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CHEMICAL GEOTHERMOMETRY AND FLUID/MINERAL EQUILIBRIA OF WATERS IN THE NW-BOURGAS SYNCLINORIUM, BULGARIA

Silviya I. Teneva Geology and Geophysics Corporation, G.M.Dimitrov str. No 16, 1113 Sofia, BULGARIA

ABSTRACT

The report focuses on the interpretation of water chemistry in the northwestern part of the Bourgas synclinorium with the aim of predicting reservoir temperature. The types of waters in this region are, a) dilute neutral pH cold springs, and b) HCO_3 -Na, Cl-HCO₃-Na and Cl-Na well waters, some of them with relatively high SO₄.

Silica and cation geothermometers are applied to predict possible subsurface temperatures using 75 chemical analysis from wells and springs calibrated by chemical equilibrium calculation with the chemical speciation programmes WATCH and SOLVEQ. The equilibrium state of thermal waters was studied by means of log Q/K diagrams, Na-K-Mg triangular diagram and the equilibrium state of cation/proton ratios at the measured chalcedony and quartz reference temperatures. In this way, it was shown which minerals are possibly in equilibrium with the fluid constituents at certain temperature. This approach facilitates the choice of geothermometers and provides a better understanding of the system. Furthermore, the silica-enthalpy mixing model was used to estimate underground temperature of the hot unmixed geothermal water. Finally, the possible subsurface temperatures were predicted. It was found that quartz solubility controls reservoir temperature in the Straldja field and water with temperatures of 100-120°C, which is 20-40°C higher than presently found, could be obtained by deep drilling. Chalcedony solubility controls reservoir temperature in the Aitos field and water with temperature 80-100°C could be obtained by drilling. The geothermal water in this region could be used for balneology, swimming pools, bathing, recreation and heating systems.

1. INTRODUCTION

Bulgaria is situated within the Balkan peninsula. Its territory is within two main tectonic structures, the Moesian platform and Alpidic-Himalayan belt. The territory of the country is a complex mosaic of platform and raised areas, deeply tectonized with extensive lithological variations and multiple magmatic manifestations, quite rich in thermal waters with temperatures between 25 and 105°C. Based on the hydrogeological conditions the country is divided into six regions, one of which is the Sredna Gora region. The Sredna Gora region is divided into several hydrogeological structures and basins of diverse dimensions,

shapes, lithology and stratigraphy. The main one is the Bourgas synclinorium filled with volcanosedimentary formations of Upper Cretaceous age and a thickness probably up to 3000 m.

Chemical methods are relatively fast, one of the most efficient and inexpensive, and should be a part of any geothermal energy exploration and evaluation programme. Chemical composition of the water can be used for estimating subsurface temperature, observing the degree of mixing and predicting possible scaling and corrosion. Chemical geothermometry is one of the major tasks of geochemistry in the exploration of geothermal reservoirs.

The report starts with a short review of the geological, tectonic and geothermal characteristics of the Bourgas synclinorium. This is necessary for the presentation of the main subject. The report focuses on the interpretation of chemical data of cold springs and wells from the northwestern part. The general aim is to estimate reservoir temperature in this part of the Bourgas synclinorium using empirical chemical geothermometers and equilibrium calculations. Comparison is made between the outcome of the various chemical geothermometers and equilibrium temperature. Various chemical geothermometers such as silica, Na-K, Na-K-Ca, K-Mg are used. Chemical analyses were used to assess the probable equilibrium temperatures. The calculations were performed using the WATCH aqueous speciation programme of Arnorsson et al. (1982) and SOLVEQ of Reed (1982). The maximum predicted temperatures are 100-120°C in the lower part of the Upper Cretaceous Complex. In the Triassic and Jurassic sediments of the region, waters with temperatures up to 150°C can be found.

This report presents my work during the last 12 weeks of a six months geothermal training at the United Nations University in Reykjavik, Iceland.

2. GEOLOGICAL, HYDROGEOLOGICAL AND GEOTHERMAL FEATURES OF THE BOURGAS SYNCLINORIUM

The Bourgas synclinorium takes up the easternmost section of the Sredna Gora structural zone and is a part of an extremely fractured and declining (in the earth's upper crust) area. To the north and south it borders with deep fractured structures, the rear Balkan Fracture and the North Strandja Flexure. To the west, the border is not so clearly marked by disrupted structures. To the east the structure is open (Bonchev, 1971).

The Bourgas synclinorium is a complex graben-like structure, consisting of Upper Cretaceous volcanic and sedimentary rocks of immense thickness and divided into four series, the Bourgas, the Michurin, the Grudovo and the Varshilovo series. In certain parts of the region deposits of Palaeogene, Miocene, Pliocene and Quaternary sediments are found covering the Upper Cretaceous complex (Figure 1).

The evolution of the Upper Cretaceous period in the synclinorium is characterised by four stages: sedimentogenic, sedimentogenic and volcanogenic, volcanogenic, and a final sedimentogenic stage. Drilling near the town of Pomorie revealed that the overall thickness of the volcano-sedimentary complex is in excess of 3,280 m. From a general point of view, it is deemed that thickness of the Upper Cretaceous sediments is smaller in the southern region of the synclinorium. No direct data is available on the underlay but, judging from some findings in Balkan and Strandja, it has a varied composition, pre-Palaeozoic crystalline, Palaeozoic magmatites and metamorphites, Triassic and Jurassic terrigenous carbonate sediments; all in different stages of metamorphosis.

Two very different structural zones can be distinguished in the tectonic make-up of the synclinorium. A northern zone, where the pattern consists of blocks and folds. It is characterised by rather complex combinations of Palaeo-volcanic formations and folds deposited at a later time, with a variety of disruptions



FIGURE 1: Geological map of the Bourgas synclinorium (Chesitev and Kanchev, 1989)

cutting through the folds. The southern zone is monoclinal and very fractured and comprises a complexity of fissures, mainly upcasts. The two zones are separated by the Krushovetz Upcast along which the southern wing ascended.

An analysis of the data on the bulk density and magnetic receptivity of the rocks revealed that they vary considerably in the different lithological types. This is probably due to the great diversity in the composition of the rocks and the extent of their metamorphism, tectonic deformation, evaporation, etc. Sedimentary rocks have the lowest bulk density, and intrusive rocks the highest. Sedimentary rocks are also the least magnetic, whereas the strongest magnetism is observed in the effusive rocks.

The geological-structural and the lithological-facial peculiarities of the Bourgas synclinorium favour the formation of the following aqueous horizons and complexes, the Quaternary, Pliocene, Miocene and Palaeogene Aquifers, and the Upper Cretaceous aqueous complex. The Upper Cretaceous complex takes up the largest area as it is practically found in all parts of the synclinorium. It is a hydrogeological environment with a fissure-type collector. The underground waters are connected to the weathered crust and the disruptive irregularities. Fissure- and layer-type waters are present in the deeper levels of the complex. In the zone of

active water interchange of the complex, the waters are fresh and cold, whereas the waters in the deepest horizons are characterised by a higher mineral content and temperature. In the geological profile of the basin features one can identify two clearly defined hydrothermal zones which differ considerably in their genetic, geochemical and energy characteristics: an upper (infiltration) zone and a lower (elision) zone. The upper hydrothermal zone is located in the volcanogenic formation of the Bourgas series and its waters are formed in the filtration environment created by lithogenic and tectonic fissures. The sub-thermal and thermal springs at Aitos, Medovo, Polyanovo, Kableshkovo, Luka, etc., are all connected to this zone. The composition of the thermal water is mainly bicarbonate-sodium. It is only slightly mineralised, highly alkaline, and the pH is in the range of 8 to 10. It can be expected that strongly mineralised overheated waters with an interesting composition have formed in the deepest layers of the lower hydrothermal zone, high temperature (over 100°C) and hydrostatic pressure. Natural sources of derivatives of these waters are known near the villages of Karageorgievo and Venetz, others have been found during drilling near Slunchev Bryag, Medovo and Primorsko.

The geothermal gradient varies considerably, both as regards areas and with depth. Regarding the volcanogenic and sedimentogenic complex the gradient reaches its highest values in the vicinity of the town Aitos, the village of Medovo, near Slunchev Bryag and the town Straldja. The values of the gradient in the Slunchev Bryag and the Straldja regions are controlled by the prevailing clay component in the Pliocene-Neogene cross section, whereas in the Aitos and Medovo regions they are influenced by the hydrogeological factor. The geothermal gradient varies from 17 to 85°C/km. In the southern part of the synclinorium the geothermal gradient have lower values. This is probably due to the age of the Sakar-Strandja tectonic zone, which is the oldest in the Alpine system in terms of time of formation, and also to the descending movement of the underground waters and the water inflows which cool down the massif. The geothermal gradient varies from 14.5 to 26°C/km. The temperature on all levels is lower in the southern part of the synclinorium. The pattern of the temperature changes is a result of the combined influence of many factors, thickness of the residual complex, hydrogeological cooling or warming, fractures, etc. The temperature anomalies are the most essential features of the geothermal pattern of the Bourgas synclinorium. They are mostly observed in the northern part of the region where the thermal spring water beds are located. The ascending, deeply circulating waters create thermal zones with high gradients. The existing temperature anomalies are a consequence of the following factors, geological-petrographic and geological-structural conditions; neotectonic movements, the northernmost part of the Bourgas synclinorium is situated between two blocks whose vertical movements have different marks; and the influence of the hydrogeological factor.

3. FLUID/MINERAL EQUILIBRIUM STATE OF THE THERMAL WATERS

The chemical composition of a geothermal system is a dynamic one. It is determined by the rate of leaching of the various chemical components from the primary rock constituents, fluid flow into the system and the kinetics of formation of alteration minerals.

Equilibrium in geothermal systems involves geothermal fluid, reservoir rock and conditions under which interaction takes place, pressure and temperature. It is believed that pressure variations in the range of 1-200 bars, occurring in geothermal systems, do not have a significant influence on the equilibrium conditions. The attainment of equilibrium in the reservoir depends on a number of factors such as the kinetics of the particular reaction, the temperature of the reservoir, the reactivity of the wall rock, the concentrations of the indicator elements in the water, and the residence time of the water in the reservoir at the particular temperature. Considering simultaneously the state of equilibrium between a specific water and many hydrothermal minerals as a function of temperature, the best estimate of reservoir temperature can be attained (Reed and Spycher, 1984). In some cases, however, the components that are potential geoindicators are not really in equilibrium with the appropriate minerals due to low temperatures in the reservoirs, mixing with cold water

or possible chemical reactions. Therefore, it is very important to study the equilibrium state of thermal waters in order to check the reliability of geothermometers. For studying equilibrium of the water, dissolved constituents, precipitation and secondary minerals are taken into consideration. Using the activity of aqueous species such as simple ions, complexes or ion pairs calculated for homogeneous equilibrium at 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 $\log (Q/K)_k$ (the saturation index - SI):

$$\log\left(Q/K\right)_{k} = \log \Pi a_{i,k}^{v_{i,k}} - \log K_{k} \tag{1}$$

where Q is the activity quotient, K is the equilibrium constant for mineral k, $a_{i,k}$ is the activity and $v_{i,k}$ is the stoichiometric coefficient of the component species i in the equilibrium mass action expression for mineral k. Values of log Q/K more than, equal to, and less than zero represent supersaturation, equilibrium and undersaturation, respectively.

Equilibrium has been a subject of different studies by many scientists. According to the phase rule Arnorsson et al. (1982 and 1983a) have evaluated that secondary minerals appear to have equilibrated with associated water of the major elements. For basaltic rocks the equilibrium is controlled by quartz, chalcedony, calcite, low albite (sodium feldspar), microcline (potassium feldspar), smectite-chlorite, pyrite-marcasite, iron hydroxides, pyrrhotite-anhydride, epidote at higher temperature, and some other Al silicates at low temperatures, fluorite and anhydride. Water in basaltic rocks is undersaturated with respect to fluorite and dilute waters below 230°C are undersaturated with respect to anhydride. In other geological environments other minerals may be involved. After studying the mineral equilibria of different geothermal waters in Iceland equations, which can be used as "equilibrium lines" for the elements, have been proposed (Arnorsson et al., 1982 and 1983a; Arnorsson and Svavarsson, 1985). The equations are given in Appendix I.

By plotting $\log Q/K$ vs. temperature for natural water, it is possible to determine whether the water has been in equilibrium with a host rock mineral assemblage, probable minerals in the assemblage, and the equilibrium temperature. The $\log Q/K$ 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. Geothermal fluids, which are formed by mixing of two or more different fluids, will show either 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 a complete lack of any identifiable equilibrium temperature, if the solution mixing with the geothermal fluid is not dilute (Reed and Spycher, 1984).

4. APPLICATION OF THE COMPUTER PROGRAMMES

4.1 The computer programme WATCH

The computer programme WATCH (Arnorsson et al., 1982; Arnorsson and Bjarnason, 1993; Bjarnason, 1994), as an aqueous speciation programme, is a useful tool for interpreting the chemical composition of geothermal fluids. It may also be used for non-thermal waters for calculating different geothermometer temperatures. It has been developed to calculate the composition and aqueous speciation of geothermal reservoir waters. The input to the programme is a component analysis of each phase (liquid, gas, steam) of the geothermal fluid at the surface, including the water pH and the temperature at which it was measured, and specification of the reference temperature at which the aqueous speciation is calculated. The temperature at which the programme calculations are performed, refers either to equilibrium with quartz, chalcedony, the Na-K geothermometry temperature, or a selected value which may be arbitrarily selected, or correspond to

the measured water temperature. All the chemical components, that occur in major concentrations in geothermal waters and/or rocks commonly found in geothermal systems, are included. The concentration of all the aqueous species (67 and H^+ and OH^- , which are treated separately) considered in the programme are expressed in terms of the component concentration by mass balance equations.

The chemical equilibria between the species are expressed as mass action equations. Solubility data of 29 commonly occurring geothermal minerals are also incorporated to facilitate comparison between water chemistry and mineral solubilities, in order to predict particular mineral/solution equilibria. The two sets of equations are solved simultaneously by an iterative procedure, which 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 is used to calculate all 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 species. From the distribution of species, a new value for the ionic strength is computed. This value is used to recompute the activity coefficients and species concentrations, still at the temperature of the pH measurement. Activity coefficients and species are taken to be equal to unity.

The pH-calculation, the calculation of the activity coefficients, the mass balance iteration, and the ionic strength calculation are repeated, in turn, a couple of times. The equilibrium gas pressures are then computed from the final equilibrium species concentration.

The output from the programme lists the components 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 are computed, from which it is straightforward to compute the corresponding saturation indices, $\log Q/K$.

The WATCH programme may also be used to study chemical changes accompanying adiabatic boiling and conductive cooling of waters in geothermal reservoirs, to compute the resulting species concentrations, activity coefficients, and activity and solubility products from the reference temperature to some lower temperature (Bjarnason, 1994).

In this report, the WATCH programme is used to study the chemical equilibria between minerals and solutions as well as to calculate the subsurface chemical equilibrium temperature (quartz, chalcedony, Na-K) of about 61 chemical analyses of geothermal and cold waters from the Bourgas synclinorium in SE-Bulgaria.

4.2 The computer programme SOLVEQ

The programme SOLVEQ was the first in a series of programmes that have been developed since the mid-70's for calculating equilibria in aqueous system. SOLVEQ can be used for computing multicomponent homogeneous and partial heterogeneous chemical equilibrium, where equilibration of a given water with specified minerals or gas fugacities can be forced (Reed, 1982). The forced equilibria are then used to fix the total concentration of specified component species. SOLVEQ's forced mineral equilibrium capability and its ability to calculate pH at high temperatures from a low temperature pH measurement (Reed and Spycher, 1989) make it useful for geothermometry and other studies of geothermal and sedimentary formation waters and for processing hydrothermal experimental run products to derive thermodynamic data or evaluate mineral equilibria. SOLVEQ solves a system of mass-balance and mass-action equations by the Newton-Raphson numerical technique (Reed, 1982; Reed and Spycher, 1984). In SOLVEQ, the chemical system is defined in terms of component species. Other species, complexes or redox species are expressed in terms of these component species. Minerals and gases are also expressed in terms of component species. The total

chemical composition of the system is, thus, given as the total molar amount of each component species in that system. In this report the SOLVEQ programme was used to enlarge the number of minerals which can be equilibrated with water at a given temperature.

5. PREDICTION OF SUBSURFACE TEMPERATURE

5.1 Outline

Determination of the subsurface temperature in a geothermal field is a major task in geothermal investigation. Various chemical geothermometers have been developed to predict reservoir temperature in geothermal systems (Fournier, 1989). In upflow zones below hot springs and shallow wells, cooling of the water may occur by conduction, boiling and/or mixing with cooler water. With the aid of solute geothermometry and mixing models, it is possible to evaluate temperatures in the geothermal reservoir at a depth below the cooling zone, using data on the chemical composition of waters from hot springs and shallow wells. The calculation of geothermal reservoir temperature, using chemical geothermometers, involves various assumptions and simplifications. The basic one is that a temperature-dependent equilibrium is attained in the geothermal reservoir between specific solute(s)/gas(es) and mineral(s). Both quantitative and qualitative methods are used in exploration for geothermal resources.

Most qualitative geothermometers are based on the distribution and relative concentration of volatile elements in waters and soils or variations in soil-gas composition. These methods consist of looking for anomalous concentration of various elements called "indicators" or anomalous ions or complexes ratio in the water. White (1970) reviewed the qualitative geothermometers that had been suggested up to 1970. Tonani (1970) suggests that enrichment of B, NH₄, HCO₃, Hg and H₂S in near-surface water may result from boiling at depth. High concentration of volatile components often accumulates above or around a relatively shallow heat source. Increasing of H₂S in water may be an indication of higher temperature at depth. Decreasing of Mg and very low concentration of this element is an indicator of thermal water. Mahon (1970) noted that high Cl/F and Cl/SO₄ ratios in liquids of a geothermal area generally indicate high temperature in the system. Fournier and Truesdell (1970) noted that the mole ratio Cl/(HCO₃+CO₃) is very useful in distinguishing waters from different aquifers in the Yellowstone National Park; higher ratios indicate waters coming from hotter aquifers. Anomalously high concentrations of non-volatile trace elements may also indicate high subsurface temperature. This would be true if the element tended to be easily leached from rocks at a high temperature and not leached at a low temperature. Often high concentration of chloride is an indication of high temperatures.

The quantitative geothermometers are widely used to estimate subsurface temperatures in geothermal reservoirs, based on the concentration of selected chemical constituents in samples from springs and shallow wells. They can be divided into two groups, chemical and isotopic geothermometers. Only the minerals, whose solubility increases strongly with temperature can be used as geothermometers. Such minerals are quartz, feldspars and zeolites. Other minerals, such as carbonates, sulphates and some Mg-silicates, undergo very fast re-equilibration during the ascend of the water from the deep reservoir to the surface. Two geothermometers are sustained by the evidence of chemical equilibria between deep solutions and mineral phases, the silica minerals and alkali feldspars, respectively.

5.2 Silica geothermometry

The earliest attempt to use water chemistry to evaluate subsurface temperature conditions in geothermal systems date back to about 1960. The first geothermometer ever used for temperature prediction was entirely empirical. Bodvarsson and Palmason (1961) detected that there was a good relation between silica content

and reservoir temperature. Later several calibrations have been proposed for the quartz and chalcedony silica geothermometers. Nowadays many equations exist to compute the silica temperature. Those used in this report are listed in Appendix II.

The silica geothermometer is based on the solubility of quartz and chalcedony and is widely used to estimate subsurface temperature. Solubilities of these minerals generally change as a function of temperature and pressure. At temperatures below 340°C the solubility of the silica minerals decreases drastically as the temperature decreases. Furthermore, silica may polymerize and precipitate from the solution as a result of conductive and/or adiabatic cooling before reaching the surface, causing low estimated reservoir temperature. At temperatures less than 300°C and at depth generally attained by commercial drilling for geothermal resources, variation in pressure has little effect on the solubilities of quartz and amorphous silica. Generally speaking, the solubility of quartz appears to control dissolved silica in geothermal reservoir, at temperatures higher than 120-180°C, so the quartz geothermometer probably works best in the temperature range of 150-250°C. At lower temperatures other silica species such as chalcedony, cristobalite, or amorphous silica may control dissolved silica (Fournier, 1977). In some cases, where water has been in a contact with rock at a given temperature for a relatively long time, quartz may control dissolved silica at temperatures less than 100°C. The reason for this is that chalcedony is a very fine-grained variety of quartz, composed of aggregates of tiny crystals. The individual quartz grains are so small, that they have relatively large surface energies compared with "normal" quartz, and this results in increased solubility. Chalcedony is unstable in contact with water at temperatures above 120-180°C, because the smallest sized crystals dissolve completely relatively quickly and larger sized crystals grow large enough, so that surface energy is no longer a factor. In some places, chalcedony may control dissolved silica at temperatures as high as 180°C.

5.3 Cation geothermometry

Cation geothermometers are widely used to calculate subsurface temperatures of waters collected from hot springs and wells. They are based on ion exchange reaction with temperature-dependent equilibrium constant, as for example

$$NaAlSi_{3}O_{g} + K^{*} = KAlSi_{3}O_{g} + Na^{*}$$
⁽²⁾

with the assumption that the activities of the solid reactions (in this case albite and K-feldspar) are unity and the activities of the dissolved species are equal to their molal concentrations in aqueous solution. The equilibrium constant *Keq* is expressed by the ratio of the molalities of the respective ions, such as Na/K. If an exchange reaction involves divalent and monovalent ions, for example K⁺ and Mg²⁺, the equilibrium constant is approximately equal to K/ \sqrt{Mg} .

Compared to the silica geothermometer, the sodium/potassium ratio is less affected by chemical reequilibration occurring during the ascent of the solution, but it may be slightly disturbed by mixing with cold dilute superficial waters. The Na/K ratio can be modified by exchange reactions with clay minerals, or by addition of potassium from sedimentary rock, especially from the volcanic materials in relatively shallow subsurface reservoirs. Experiments at high temperatures and pressure by Orville (1963) and Hemley (1967) showed, that reactions involving base exchange of Na and K between alkali feldspars and an aqueous solution, proceed very slowly at temperatures below about 300°C. The Na/K ratio generally works well for estimating temperatures of waters above 200°C. The application of this geothermometer for diluted waters or systems below 150°C often results in an overestimated temperature, because the basic assumption of this geothermometer, which is the presence of feldspars in equilibrium with water, is not fulfilled. Many temperature functions have been presented for the Na-K geothermometer, but those which have been used for prediction of subsurface temperature in the NW-Bourgas synclinorium are listed in Appendix II. The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) has proved to be more reliable than the Na-K geothermometer for low temperature waters. It is completely empirical, based on more than one exchange reaction. It takes into account reactions involving the exchange of Na⁺, K⁺ and Ca²⁺ with mineral solid solution. The Na-K-Ca geothermometer appears to give excellent results for most waters above approximately 200°C, but erratic results are obtained for waters from reservoirs at less than 200°C. These erratic results are connected to samples with high CO₂ partial pressure (Paces, 1975) and probably with exchange reaction between Na, K and Ca with additional ions, such as Mg. Precipitation of calcium as carbonate after boiling of solution on the way from reservoir to the surface is another likely source of error. To avoid the influence of the partial pressure of CO₂ on the Na-K-Ca geothermometer, Paces (1975) recommended a correction. Correction is also suggested for Mg, when this geothermometer is applied to Mg rich waters (Fournier and Potter, 1979). Generally, the Mg concentration in geothermal fluids decreases rapidly as the temperature increases, and all Mg-rich fluids found in nature have undergone water-rock reaction at a relatively low temperature.

Various other cation geothermometers have been proposed that may be of use in some situations. Geothermometers such as K/\sqrt{Mg} (Giggenbach, 1988) and Li/\sqrt{Mg} (Kharaka and Mariner, 1988). Both of these appear to be good indicators of the last temperature of water-rock equilibration in ascending water, as water-rock exchange reactions involving Mg proceed relatively fast at low temperature. The Na/Li geothermometer (Fouillac and Michard, 1981) appears to be particularly sensitive to total dissolved solids and to rock type. It is very sensitive to slight changes of Li that result from exchange involving other ions than Na. Therefore, this geothermometer should be used in combination with others, but not alone.

Ionic solute geothermometers, based on Na-K, Na-K-Ca and K-Mg contents, are useful tools for the evaluation of the subsurface temperature. Most of the problems in their use arise from their application to unsuitable samples. Recently a "self-policing" technique was devised giving an automatic indication as to the suitability of a given water for the application of ionic solute geoindicators. It is essentially based on the temperature-dependence of the two reactions

$$K-feldspar + Na^* = Na - feldspar + K^*$$
(3)

$$2.8K - feldspar + 1.6H_{2}O + Mg^{2^{*}} = 0.8K - mica + 0.2Chlo. + 5.4Sil. + 2K^{*}$$
(4)

where *Chlo*. and *Sil*. refer to chloride and silica, respectively. Both of them involve minerals of the full equilibrium assemblage expected to form after the isochemical recrystallization of an average crustal rock under condition of geothermal interest. Na, K and Mg contents of waters in equilibrium with this assemblage are accessible to rigorous evaluation. Evaluation of the Na-K-Mg geothermometer is best carried out by use of the triangular diagram provided by Giggenbach (1988). It can be used to classify waters as fully equilibrated with rock at given temperatures, partially equilibrated, and immature (dissolution of rock with little or no chemical equilibrium). The Na-K-Mg equilibrium diagram from Giggenbach (1988) is presented in Figure 2. It shows a plot of the relative Mg, Na and K concentrations in the natural water in the Bourgas synclinorium. The data point from the wells plot very close to the "fully equilibrated line", indicating that the Na-K geothermometer presented by Giggenbach can be applied in order to estimate the subsurface temperature. The temperature, t_{kn}, of the well waters is about 75-100°C and closely approaches the equilibrium of the reservoir water with quartz, albite, analcime, microcline and montmorillonites. One point plots in the partial equilibrium area (well JA-12) and several points are in the area of immature waters, very close to the \sqrt{Mg} corner of the diagram, which may arise from admixture with shallow cold water. Although JA-12 departs from the equilibrium line its position on the diagram probably infers a potentially high temperature in the deep reservoir.



FIGURE 2: Na-K-Mg triangular diagram used for water samples from the Bourgas synclinorium

5.4 Mixing models

Geothermal water ascending from geothermal reservoir to the surface and emerging in hot springs may cool on the way, either by conduction, boiling, or mixing with shallow cold water or by combination of these three processes. Fluid geothermometry provides evidence of the location mechanism of and these processes. Waters that ascend relatively rapidly and directly from the reservoir with little conductive cooling are likely to have chemical composition that reflect rock-water equilibrium at the reservoir temperature. Other thermal waters which have ascended from deep reservoirs so slowly that much of their

chemistry has been altered by lower temperature reaction. Where the aquifer is at temperatures below atmospheric boiling, the water can emerge at about the temperature of the aquifer. The chemical composition of the mixed water can be used for temperature estimation applying a mixing model (Fournier and Truesdell, 1973). This model can be applied if there is an independent indication for mixing. If it is used for unmixed water the predicted temperature could be too high. The chemical characteristics of mixed water which should be used as evidence for mixing are discussed by Fournier (1981) and Arnorsson (1985). Some of them are large discrepancy between the temperatures indicated by the silica and the cation geothermometers; cold springs with large mass flow rates and relatively high estimated subsurface temperatures by chemical geothermometers; low pH relative to the water salinity; variation in oxygen and hydrogen isotopes; the tendency of calcite undersaturation and low calcium/proton activity ratio compared to geothermal water; variation in chloride concentration; systematic variation in temperature and composition of water in springs from the same area.

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 or chalcedony controlled (Fournier, 1989).

6. ESTIMATION OF SUBSURFACE TEMPERATURE

6.1 The Straldja geothermal field

The Straldja geothermal field is located in the western part of the Bourgas synclinorium in the Straldja graben (Figure 1). It is a part of the Sredna Gora zone and has developed on a foundation of Pre-Cambrian metamorphics, Triassic and Jurassic sediments. They are probably covered by not so thick layers of Cenomanian and Turonian sediments. This deep graben is filled with Palaeogene-Neogene sediments,



FIGURE 3: Location of wells in Straldja field

consisting mainly of clayish sandstones and conglomerates, tuffs and tuff breccias of Upper Cretaceous age in alternation with limestone layers in the deeper parts. The major reservoir rock types are Upper Cretaceous limestones, andesites and tuffs. The Straldja geothermal field is affected by recent water-bearing faults.

Drilling for cold and hot water and other purposes was carried out in the period 1965-1975. Figure 3 shows the location of the wells. Seven of the boreholes passed through Palaeogene-Neogene clays and reached the bedrock of the field at different depths, from 120 (well B-71) to 439 m (well JA-18) and only one (well B-70)

was completed to a vertical depth of 55 m into the Palaeogene clays. The deepest well, JA-18, reached down to 1185 m. Most of the wells started as artesian with a piezometric level of up to 21.5 m above the surface and flowrate in the range of 0.23-7.5 l/s. The maximum temperature of the natural hot water is 78°C (well JA-1). Pumping tests at different flow rates, temperature loggings and resistivity measurements have been done in all wells. Water samples were collected during the pumping tests. Figure 4 shows temperature E logs of the wells indicating that feed zones are located at different levels, mainly in fractured tuffs. The fractured zones are most likely structures that control the circulation of hot water in this hydrothermal system. The geothermal gradient is in the range 22-88°C/km for Palaeogene sediments and 45-62°C/km for Upper Cretaceous volcanic rocks.

In the present study, the chemical composition of water samples from 8 geothermal wells was taken into consideration (Table 1).



FIGURE 4: Temperature profiles for wells from the Straldja field

No.	Well	T _{meas.} (°C)	TDS	pН	Na	K	Ca	Mg	Cl	SO4	CO ₂	SiO ₂
1	B-69	24	336	7.9	73.4	0.5	7	4	16	41	128	28.5
2	B-70	14	520	7.6	27.8	0.5	61	27	17	13	236	33.9
3	B-71	21	400	8.8	87.2	0.8	4	2	17	31	120	50.8
4	JA-1	78	1105	8.8	360		32		340	269	60	52.4
5	JA-2	43	1000	8.9	333	5	20		333	224	17	47.8
6	JA-12	73	1180	9.2	339	10.7	44	0.8	358	240	27	62.4
7	JA-18	31	1120	8.7	347	2.4	26	2	391	210	48	53.1
8	JA-37	28	1030	7.1	310	2	26		333	235	37	30.8

TABLE 1: Chemical composition of thermal water from the Straldja field (in mg/l)



FIGURE 6: The Straldja field, the silica-enthalpy mixing model

The water samples can be divided into two groups according to their chemical composition. Na-HCO3 type waters were observed from two of the wells and Ca-HCO₃ from one well. These wells are shallow and the main inflow zone is in the depth range of 285-293 m for both of them. One water sample from well B-70 is from Quaternary aquifer. Na-Cl type waters were found in the remaining 5 wells as inflow zones in them are located at 437-960 m. The total concentration of dissolved solids ranges from 336 to 1180 mg/l. The thermal water has a chloride content of 333-391 mg/l. This is a relatively high concentration compared to the chloride content in underground waters in the Bourgas synclinorium. It is well known that chloride is not incorporated in alteration minerals and its concentration in the water is determined by its availability in the source. Normally this

element tends to occur in low concentration in water located far from the coast. It may be assumed that the higher chloride content in waters in the Straldja geothermal field, relatively far from the coast, may be the result of heated sea water at a great depth and a different aquifer.

Figure 5 shows the sulphate and silica concentrations of the water plotted against chloride. No direct correlation can be seen between the silica and chloride contents of the waters, where as a correlation can be envisioned between sulphate and chloride. However, due to lack of sufficient data, this correlation could also be interpreted as two groups of waters, one with low chloride and sulphate content, and the other with Cl > 300 mg/l and SO₄ > 200 mg/l. Figure 6 shows the silica concentration of the water plotted versus the discharge enthalpy, indicating a

good linear relationship. Taking sample 2 (well B-70) to represent the cold water component, the silica-enthalpy plot intersects the chalcedony saturation curve and quartz saturation curves at 361 and 552 kJ/kg, respectively. These values correspond to a subsurface temperature of 86 and 130°C, respectively.

The analytical data from all 8 wells were used to calculate the equilibrium state of 23 minerals using the WATCH programme of Arnorsson et al. (1982). The log values O/Kat different temperatures were also calculated using the SOLVEQ programme of Reed and Spycher (1984) for fluids from wells JA-12, JA-18 and JA-2. The log O/K values were plotted versus temperature to find the equilibrium temperature. An example of the mineral equilibrium diagram (log O/Kversus temperature) obtained using WATCH is shown in Figure 7a for well JA-12 in Straldja. Figure 7b shows the results obtained by the computation for the same sample using SOLVEQ. There are some differences between the results obtained by the two programmes for all samples, in particular for well JA-12.

The range of equilibrium temperatures obtained is rather large, being about 50-130°C for SOLVEQ and 70-130°C for WATCH. The number of mineral curves that cross the zero $\log O/K$ horizontal line at the same temperature, or the number of minerals that co-exist in equilibrium, is not great, 5-6 is the maximum in most cases. Since different minerals do not reach equilibrium at exactly the same temperature, statistical methods







were used to search for the temperature range where most minerals cross the horizontal zero line. As demonstrated in Figure 7a and 7b, chalcedony equilibrates with the water at about 76-77°C, and four and two mineral curves converge in the temperature range 75-85°C for the SOLVEQ and WATCH calculations, respectively. On the other hand, the water reaches equilibrium with guartz at about 103-109°C and five mineral curves converge in the temperature range of 95-105°C, for the SOLVEQ calculations and three curves converge in the temperature range of 105-115°C according to the WATCH calculations. It is thus inferred that quartz rather than chalcedony controls the fluid-silica equilibrium in the geothermal system. As for well JA-12, equilibrium temperature is assumed to be about 90-100°C. Similar equilibrium temperatures were obtained for all wells. For both silica minerals, chalcedony and quartz, the programmes gave approximately the same results. Unfortunately, only the analytical data from three wells that included aluminium and iron concentration could be interpreted by this method. Calcium carbonate equilibrium temperature for two samples show that the samples are supersaturated with respect to calcium. Thus, a calcite scaling problem could occur in these cases. The geothermal fluid is undersaturated with respect to amorphous silica. The montmorillonite minerals in JA-18 (Table 2) give higher reservoir temperature than obtained in the other wells. Either the montmorillonites do not represent minerals in equilibrium with the water, or they are representative of deeper circulation within the reservoir. The known and esitic-tuff cover in the Straldja field, which is very thick, could contain zeolites and feldspars, or montmorillonite as a part of the hydrothermal alterations. The rock of the Cenomanian, Turonian, Jurassic and Triassic basement could contain feldspars, carbonates and clay minerals. Both mineralogic assemblages could reflect systems that exist at different depths.

Mineral	System			
		JA-2	JA-12	JA-18
Laumontite	Ca-Al-Si-O-H	102	137	ss*
Ca-montm.	Ca-Al-Si-O-H	85	97	138
Calcite	Ca-C-O	143	SS*	50
Mg-montm.	Mg-Al-Si-O-H		95	138
Albite, low	Na+-Al-Si-O	93	112	139
Na-montm.	Na-Al-Si-O-H	79	90	127
Analcime	Na-Al-Si-O	85	102	160
Adularia	K-Al-Si-O	66	86	90
K-montm.	K-Al-Si-O-H	70	79	112
Chalcedony	Si-O	69	80	73
Quartz	Si-O	99	106	102

TABLE 2: Equilibrium temperature values, calculated for sodium-chloride type waters (by WATCH)

* ss = supersaturated over 20°C

Figures 8 and 9 describe the temperature dependence of cation/proton ratios at chalcedony and quartz reference temperatures, respectively. They were drawn to estimate the equilibrium state between waters and minerals, to further reveal the water-mineral equilibrium state. The applied equations describing the temperature-dependence of cation/proton ratio (Arnorsson et al., 1983a) are listed in Appendix I. Generally, it is impossible for all chemical reactions to reach water-rock equilibrium, but it is possible to evaluate the equilibrium state of a water sample from a reaction between the equilibrium concentrations at different

temperatures in the reservoir. As can be seen, all the points are closer to the equilibrium curves at the quartz temperature than at the chalcedony temperature. Some of the points are still off the equilibrium curves, B-69, B-70 and JA-37 at quartz temperature except for the log $\sqrt{Mg/H}$ vs. temperature equilibrium curve. This result can be used as an evidence that quartz controls the concentration of silica in the deep reservoir, or at least that quartz is a better geothermometer for the estimation of the subsurface temperature at depth in the Straldja field than the chalcedony geothermometer. Figure 10 shows, that there is a slight correlation between the silica concentration of the water and the measured temperature, indicating increased solubility of silica with measured temperature.

The chalcedony, quartz and Na-K-Ca temperature are plotted versus measured temperatures in Figure 11, in order to evaluate the applicability of the geothermometers. It can be seen that there is a relatively good correlation between the chalcedony, quartz and Na-K-Ca temperatures and the measured temperature. The water sample from well B-70 has measured temperature of 14°C, which is exceptionally low compared to the calculated quartz temperature of 85°C. This discrepancy can be explained by cooling of geothermal water due to accumulation in a secondary reservoir made of Quaternary clay and sand.



FIGURE 8: The Straldja field, equilibrium state for waters at the chalcedony geothermometer temperature



FIGURE 9: The Straldja field, equilibrium state for waters at the quartz geothermometer temperature

The conventional chalcedony, quartz and Na-K geothermometry temperatures were calculated using the WATCH programme. In addition some others geothermometric equations (reported in Appendix II) were applied to the chemical analyses. The results are given in Table 3.

Sample no.	T _{meas} (°C)	T _{chal-1} (°C)	T _{chal -2} (°C)	T _{qtz -1} (°C)	T _{qtz-2} (°C)	T _{NaK-1} (°C)	T _{NaK-2} (°C)	T _{NaK-3} (°C)	T _{NaKCa} (°C)	T _{KMg} (°C)
1	24	49	46	77	81	82	60	51	67	29
2	14	56	53	85	88	125	104	93	76	21
3	21	74	73	103	103	94	73	63	81	36
4	78	75	74	104	104					
5	43	71	70	100	101	116	95	85	105	
6	73	84	83	112	112	154	135	123	130	68
7	31	76	75	105	105	82	61	51	77	47
8	28	52	49	80	84	80	58	49	73	

TABLE 3: Geothermometer temperatures for chemical samples from Straldja field



It can be concluded, that for the Straldja field, the quartz geothermometer is found to be the most reliable of the geothermometers that were studied and base exchange reactions involving quartz, clay and feldspars are a major controlling factor. The maximum measured temperature is 78°C in well JA-1. According to the quartz geothermometer the highest predicted temperatures in the geothermal reservoir are 100-120°C. All results show that water ascends either slowly or indirectly to the surface and as a result conductive cooling is likely to occur. In addition, the hot ascending waters may cool by means of mixing with cooler groundwater and chemical equilibrium is not established after mixing. According to the temperature estimated by the geothermometers, one can have a rough idea about reservoir depth. On average, the geothermal gradient is 45-50°C/km and the mean annual surface temperature 13.5°C, hence, the reservoir depth is likely to be about 2 km.

6.2 Aitos geothermal field

The Aitos field is located within the northern part of the Bourgas synclinorium (Figure 1). The main geological features of this area are the same as in the Bourgas synclinorium, Upper Cretaceous volcano - sedimentary rocks, mainly flysch formation, inderbedding of sandstones, siltstones, limestones and marls and to lesser extent tuffs, tuff breccias and argillites. In the Karnobat-Aitos graben, part of which is included in the Aitos area, deposits of Pliocene and Quaternary sediments, mainly clays and sandstones cover the Upper Cretaceous complex. The area is transected by a E-W trending fault, approximately parallel to the rear Balkan fracture, which borders the Bourgas synclinorium on its northern side and several closely spaced faults sub-parallel to it. Most of the wells which detected thermal waters are located along these E-W striking faults, suggesting that these sets of structures control the flow of the rising geothermal fluid. For a long time two mineral springs have been known in the Aitos area. One of them "Ladjata", with a flow rate of 5 l/s, is used for baths after the water has been heated.

During the years 1968-1970 six wells were drilled in the Aitos area, 100 to 300 m deep. Since 1974 a number of shallow wells for hot or cold waters have been drilled in the area. The location of the wells is shown on Figure 12.



The depth of the wells is between 40 m (2B-7) and 1115 m (B-83). The wells cross Upper Cretaceous rocks from the surface down to 110.5 m (B-16). Pumping tests at different flow rates and temperature loggings at different depths have been done in most of the wells. Feed zones are situated at different depths in the wells which has big a influence the on interpretation of chemical composition of the thermal fluid. The geothermal gradient. which provides good a indication as to the of distribution the

FIGURE 12: Location of cold springs and wells in the Aitos geothermal field temperature, varies considerably. The values of the gradient in the Aitos field are influenced by the hydrogeological factor. The high values of the geothermal gradient account for the high values of the thermal flow in this part of the synclinorium. The thermal anomaly in the northern part of the synclinorium (75-80 mW/m²) is due to the influence of thermal waters.

The Aitos area is characterized by the presence of many cold springs and wells. The geological and lithological features of this area containing a Pliocene aquifer, which contains fresh cold water and Upper Cretaceous aquifer, which contains fissure waters connected mainly to genetically different fissures in the flysch and flysch-like sediments. The chemical composition of the geothermal waters from the Aitos field is given in Table 4. For the present work cold springs within and close to the Aitos field were selected. The selection was based on complete water analyses with a good ionic balance. The springs chosen, cover the whole territory of the Aitos field (Figure 12). Measured temperature ranges from 12 to 21°C and discharge rates range from 0.023 to 1.5 l/s. Studied springs show mainly HCO₃-Ca type waters with pH from 7.1 to 7.9, and salinity from 447 to 1139 mg/l. All these springs seem to belong to a shallow hydraulic circulation.

The thermal water, mainly from wells, has a Cl-SO₄-Na or HCO₃-Na composition, pH from 7.4 to 9.5, low salinity and temperature between 21 and 49°C, representing the regional volcanic aquifer. The major difference between the two fluids concerns the Ca, Mg, F and particulary SiO₂ contents and could be due to both secondary processes during the upflow and to a lower equilibrium temperature of the water. The chemical composition of the water shows relatively high chloride concentration compared to other regions in Bulgaria. The chloride is believed to have originated from seawater when the area was covered by sea in Paleogene (Priabone) and Neogene time, or it could be supplied by seawater spray or aerosol through precipitation. The chemical analyses of water from some of the sampled wells, including aluminium and iron, were used to calculate the equilibrium temperature, with the WATCH programme. By using the conventional geothermometer temperatures that are calculated by WATCH as a reference, the temperature range for the

No.	Well	T _{meas.} (°C)	TDS	pH	Na	К	Ca	Mg	Cl	SO4	CO ₂	SiO ₂	F
9	B-13	18	486	9.5	148	2	2		49	41	104	63.2	
10	B-16	20	555	7.6	123	1	19	4	14	60	218	22.3	1.7
11	B-17	18	391	8.8	109	1	3		14	25	144	13.9	
12	B-18	42.5	552	9.8	169	0.4	2		59	58	85	54.7	7
13	B-19	19	789	8.4	188	1	25	6	30	168	238	26.2	2
14	B-21	18	1089	7.8	175*		61	56	112	332	224	27	
15	B-27	16	577	7.4	151*		9	9	95	120	112	29.3	
16	B-34	16	522	7.6	24	1.1	80	16	23	51	203	30	0.6
17	B-36	16	523	9	131*		11	4	43	58	138	35	
18	B-40	13	392	7.6	60	0.3	28	9	14	29	164	18.5	0.5
19	B-63	44	606	8.3	155	1.9	2		63	93	113	84	5
20	B-75	31	463	7.2	116	1.5	6.5	2	43	51	137	39.3	1.6
21	B-80	36	456	8.4	120	0.9	1	0.6	23	49	120	54	3.2
22	B-83	39	884	9.2	240	3	4		76	132	133	134	2.8
23	B-86	13	747	8.7	92	0.9	21	58	50	34	291	41	0.6
24	B-20	29	346	10	103	0.2	2		19	19	63	42	
25	B-88	31	390	9.5	113	0.2	2		20	22	105	66	5.5
26	B-94	33	568	8.9	152	1.3	3	32	66	189	17	66	1
27	BD-60	19	1080	7.7	78	5.1	74	100	153	192	255	39.3	
28	2B-7	13	540	8	28	1.6	76	20	29	28	213	26.2	0.3
29	B-111	49	700	9.5	228	1.1	3		166	126	40	71	8
30	B-114	26	640	8.4	180	0.9	12	4	138	124	83	32	7.5
31	B-115	23	600	7.9	186	0.4	5	7	127	111	98	18	5
32	B-118	15	730	8.3	72	1.6	88	27	49	106	226	18.5	1.8
33	B-120	18	810	8.3	187	1.6	34	13	94	127	212	20	6
34	B-124	21	680	8.3	190	0.9	17	5	146	145	92	17	10
35	B-135	49	670	9.5	204	0.9	4		168	128	42	59	10

TABLE 4: Chemical composition of thermal water from the Aitos field (in mg/l)

* Na+K

log Q/K values was chosen to be 10-160°C. As an example of geothermal water from the Aitos field, Figures 13 a and b show the results of equilibrium calculation for one sample, using a log Q/K vs. temperature plot. The equilibrium temperature was calculated on the basis of the equilibrium temperature values corresponding to log Q/K = 0, for albite, Ca-, Na- and K-montmorillonite, calcite, analcime, albite, chalcedony, quartz, adularia and microcline. The equilibrium temperatures obtained are in the range 50-70°C (wells B-13, B-17, B-18 and B-20); 70-100°C (B-16, B-19, B-34 and B-40); 100-120°C (B-63) and 120-150°C (B-83 and B-94).



FIGURE 13: The Aitos field, mineral equilibrium curves for waters from well B-63, a) by the WATCH programme, b) by the SOLVEQ programme

Since, in some of the wells different minerals do not reach equilibrium at a specific temperature, the SOLVEO programme was used in order to expand the spectrum of involved minerals (Figure 13b). Statistical methods were also used to search for the temperature range where most minerals cross the zero line (Figure 13a and b). The water is supersaturated with respect to calcite in most cases, but undersaturated with respect to amorphous silica and fluorite. The similarity between equilibrium temperatures for some of the wells suggests that these wells probably draw fluid from the same aquifer, but at different depths and consequently in different proportions. Based on these results it can be concluded that the equilibrium temperature is 50-70°C for the upper (infiltration) zone and 100-120°C and even higher for the lower (elision) zone. The relatively low measured temperatures in these wells compared with the equilibrium temperature obtained by this method do not exclude the possibility of a mixing with shallow cold water.

Figures 14 and 15 show the relationship between chloride and silica, and chloride and sulphate respectively. The thermal water show nearly linear relationships. However, the silica-chloride diagram may also indicate two groups of waters. Some of the wells draw water with high content cloride and approximately constant silica content. It can be considered that wells B-111 and B-135 intersect a waterbearing fracture with water ascending from a deep aquifer to the surface.

Unfortunately the chemical analysis for the waters from these wells do not include aluminium and iron and equilibrium temperature can not be found.

The relationship between these constituents were investigated for another group of cold springs located approximately 30 km southwest of the Aitos area (Figure 12, samples no. 62-75). It was found that there is no clear relationship. As Arnorsson (1985) described, the relationship between chloride and silica and chloride and sulphate could be used as strong evidence for the mixing nature of the thermal water. High sulphate content of some samples (B-83, B-94, B-21 etc.) can be explained by assuming oxidation of sulphide to sulphate by atmospheric oxygen in the cold water, which is mixed with the hot geothermal water. All the waters are undersaturated with respect to anhydrite. Therefore, the assumption for high sulphate content of the water due to mixing is reasonable. Some cold springs located close to the major inflow zone (the Hadjiite area) are considered to have formed by mixing of thermal water with cold groundwater to a considerable extent.

Since water in some wells and cold springs in this field are found to be mixed waters the use of a mixing model is necessary. Figure 16 shows a dissolved silica-enthalpy graph and how the temperature of the hot water component is determined with respect to quartz and chalcedony solubility (Fournier, 1977). The silica content of the cold water is 19 mg/l with a temperature of 15°C. The temperature of the deep geothermal hot water is found to be 199°C and 154°C with respect to the quartz and chalcedony solubility. These temperatures, especially the one based on the solubility of chalcedony, correspond well with the estimated equilibrium temperature. They are higher than those encountered by drilling, but as previously mentioned, most of the wells are shallow.

The relative activities of all the major cations in the



FIGURE 14: The Aitos field, Cl vs. SiO₂





geothermal system (Na, K, Ca, Mg, Fe and Al) and protons are fixed at a particular temperature. Equations describing the temperature dependence of the cation/proton ratio (Arnorsson et al., 1983a) are listed in Appendix I. Generally all the points are closer to the equilibrium curves at the chalcedony temperature than at the measured temperature as seen in Figures 17 and 18. Thus, we can assume that the chalcedony geothermometer should give a more correct subsurface temperature. Therefore, we can accept that chemical equilibrium is approximately established after mixing and that chemical geothermometers indicate temperature of the mixed water, not the hot water component (wells B-135, B-111, B-18, B-83, B-13). As it is known, the activity ratio $\sqrt{Ca^{2+}/H^+}$ tends to be low in cold and surface waters compared with thermal



waters (Arnorsson, 1983). This was used for distinguishing equilibrated geothermal waters from non-equilibrated surface waters. Some of the points are still off the equilibrium curve, but most of them are cold water. As it is visible in Figures 17 and 18, the cold springs from the Aitos field have activity ratio very close to that for waters from wells. It can be concluded that due to the shallow depth most of the wells draw water from aquifers located within the upper part of Upper Cretaceous complex (infiltration zone) and only few of them intersect main waterbearing fractures.

All water samples from wells and cold springs in the Aitos and the Hadjiite areas (Figure 12, samples no. 9-61), have been used to predict possible subsurface FIGURE 16: The Aitos field, silica-enthalpy mixing model



FIGURE 17: The Aitos area, equilibrium state for water samples at measured temperature

geothermometers. The results are shown in Table 5. The silica geothermometry for the thermal fluid gives a value in the range of 22-126°C for chalcedony equilibrium, and 50-154°C for quartz equilibrium. The silica temperature tends to be higher than the measured temperature in drillholes. The geothermometers indicate high subsurface temperatures for eight of the wells which probably intersect the main upflow zone of the field. Using Na-K and Na-K-Ca thermometers, which are less sensitive than silica to mixing with cold water, we obtain temperatures equal or higher than silica (Figure 19). Results of the Na-K-Ca geothermometer indicated that this empirical geothermometer appears to be applicable for low-temperature waters. The Na-K geothermometer gives higher temperatures than the chalcedony geothermometer, but often they are only slightly higher. Thus, there is a relatively good correlation between Na-K and chalcedony temperatures. The computed temperatures are plotted versus measured temperature in Figure 20. It is possible that water with higher temperature can be found in this area.



FIGURE 18: The Aitos field, equilibrium state for water samples at chalcedony geothermometer temperature

No. sample	T _{meas} (°C)	T _{chal -1} (°C)	T _{chal-2} (°C)	T _{qtz-1} (°C)	T _{qtz -2} (°C)	T _{NaK-1} (°C)	T _{NaK-2} (°C)	T _{NaK-3} (°C)	T _{NaKMg} (°C)	T _{KMg} (°C)
9	18	84	84	113	112	111	90	80	105	
10	20	39	36	68	73	89	67	58	73	35
11	18	22	18	50	57	94	73	63	85	
12	42	77	76	106	106	45	23	14	50	
13	19	45	42	74	78	72	51	41	63	33
14	18	47	44	75	79	12	51	44	05	55
15	16	50	47	78	82					
16	16	51	18	70	82	177	159	146	105	20
17	16	57	55	96	00	1//	150	140	105	50
18	13	32	20	60	66	70	10	20	40	21
10	13	00	100	100	105	107	40	39	49	21
19	44	99	100	128	125	107	80	15	102	10
20	31	02	00	91	93	109	88	/8	93	42
21	36	11	/6	105	106	86	64	55	86	43
22	29	126	130	154	147	107	86	76	104	
23	13	64	62	93	95	97	75	65	75	22
24	29	65	63	93	95	38	17	9	41	
25	31	87	86	115	114	36	14	6	39	
26	33	87	87	115	114	91	70	60	87	28
27	19	62	60	91	93	201	183	171	136	35
28	13	45	42	74	78	191	173	161	116	32
29	49	90	90	119	117	69	47	38	72	
30	26	53	51	82	85	70	48	30	64	34
31	23	31	27	60	65	42	20	12	45	36
32	15	32	28	61	66	135	115	104	02	31
32	18	35	20	63	60	01	70	60	76	24
24	21	20	25	57	64	60	10	27	10	22
25	40	29	25	5/	100	08	40	37	01	33
35	49	81	80	110	109	65	44	35	0/	
30		33	29	62	6/	159	140	128	101	28
37		43	40	72	77	154	135	123	88	22
38		50	47	78	82	176	158	146	111	31
39		44	41	73	77	235	220	207	138	37
40		60	57	88	91	133	112	102	83	21
41		37	33	65	71	121	100	90	72	22
42		64	62	93	95	124	104	93	80	26
43		64	62	93	95	125	104	94	84	27
44		74	73	103	103	184	166	154	126	35
45		58	56	87	90	67	45	36	46	19
46		52	49	81	84	86	64	55	56	15
47	17	93	93	121	119	156	137	125	131	
48	14	60	57	88	91	86	65	55	53	15
40	1.4	55	52	84	87	152	122	122	04	24
50		00	00	110	117	190	161	140	120	24
51		50	50	02	05	120	100	00	74	17
51		55	51	82	85	130	109	99	/4	17
52		13	12	102	103					
53	14	37	33	71	66					
54	13	63	61	92	94					
55	21	64	62	93	95					
56	17	60	57	88	91					
57	14	67	66	96	97					
58	17	49	47	78	82					
59	16	81	80	110	109					
60	16	43	40	72	77					
61	12	53	51	82	85					

TABLE 5: Geothermometer temperatures for chemical samples from Aitos field



FIGURE 19: The Aitos field, chalcedony geothermometer temperature vs. Na-K-Ca geothermometer temperature



7. SUMMARY AND CONCLUSIONS

The main aim of the report is to predict subsurface temperatures in the northwestern part of the Bourgas synclinorium. The calculations of the predicted temperatures are based on analytical results from 35 wells and 26 cold springs. The samples are from two different geothermal fields, the Straldja and Aitos fields. A brief description is given on the geology, hydrogeology and hydrogeothermal exploration of these fields as background information. The geotectonic conditions play an important role in controlling geothermal activity and the distribution of thermal water. The tectonic structures, like faults and fissures, provide the flow paths and the storage space for hot water. The volcanogeno-sedimentary complex is clearly anisotropic with regard to hydrogeological conditions, both in horizontal and in vertical directions, due mainly to processes of disruptive tectonics.

The composition of the thermal and sub-thermal waters discovered is mostly bicarbonate-sodium, chloridesodium and chloride-bicarbonate-sodium. The bicarbonate-sodium waters are connected to the upper hydrothermal zone in both of the fields. They are only slightly mineralized, highly alkaline, and their pH is in the range 8-10. The chloride-sodium and chloride-bicarbonate-sodium waters have been located through drilling. These waters have a higher chloride and fluoride content. Besides in-depth genesis, the higher chloride content observed in the Aitos field could also be due to impulverisation of seawater as a result of rain and air draughts. Temperature and chemical composition of thermal waters from wells suggest that their sources may be different. By using the computer programmes WATCH and SOLVEQ and plotting the log Q/K diagrams, possible equilibrium and non-equilibrium situations between studied fluid components and minerals can be identified.

The chemical geothermometers which have been used to estimate the subsurface temperature of the geothermal water give an overall picture of these fields. The Na-K geothermometer gives very high and sometimes unrealistic temperatures for all cold springs and some of the wells very high, so it should not be applied to waters which are non-thermal or only slightly thermal, with chloride content similar to that of the

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local surface water. The K-Mg geothermometer gives low values for the thermal waters, but sometimes values similar to the chalcedony geothermometer temperatures for cold waters. Generally, this geothermometer can not be used alone. For the thermal waters in the Aitos area, Na-K geothermometry temperatures are lower than that of the mixed water, because waters of the approximately the same salinity mix. Results of Na-K-Ca geothermometers indicate that this empirical geothermometer appears to be applicable for low-temperature waters. Quartz geothermometry temperatures realistic for waters in the Straldja field correspond well with estimated mineral-equilibrium temperatures. In the Aitos area, where almost all wells draw fluid from two or more aquifers, and where the discharge represents mixed water, the quartz geothermometer yields higher temperatures than the average temperature of the mixed water. The chalcedony geothermometer provides the most reliable temperatures for this field. According to it, the predicted temperatures are in the range 22-126°C.

The results from the geochemical investigation are in agreement with the results of previous investigations. It is to be expected that the main and, from a practical point of view, most important hydrothermal waters in the northwestern part of the Bourgas synclinorium are to be found in the Pre-Cretaceous aqueous horizons and complexes of the lower elision zone. These are the Triassic and Jurassic carbonate complexes and the terrigenous sediments. All of them have been repeatedly and extensively exposed to the action of continental conditions and have been subject to karstification and cracking. It is therefore to be expected that everyone of them could accumulate considerable amounts of relict, syngenetic haline or epigenetic seawater with temperatures of 120-150°C as predicted by the quartz geothermometer.

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APPENDIX I: Equations describing the temperature dependence of cation/proton ratios (from Arnorsson et al., 1983a)

$$\log \frac{\sqrt{Ca^{2*}}}{H^*} = 1.733 + 0.01117T + \frac{3890.51}{T} - 3.9977 \log T$$
$$\log \frac{Na^*}{H^*} = 2.694 + 0.02023T + \frac{4243.47}{T} - 6.2069 \log T$$
$$\log \frac{K^*}{H^*} = 2.505 + 0.01917T + \frac{3325.71}{T} - 5.7814 \log T$$
$$\log \frac{\sqrt{Mg^{2*}}}{H^*} = 1.816 + 0.01078T + \frac{3727.48}{T} - 4.1640 \log T$$

APPENDIX II: Equations for chemical geothermometers used in the report

$$T_{chal-1} = \frac{1112}{4.91 - \log SiO_2} - 273.15$$
 Arnorsson et al., 1983b

$$T_{chal-2} = \frac{1023}{4.69 - \log SiO_2} - 273.15$$
 Fournier, 1977

$$T_{qtr-1} = \frac{1309}{5.19 - \log SiO_2} - 273.15$$
 Fournier, 1977

$$T_{qr-ad-2} = \frac{1522}{5.75 - \log SiO_2} - 273.15$$
 Fournier, 1977

$$T_{Na-K-1} = \frac{1390}{1.75 + \log \frac{Na}{K}} - 273.15$$
 Giggenbach, 1988

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$$T_{Na-K-2} = \frac{1217}{1.483 + \log \frac{Na}{K}} - 273.15$$
 Fournier, 1979

$$T_{Na-K-3} = \frac{1178}{1.470 + \log \frac{Na}{K}} - 273.15$$

Nieva and Nieva, 1973

$$T_{Na-K-Ca} = \frac{1647}{\log \frac{Na}{K} + \beta(\log \frac{\sqrt{Ca}}{Na} + 2.06) + 2.47} - 273.15$$

$$\beta = \frac{4}{3}$$
 for $t < 100 \,^{\circ}C$; $\beta = \frac{1}{3}$ for $t > 100 \,^{\circ}C$

$$T_{K-Mg} = \frac{4410}{14.0 - \log \frac{K}{\sqrt{Mg}}} - 273.15$$

Giggenbach et al., 1983