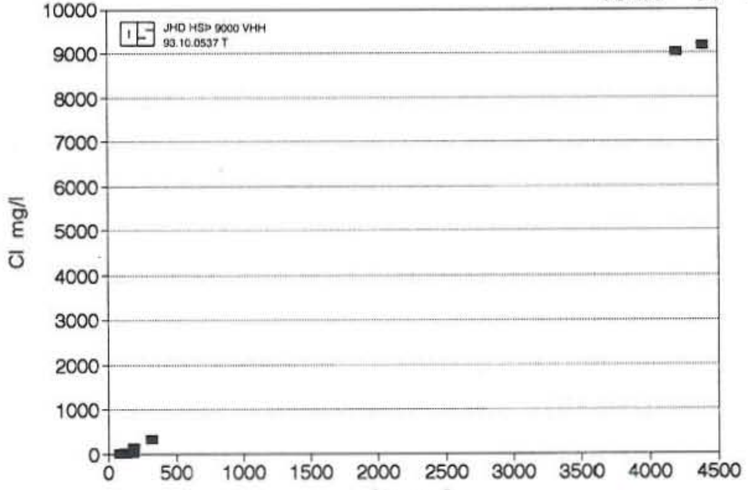

FIGURE 20: The Burgas field, Cl vs. Na

chalcedony and measured temperatures is not clear in this case.

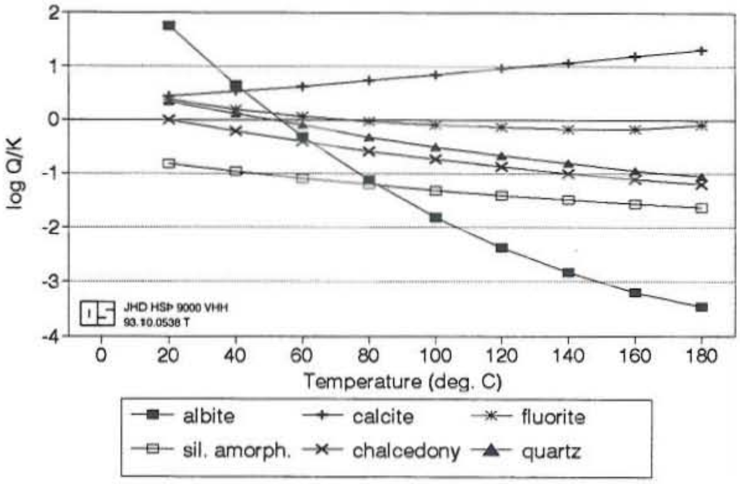

FIGURE 21: The Burgas field, equilibrium temperature graph (S. briag)

A correlation exists only for some of the samples but it is unrealistic for the highest measured temperature in this region (77°C) because the predicted temperatures are lower than the measured temperatures (Figures 2 and 3). The Na-K geothermometer usually gives higher temperatures but they are still realistic (about 90°C) for the samples with highest measured temperatures in this field. The results for the Na-Li geothermometer are considerably higher than those for the other geothermometers used in this field and therefore they were ignored here. The K-Mg and Na-K-Ca temperatures were calculated for all the samples.

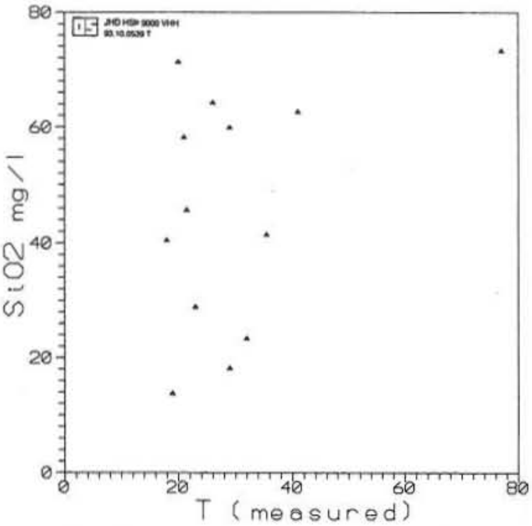

FIGURE 22: The Burgas field, SiO_2 vs. measured temperature (°C)

Figure 23 shows poor correlation both for measured temperatures and chalcedony, K-Mg and Na-K-Ca geothermometer temperatures. It can be concluded that Na-Li, K-Mg and Na-K-Ca temperatures are unrealistic for the waters in this area. The chalcedony and Na-K geothermometers can be used for some of the waters in this field. Figure 3 shows that the highest predicted water temperature can be expected in the Medovo area (No. 78-80), but it is not likely to be higher than 70°C. Although the thickness of the reservoir is very great, of the

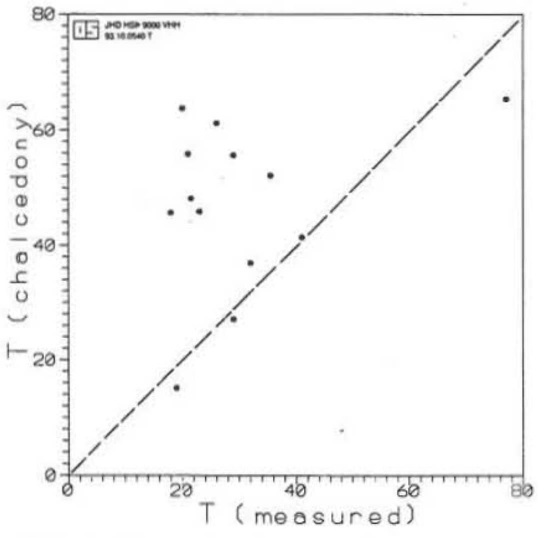

FIGURE 23: The Burgas field, chalcedony temperature vs. measured temperature (°C)

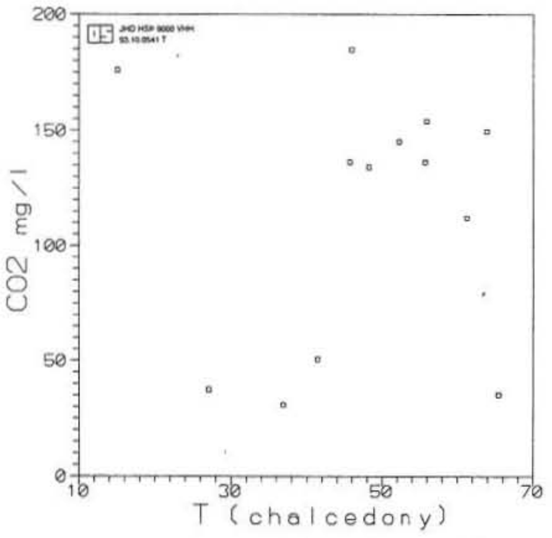

FIGURE 24: The Burgas field, CO_2 vs. chalcedony temperature (°C)

order of 3000 m, no indication of water with higher temperature than presently exploited (No. 86-77°C, Figure 2) was noted. Future drilling should be located within the Medovo area, which seems to be the most promising area of the Burgas field, as regards geothermal energy.

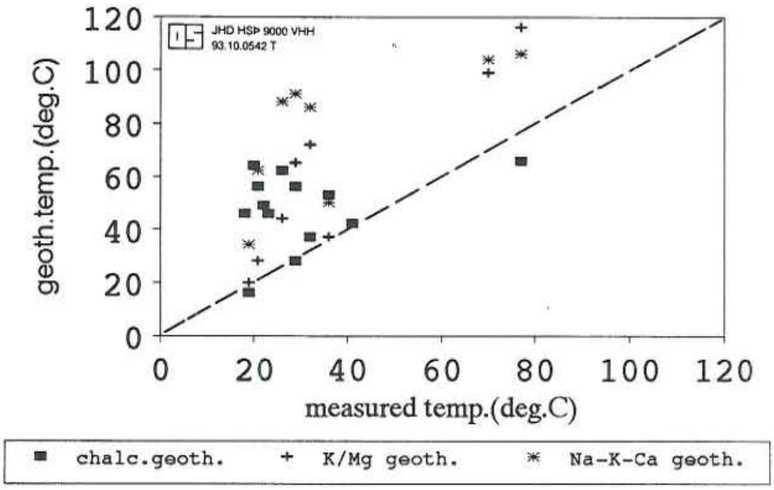

FIGURE 25: The Burgas field, geothermometer temperature vs. measured temperature

7.4 The Razlog field

The Razlog field is situated among the mountains of Rila, Pirin, and Rodopi in the southwestern part of Bulgaria. There are several geothermal areas in this field. Three of them (Gulijna bania, Eleshnitza and Dobrinishte) are near the river of Mesta and the others (Bachevo, Katarino, Razlog, Belitza, Dagonova mahala and Iakoruda) are north-west of the first group. Initially, there were about 70 natural hot springs in the area. The total flowrate was approximately 100 l/s and the maximum water temperature 56°C.

More than 20 wells were drilled 1960-1980. Today, most of them are producing wells. The surface manifestations decreased or disappeared altogether in some places after drilling. The flowrate increased up to 160 l/s but the maximum temperature did not change. The rock strata underlying the Razlog field are made up of gneiss and granite. These metamorphic and intrusive rocks are capped with Palaeogene, Neogene and Quaternary sediments with a thickness of 50 m to several hundred meters.

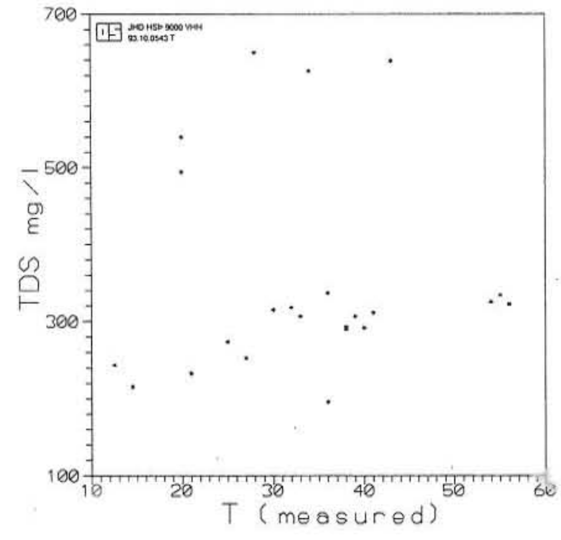

FIGURE 26: The Razlog field, total dissolved solids vs. temperature (°C)

The chemical composition of 24 natural springs and geothermal wells in the Razlog field were taken into consideration (Table 5) (for location, see Figures 2 and 3). A homogeneous chemistry of the water from different sources was observed. For instance, the total dissolved solids concentration ranges from 200 to 400 mg/l in most of the samples but is slightly higher (500 mg/l to 700 mg/l) in five samples from Katarino and Iakoruda (Figure 26). The other chemical diagrams (e.g. Figure 27) show a similar situation to that shown in Figure 26. The above mentioned five waters are more variable in chemical composition than the others. Only the SiO_2 value increases gradually with the temperature of the waters (Figure 28).

The log(Q/K) versus temperature plot for a geothermal water from the Razlog field (Katarino area) demonstrates its equilibrium characteristics (Figure 29). The six geothermal minerals, that were used, are the same as the ones used for the Burgas and Kazanlak fields: albite,

TABLE 5: Chemical composition of geothermal waters in the Razlog field (mg/l)
(the location of samples is shown in Figure 2)

No.	pH	TDS	Cl	SO_4	CO_2	Na	K	Ca	Mg	SiO_2
9	9.30	334	4.9	49.4	79.2	83.0	0.9	1.7		52.4
10	9.30	323	5.7	45.7	77.0	80.8	0.9	2.2	0.4	52.8
11	8.81	325	5.4	61.3	68.2	86.4	0.9	1.9	0.3	50.8
12	9.30	196	3.7	19.3	47.8	47.6	0.4	2.6		36.3
13	9.40	321	4.7	45.7	63.8	83.7	0.9	1.9		61.4
14	8.60	274	4.2	51.4	74.8	59.8	1.8	9.7	1.6	30.8
15	9.40	253	4.2	47.7	59.4	64.9	1.5	2.4	0.4	34.6
16	9.65	216	3.9	28.4	52.8	67.2	0.1	2.0		22.6
17	9.40	244	11.7	17.3	79.2	75.8	0.3	1.3		14.5
18	8.90	540	7.8	288.0	26.4	148.1	1.5	15.2		28.7
19	8.90	494	7.8	266.7	19.8	135.7	1.4	14.4		27.1
20	7.61	233	1.8	2.2	118.6			29.8	13.9	17.2
21	8.22	650	9.5	244.4	92.4	175.1	2.6	10.8		51.5
23	9.17	307	8.6	39.5	70.4	70.1	1.9	3.0	0.1	63.2
24	9.16	318	6.3	38.7	74.8	73.5	2.1	2.6		66.9
25	9.08	307	5.7	37.9	63.8	68.9	2.4	2.9	0.4	74.4
26	9.19	292	5.9	36.6	70.2	69.5	2.0	2.6	0.2	56.8
27	9.18	337	7.5	37.9	79.2	73.3	2.3	2.6	0.2	77.0
28	9.18	311	6.8	38.3	74.8	73.4	1.8	2.6	0.2	61.3
29	9.09	315	5.7	42.8	70.4	71.2	2.0	2.4	0.5	68.8
30	8.81	290	8.6	29.2	79.2	61.6	2.3	4.6	1.0	53.0
31	9.16	293	8.6	37.4	66.0	71.5	2.1	2.6	0.2	58.1
32	8.29	626	9.1	226.3	88.0	165.6	2.6	10.8		58.6
33	8.27	639	9.1	242.4	83.6	171.5	2.2	11.6		56.4

calcite, fluorite, amorphous silica, chalcedony and quartz. The results are very similar to those for the Kazanlak field. The calcite curve crosses the equilibrium line at approximately 100°C, whereas the curves for quartz and albite cross the line in the temperature range 35-55°C. Chalcedony and fluorite cross the equilibrium line at very low temperatures (approx. 20°C) and the water is undersaturated at all temperatures with respect to amorphous silica. The equilibrium temperature is likely to be 40°C.

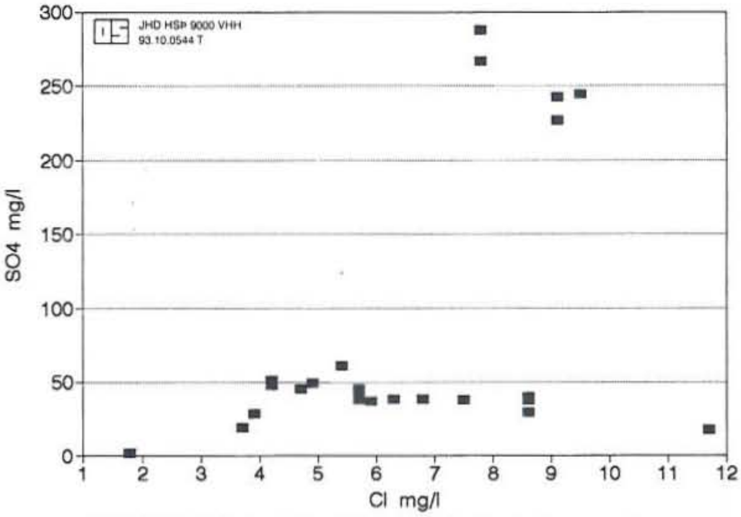

FIGURE 27: The Razlog field, SO_4 vs. Cl

As for water from the other fields, the chalcedony and Na-K geothermometer temperatures were calculated using the WATCH programme. Figure 30 shows the relation between CO_2 concentrations and chalcedony temperatures. At higher temperatures CO_2 shows a tendency to

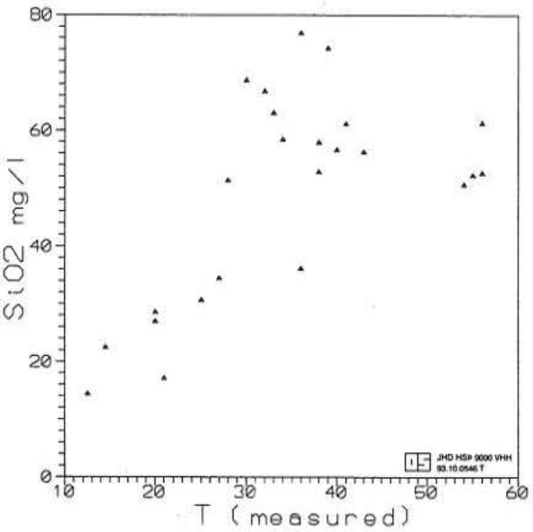

FIGURE 28: The Razlog field, SiO_2 vs. measured temperature(°C)

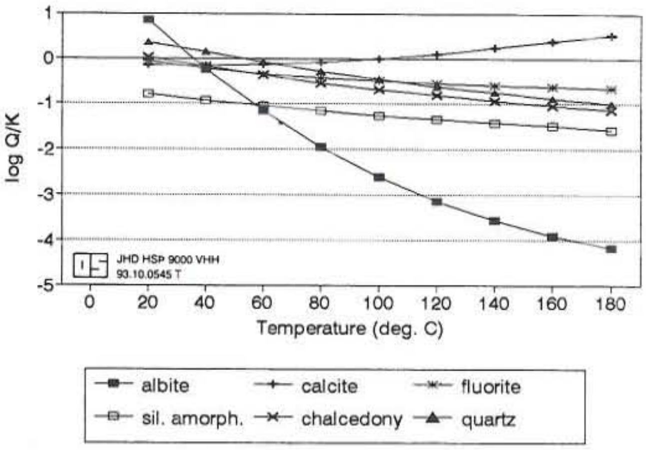

FIGURE 29: The Razlog field, equilibrium temperature graph (Katarino)

increase with temperature. The predicted chalcedony temperatures are higher than the measured temperatures (Figure 31). Furthermore, they are very realistic for this field because almost all of them are below 80°C (the maximum measured temperature is 56°C).

The Na-K geothermometer usually gives higher temperatures than the chalcedony geothermometer for low-temperature waters of the fields in Southern Bulgaria. But in this case, they are slightly higher than chalcedony temperatures. Thus, there is a relatively good correlation between the Na-K and chalcedony temperatures. The computer programme CAT_TEMP was used for calculating the K-Mg and Na-K-Ca geothermometer temperatures. The results are plotted versus measured temperature in a diagram (Figure 32).

The data for measured and chalcedony temperatures are shown in Figures 2 and 3, respectively. The measured temperatures for most geothermal waters in the Razlog field are between 20°C and 50°C but the predicted chalcedony temperatures are in the range 60-80°C. It is possible that water with higher temperatures (10-20°C above measured values) can be found by drilling deeper in the Dobrinishte and Iakoruda areas.

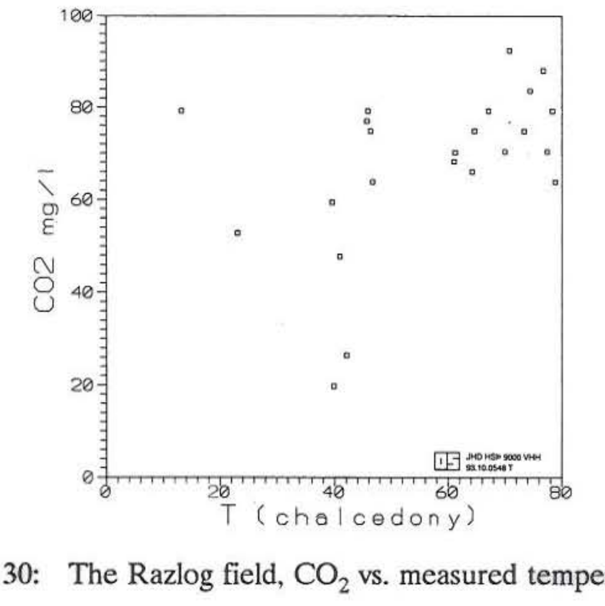

FIGURE 30: The Razlog field, CO_2 vs. measured temperature (°C)

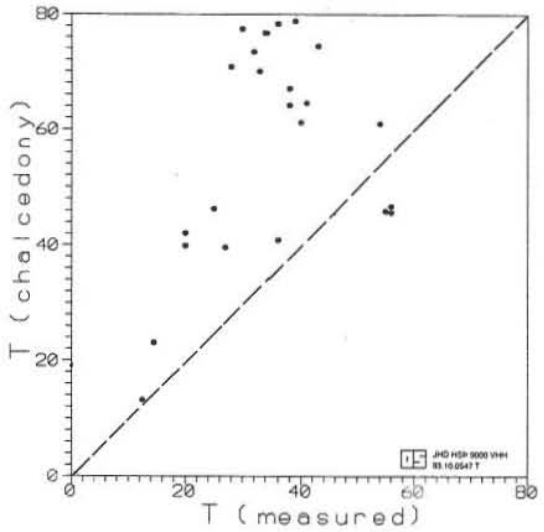

FIGURE 31: The Razlog field, chalcedony temperature vs. measured temperature (°C)

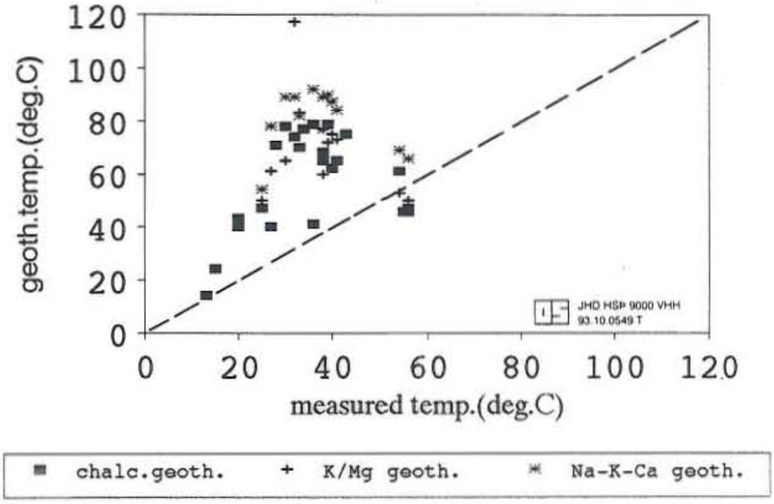

FIGURE 32: The Razlog field, geothermometer temperatures vs. measured temperature

8. PREDICTED TEMPERATURES IN SOUTHERN BULGARIA

The main goal of this report is to predict subsurface temperatures for geothermal water in Southern Bulgaria. The calculations of the predicted temperatures are based on analytical results for more than 200 samples from natural springs and geothermal wells. The samples are from 18 different geothermal fields from this part of the country. Four of these fields (Sofia, Kazanlak, Burgas and Razlog) were selected as typical geothermal areas. A brief description was given of the geology and geothermal exploration of these fields as background information. It was found out (Figure 33) that more than 90% of these geothermal waters have low concentration of total dissolved solids (TDS), below 1000 mg/l although they occur in different geological environments (volcanic, intrusive, and metamorphic rocks). The exceptions are the waters from sedimentary rocks which have TDS concentrations up to 5000 mg/l, and mixed waters which occur near the seashore with a TDS concentration of about 14000 mg/l (Slanchev briag in the Burgas field).

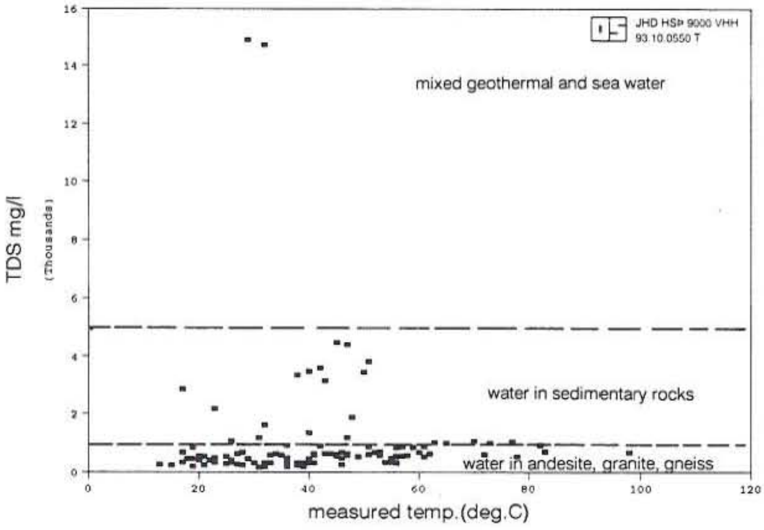

FIGURE 33: Southern Bulgaria, total dissolved soldids vs. measured temperature

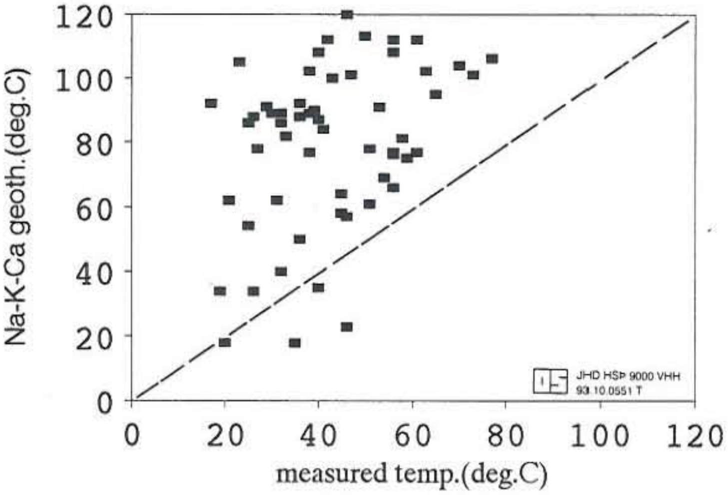

FIGURE 34: Southern Bulgaria, Na-K-Ca geothermometer temperature vs. measured temperature

A comparison was made between various chemical geothermometer temperatures (chalcedony, Na-K, Na-Li, Na-K-Ca, and K-Mg). Application of these geothermometers indicates different underground temperatures for the four chosen fields. Furthermore, the 200 chemical analyses from Southern Bulgaria were interpreted using three chemical geothermometers (chalcedony, Na-K-Ca and K-Mg) employing the WATCH and CAT_TEMP computer programmes. The data are shown in Table 1.

The results for each of the three geothermometers are given in Figures 34, 35 and 36, which show the Na-K-Ca temperature, the K-Mg temperature and the chalcedony temperature, respectively, plotted against measured temperature. It is concluded that as for the selected fields discussed above, the chalcedony geothermometer is the most appropriate to indicate reservoir temperatures in all of Southern Bulgaria (Figure 36).

Figure 37 shows that the maximum predicted temperatures are between 100°C and 110°C but most of them are in the range 40-

70°C. Most of the measured temperatures are in the range 30-60°C, so the possibilities of finding geothermal water with significantly higher temperature than is presently known, are only scarce. Nonetheless, according to the predicted chalcedony temperatures (Figure 37), the additional water that can be found by drilling new wells, could at least double the water supply presently utilized for heating purposes.

At present only 5% of the sources can be directly used for heating. Based on the present data, it has been observed that the areas of Blagoevgrad, Pchelin bania and Sandanski in Southern Bulgaria seem to be the most promising ones with respect to geothermal energy. These areas are not parts of the four fields that have been described in this report.

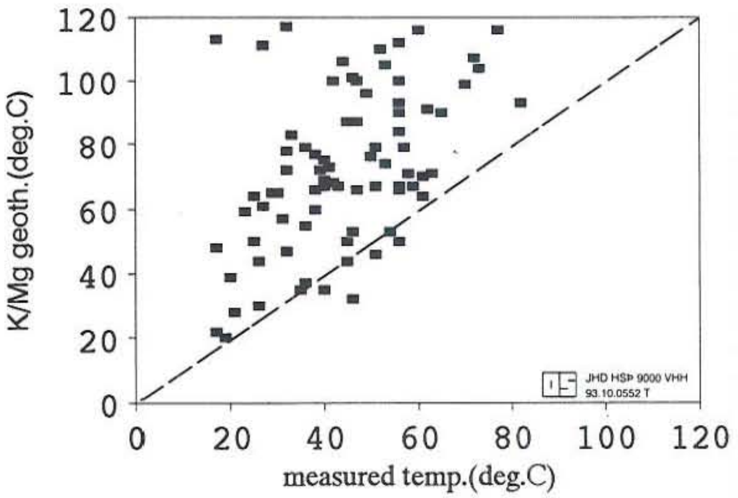

FIGURE 35: Southern Bulgaria, K-Mg geothermometer temperature vs. measured temperature

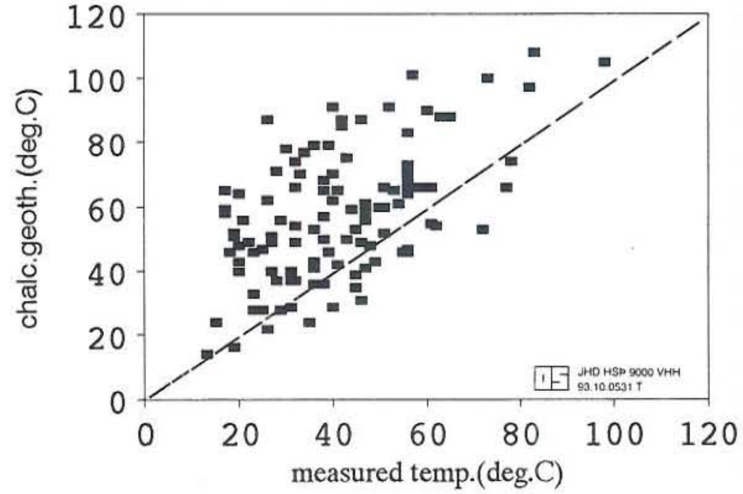

FIGURE 36: Southern Bulgaria, chalcedony geothermometer temperature vs. measured temperature

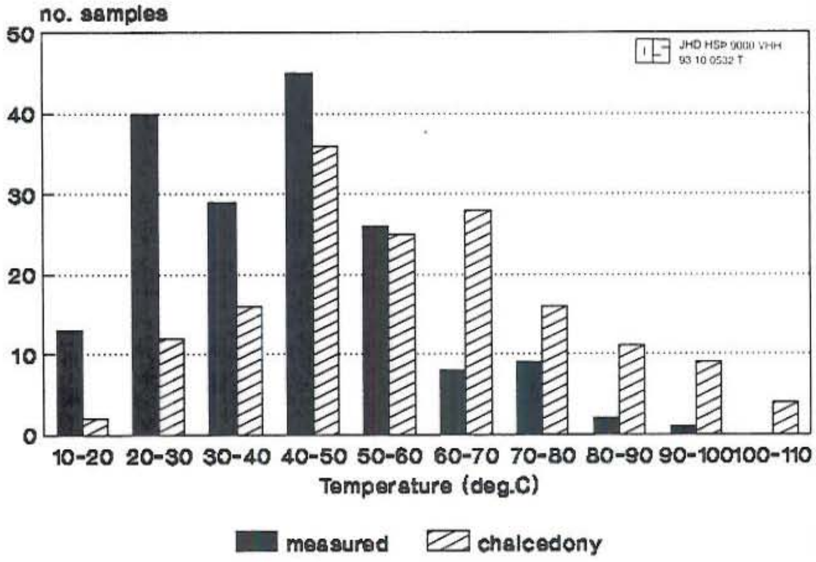

FIGURE 37: Southern Bulgaria, chalcedony and measured temperature histogram

9. CONCLUSIONS AND RECOMMENDATIONS

Chemical geothermometers are relatively simple and inexpensive indicators of subsurface temperatures, and should be an integral part of every geothermal exploration. Various quantitative chemical geothermometers have been developed to predict reservoir temperatures. Five of them (Na-K, chalcedony, Na-Li, Na-K-Ca and K-Mg) were used for the preparation of this report. The chemical compositions of thermal waters from Southern Bulgaria were interpreted using these geothermometers. Temperature calculations can be carried out in the temperature range 0-150°C employing these geothermometers. It should be realized that a considerable part of the data used may not be reliable above 150°C because the maximum geothermal gradient is about 45°C/km for the country. The Na-K and the Na-Li geothermometers gave unrealistically high predicted temperatures. The K-Mg and the Na-K-Ca geothermometers yielded lower results for spring and well waters than the Na-K and the Na-Li geothermometers but in many cases, they were likewise unrealistic. It was the chalcedony geothermometer that proved most reliable for Southern Bulgaria compared to the other four geothermometers. According to the chalcedony geothermometer, the maximum predicted temperatures are in the range 100-110°C. Results also revealed that geothermal waters with 10-20°C higher temperatures could be obtained if deeper drilling were performed in some areas.

When the chemical geothermometers are applied, it is necessary to take into consideration all the available data such as the geology of the fields; and the present and previous processes and conditions. In this report, the application of cation geothermometers for geothermal waters in Southern Bulgaria, was shown to be unreliable. Thus, new calibrations are recommended. In cases where equilibrium was not attained (Burgas and Sofia fields, for instance), the samples represent mixed water or non-equilibrium waters. For all fields where there is an indication of mixing, further study is necessary. Finally, it is recommended that comparisons be made between the results of quantitative chemical geothermometry, which are found in this report, and the results of the more widely-applied qualitative chemical geothermometry in Bulgaria.

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APPENDIX I: An example of the output data of the computer programme WATCH

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VHH, 03.09.93
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Sample number -   Dobrinishte S-3

Program WATCH

Water sample (mg/kg)           Steam sample

pH/deg.C           9.17/ 33.0  Gas (volume %)                 Reference temperature    deg.C :   33.0  (Measured)
CO2               70.40        CO2                 .00
H2S                 .00        H2S                 .00        Sampling pressure     bar abs. :    1.0
NH3                 .00        NH3                 .00        Discharge enthalpy       kJ/kg :   138.  (Calculated)
B                   .00        H2                  .00        Discharge                 kg/s :   10.0
SiO2              63.20        O2                  .00        Steam fraction at collection   :  .0000
Na                70.10        CH4                 .00
K                  1.90        N2                  .00        Measured temperature     deg.C :   33.0
Mg                 .100
Ca                 3.00        Liters gas per kg
F                 5.100        condensate/deg.C   .00/  .0   Condensate (mg/kg)
Cl                 8.60                                       pH/deg.C             .00/  .0
SO4               39.50        Total steam (mg/kg)            CO2                  .00
Al                 .080        CO2                 .00        H2S                  .00
Fe                 .108        H2S                 .00        NH3                  .00
TDS              253.00        NH3                 .00        Na                   .00


Ionic strength =   .00388
Ionic balance :   Cations (mol.eq.)    .00322605    Anions (mol.eq.)    .00330833    Difference (%)  -2.52


Deep water components (mg/kg)                        Deep steam (mg/kg)          Gas pressures (bars-abs.)

B              .00        CO2          70.40         CO2              .00        CO2        .679E-04
SiO2         63.20        H2S            .00         H2S              .00        H2S        .000E+00
Na           70.10        NH3            .00         NH3              .00        NH3        .000E+00
K             1.90        H2             .00         H2               .00        H2         .000E+00
Mg            .100        O2             .00         O2               .00        O2         .000E+00
Ca            3.00        CH4            .00         CH4              .00        CH4        .000E+00
F            5.100        N2             .00         N2               .00        N2         .000E+00
Cl            8.60                                                               H2O        .503E-01
SO4          39.50                                                               Total      .504E-01
Al           .0800
Fe           .1080
TDS         253.00        Aquifer steam fraction =   .0000


Ionic strength =   .00388                                           1000/T (Kelvin) =   3.27
Ionic balance :   Cations (mol.eq.)    .00322605    Anions  (mol.eq.)    .00330832    Difference (%)  -2.52

Chemical geothermometers (degrees C)
Quartz       101.5   (Fournier & Potter, GRC Bulletin, pp. 3-12, Nov. 1982)
Chalcedony    71.1   (Fournier, Geothermics, vol. 5, pp. 41-50, 1977)
Na/K          90.3   (Arnorsson et al., Geochim. Cosmochim. Acta, vol. 47, pp. 567-577, 1983)

Oxidation potential (volts) :     Eh H2S= 99.999   Eh CH4= 99.999   Eh H2= 99.999   Eh NH3= 99.999
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Activity coefficients in deep water

H+           .939        KSO4-         .935        Fe++           .769       FeCl+          .934
OH-          .933        F-            .933        Fe+++          .571       Al+++          .571
H3SiO4-      .934        Cl-           .933        FeOH+          .935       AlOH++         .766
H2SiO4--     .766        Na+           .934        Fe(OH)3--      .935       Al(OH)2+       .935
H2BO3-       .932        K+            .933        Fe(OH)4--      .765       Al(OH)4-       .934
HCO3-        .934        Ca++          .769        Fe(OH)++       .765       AlSO4+         .934
CO3--        .763        Mg++          .776        Fe(OH)2+       .935       Al(SO4)2-      .934
HS-          .933        CaHCO3+       .936        Fe(OH)4-       .935       AlF++          .766
S--          .765        MgHCO3+       .934        FeSO4+         .935       AlF2+          .935
HSO4-        .934        CaOH+         .936        FeCl++         .765       AlF4-          .934
SO4--        .761        MgOH+         .937        FeCl2+         .935       AlF5--         .763
NaSO4-       .935        NH4+          .932        FeCl4-         .934       AlF6---        .544


Chemical species in deep water - ppm and log mole                     Deep water pH is  9.170

H+            .00   -9.143        Mg++            .09   -5.450        Fe(OH)3        .00      .000
OH-           .49   -4.538        NaCl            .00   -7.668        Fe(OH)4-       .00      .000
H4SiO4      78.77   -3.086        KCl             .00   -9.476        FeCl+          .00   -10.013
H3SiO4-     21.22   -3.651        NaSO4-          .21   -5.753        FeCl2          .00   -30.389
H2SiO4--      .10   -5.994        KSO4-           .02   -6.933        FeCl++         .00      .000
NaH3SiO4      .95   -5.093        CaSO4           .24   -5.749        FeCl2+         .00      .000
H3BO3         .00     .000        MgSO4           .02   -6.703        FeCl3          .00      .000
H2BO3-        .00     .000        CaCO3           .84   -5.074        FeCl4-         .00      .000
H2CO3         .13   -5.680        MgCO3           .03   -6.523        FeSO4          .01    -7.440
HCO3-       88.59   -2.838        CaHCO3+         .10   -6.025        FeSO4+         .00      .000
CO3--        8.16   -3.867        MgHCO3+         .00   -7.304        Al+++          .00   -19.775
H2S           .00     .000        CaOH+           .00   -7.596        AlOH++         .00   -15.186
HS-           .00     .000        MgOH+           .00   -7.850        Al(OH)2+       .00   -11.029
S--           .00     .000        NH4OH           .00     .000        Al(OH)3        .00    -7.588
H2SO4         .00  -22.584        NH4+            .00     .000        Al(OH)4-       .57    -5.532
HSO4-         .00  -10.552        Fe++            .05   -6.030        AlSO4+         .00   -20.441
SO4--       39.13   -3.390        Fe+++           .00     .000        Al(SO4)2-      .00   -22.044
HF            .00   -9.528        FeOH+           .07   -6.023        AlF++          .00   -16.510
F-           5.10   -3.571        Fe(OH)2         .00   -7.839        AlF2+          .00   -14.567
Cl-          8.60   -3.615        Fe(OH)3-        .00  -11.437        AlF3           .00   -14.141
Na+         69.87   -2.517        Fe(OH)4--       .00  -16.341        AlF4-          .00   -15.331
K+           1.90   -4.314        Fe(OH)++        .00     .000        AlF5--         .00   -17.500
Ca++         2.55   -4.196        Fe(OH)2+        .00     .000        AlF6---        .00   -20.484


Log solubility products of minerals in deep water

               Theor.    Calc.                    Theor.    Calc.                   Theor.    Calc.
Adularia      -20.744  -19.162    Albite, low    -19.702  -17.364    Analcime      -15.635  -14.277
Anhydrite      -4.786   -7.819    Calcite         -8.552   -8.295    Chalcedony     -3.486   -3.086
Mg-Chlorite   -84.393  -84.718    Fluorite       -10.881  -11.513    Goethite       -7.008   99.999
Laumontite    -31.584  -27.771    Microcline     -22.689  -19.162    Magnetite     -34.962   99.999
Ca-Montmor.  -108.156  -95.200    K-Montmor.     -53.826  -49.789    Mg-Montmor.  -108.870  -96.449
Na-Montmor.   -53.531  -47.992    Muscovite      -26.677  -21.140    Prehnite      -40.532  -38.131
Pyrrhotite   -133.943   99.999    Pyrite        -200.137   99.999    Quartz         -3.836   -3.086
Wairakite     -27.424  -27.771    Wollastonite    13.342   10.943    Zoisite       -39.022  -39.121
Epidote       -49.362   99.999    Marcasite     -171.621   99.999    Talc           20.853   25.995
Chrysotile     30.526   32.168    Sil. amorph.    -2.647   -3.086
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APPENDIX II: An example of the output data of the computer programme CAT_TEMP

```
Sample number = 10  (Gulijna bania W-6)


Na-K temperature (SA, 1983 -  25-250C)..............(C) =   44
Na-K temperature (SA, 1983 - 250-350C)..............(C) =   88
Na-K temperature (Fournier, 1979)...................(C) =   82
Na-K temperature (Truesdell, 1976)..................(C) =   32
Na-K temperature (Tonani, 1980).....................(C) =   32
Na-K temperature (Nieva, 1987)......................(C) =   71
Na-K temperature (Giggenbach, 1988).................(C) =  103

K-Mg temperature (Giggenbach, 1988).................(C) =   50

log(sqrt(Ca)/(Na)+2.06 = 0.32
             R-factor = 19.83
Na-K-Ca temperature (Fournier & Truesdell 1973).....(C) =   66

Na-K-Ca temperature (beta=4/3)........(C) =   66
Na-K-Ca temperature (beta=1/3)........(C) =   91

No Mg correction !!
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