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**CHEMICAL GEOTHERMOMETERS AND
MINERAL EQUILIBRIA OF SOME HOT WATERS
IN YUGOSLAVIA**

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CHEMICAL GEOTHERMOMETERS AND MINERAL EQUILIBRIA OF SOME HOT WATERS IN YUGOSLAVIA

- Vardar zone and Serbo-macedonian mass -

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ABSTRACT

Geochemistry is a relatively young branch of hydrochemistry which is applied in each step of geothermal research and is also one of the less expensive investigation methods. The main goal of geochemistry in surface exploration is predicting of subsurface temperatures. In later stages monitoring of chemical changes in the reservoirs and solving scaling and corrosion problems are common. Yugoslavia is situated within an active tectonic and seismic belt known as the Alpic-Kavkaz-Himalayan belt and in its territory there are found about 300 hot occurrences both springs and wells with temperatures of 20-111°C. The geothermal energy in this country is used in health spas, for greenhouse farming and heating. This report deals with chemical data from a part of Yugoslavian hot waters belonging to two tectonic units, the Vardar zone and the Serbo-macedonian mass. The main geological and tectonical features of the Vardar zone are ophiolites, melange and flysch sediments and young magmatic rocks of Quaternary age. The Tertiary grabens covered by young sediments are found in this zone. The Vardar zone is a very active tectonic and seismic zone. The Serbo-macedonian mass represents an older tectonic unit where rocks from Precambrian to Quaternary age are spread. This unit is not as active as the Vardar zone but some seismic areas are found, mostly related to regional faults. In the report 52 chemical analysis from hot springs or wells are taken into consideration. The samples belong to two republics, Serbia and Macedonia. In Serbia the waters are mainly of Na-HCO₃ or Na-Cl type but in Macedonia the waters show complex compositions. The waters are mainly Ca-Mg-Na-HCO₃ or Na-HCO₃ type. Chemical geothermometry, mixing models and mineral equilibria were used to interpret the samples. Waters of Na-Cl type often show mineral equilibria but bicarbonate waters often show disturbed equilibria. Waters with extremely high magnesium are often very difficult in interpretation. In Serbia, reservoir temperatures in the range of 120-140°C were obtained for a few samples and in Macedonia the highest predicted temperature is in Bansko, 110-115°C.

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1. INTRODUCTION

Yugoslavia as Balcan peninsula countries is situated within Alpidic-Kavkaz-Himalayan active tectonic and seismic belts. It is manifested with active seismic area in Yugoslavia associated with geothermal manifestations. There are more than 300 geothermal known occurrences mainly as hot springs with temperatures above 20°C, which is lower limit for geothermal classification.

Owing to regional heat flow as source heat and Moho discontinuity spreading in Yugoslavia it was believed that only low temperature fields exist. But last year drillings in Serbia, Vrantska banja indicated possibility of higher temperatures in some fields. In this area temperature of 111°C and both water and steam in a 1000 m deep borehole was obtained. Indications of higher temperatures are present according to presence of young magmatic intrusions close to the surface and at shallow depth.

This report consists of a short review of the geological environment, tectonic and geothermal characteristics of Yugoslavian territory with more details about Bosnia-Serbia-Macedonian geothermal provinces necessary for presentation of the main subject. This report deals with thermal activity in the eastern part of this province belonging to the two uniform tectonic units. The general aim of this report is geochemical interpretation of chemical analysis of some minerals, thermal and thermomineral waters, where geothermometers, mineral equilibria, mixing and scaling were given special attention. The reader can remark that here is a more detailed description about geothermal waters from the Republic of Macedonia where the author lives and works.

2. GEOTHERMAL PROVINCES IN YUGOSLAVIA

Milojevic and Peric (1982), distinguished four main geothermal provinces in Yugoslavia, shown in Fig. 1. These are: Serbian-Bosnian-Macedonian province which is the largest, Pannonian, Dinaridic and Alpidic provinces. Each province has special geological, tectonical and geothermal characteristics.

2.1. The Serbian-Bosnian-Macedonian province

The province consists of different geological formations with different lithological composition and age. The age of the rocks are from Precambrian to Quaternary and the types are sedimentary, magmatic and metamorphic. There are represented by acidic, mafic and ultramafic bodies older than Quaternary age as well as volcanic and intrusive formations of Quaternary age. The hottest geothermal manifestations in Yugoslavia are found in this province. According to geophysical data, mainly seismic profiling, the crustal thickness is 25-40 km in this area.

2.2. The Dinaric geothermal province

As shown in Fig. 1 the Dinaric geothermal province spreads over the Adriatic coast. Comparing Fig. 1 and Fig. 2 it becomes obvious that it covers the Outer Dinaric tectonic unit. This province consists mostly of Mesozoic limestone with thickness in excess of 1000 m. The MOHO discontinuity in Yugoslavia is at most depth in this province, about 50 km. Thermal manifestations are not known within this province.

2.3. The Pannonian geothermal province

Pannonian geothermal province covers the Yugoslavian part of the Pannonian Tertiary basin. This province is characterized by Quaternary sediments with thickness over 2000 m. The geothermal potential in Yugoslavia is highest in this region but geothermal waters with high temperatures are found at great depth, making exploitation expensive. About 100 thermal springs are known mostly in the southern part where sedimentary strata reach the surface. Within the basin geothermal waters were obtained by drilling, mostly oil drilling. The crustal thickness in the province amounts to about 25 km.

2.4. The Alpidic province

This province is the smallest one and it is situated in the north-western part of the country within the Alpidic mountain range. The main characteristics of this province are intermountain sedimentary basins where thermal springs and boreholes account. MOHO discontinuity is at 30-40 km depth.

3. GEOTECTONIC SETTING OF YUGOSLAVIA

Geotectonically Yugoslavia is divided into six main units, (Andjelkovic, M.,1978): Dinarides, Alpides, Pannonides, Vardar zone, Serbo-Macedonian massif and Carpato-Balcanides, shown in Fig. 2. The largest tectonic unit, Dinarides, is divided into three zones, Outer Dinarides, Central Dinarides and Inner Dinarides. In the Republic of Macedonia which is mostly situated in this unit it is separated into two subunits called West Macedonian zone and Pelagon horst anticlinorium, located in the central and southern part of Macedonia.

3.1. Alpides

The Yugoslavian Alpides are presented by Eastern Alps consisting mainly of metamorphic and magmatic rocks and also of sediments, ranging in ages from Paleozoic to Cenozoic.

3.2. Dinarides

The Outer Dinarides are built mainly of Paleozoic to Cenozoic calcareous and clastic series with predominating Mesozoic carbonate formations. The western part is known as a High Karst zone. The Central Dinarides extend the Outer and Inner Dinarides. It is built of calcareous rocks, flysch, volcano-sedimentary sequences and magmatic rocks of different ages but Triassic age is dominated. The Inner Dinarides consist of Paleozoic terrigenous and marine sediments with characteristic Triassic calcareous, Jurassic volcano-sedimentogenic rocks, Cretaceous ophiolitic-radiolaritic series, Paleogenetic flysch and Neogenetic molasse. Magmatic rocks of Paleozoic to Neogene age are associated with these rocks.

3.3. Pannonides

This tectonic unit extends to the north of Dinarides in the southern part of Pannonian basin which covers the north regions of Yugoslavia. The bedrock consists of old metamorphic rocks, mainly marbles and magmatic rocks. It is covered by over 2000 m thick Tertiary strata.

3.4. Carpato-Balcanides

The rocks belonging to this tectonic unit are the oldest rocks in Yugoslavia. It is located in the eastern part of Serbia and it consists of formations from Riphean to Paleogene. Lithologically the rocks are mostly metamorphic and magmatic but also young sediments are present covering intermountain depressions and grabens.

3.5. Serbo-Macedonian massif

The location of this tectonic unit can be seen on Fig. 2. Its beginning is related to the basement of the Pannonian basin in Yugoslavian and Romanian territory. Serbo-Macedonian massif pass through the central part of Serbia, Eastern Macedonia continuing into the Greece territory under the same name. Geological basement consists of metamorphic and magmatic rocks. Its characteristic features are the tectonic grabens covered by sediments of Neogen and Quaternary age. At lower elevation the geothermal manifestations are related to active seismic faults and fissures, so their appearances are associated with grabens and neotectonic active regional dislocations.

3.6. Vardar zone

The Vardar tectonic zone extends along the Serbo-macedonian mass and it is bordered on its western side by the Inner Dinarides. The main features of this unit are ophiolites and sediments ranging in age from Jurassic to Quaternary. In the northern part it is covered by Pannonian sediments. The Vardar zone extends from Belgrade in the north, through Western Serbia and central Macedonia and continues to Greece under the name, Axios zone (Axios-Vardar river originate in Macedonia and pouring in Aegean sea in Greece). Magmatic activity in Vardar zone was intermittent in the period from Jurassic to Quarter. Nowadays very active seismic zone is present, where strong earthquakes frequently take place. According to many scientists Vardar zone was an active subductional zone during Jurassic when the ophiolites mass was formed.

3.7. Part of Yugoslavia subject of the report

The Bosnia-Serbia-Macedonian geothermal province covers a large area. Therefore it was decided to deal only with geothermal waters belonging to the Vardar tectonic zone and Serbo-Macedonian. Another reason for this limitation was that this province

belongs to four different republics and it is difficult to get suitable data. The observing part extends into the territory of two republics, Serbia and Macedonia.

4. DISTRIBUTION AND CLASSIFICATION OF GEOTHERMAL WATERS IN VARDAR ZONE AND SERBO-MACEDONIAN MASS

The distribution of the main hot waters in Vardar zone and Serbo-macedonian mass is shown in Fig. 3. In this report the geothermal areas are grouped on the bases of geography, geology and chemical composition. Geographically it is distinguished between samples from Serbia and samples from Macedonia. The reason for this division is that analytical methods for chemical analysis may be different in each republic. Geologically, the samples from Serbia are divided into samples from Tertiary sediments, samples from wells drilled in Tertiary sediments where bedrock is represented by metamorphic rocks, samples from flysch environment, samples from metamorphic and samples from magmatic environment. In Macedonia the thermal waters issue mainly through Tertiary sediments covering metamorphic basement and through magmatic rocks.

The chemical composition of geothermal waters from Vardar zone and Serbo-macedonian mass is given in Tab. 5 and shown in Fig. 6 on two triangle plots, part of Piper diagram (Piper, 1953), representing cations and anions, respectively. It is obvious that the dominating cation is sodium although in some waters other cations are the main ions. Bicarbonate and chloride are the main anions. There is a difference between the chemical composition of thermal waters from Serbia and Macedonia, Fig. 6. In Serbia the waters are of Na-HCO₃ or Na-Cl type but in Macedonia the waters show a more complex chemical composition. The waters are of Ca-Mg-Na-HCO₃ or Na-HCO₃ type.

Chemical analysis from Serbia used in the report were obtained from The Faculty of Mining and Geology, University of Belgrade (Milojevic, written communication). The chemical analysis from Macedonia are taken from Gunnlaugsson (1985). A few analysis from Macedonia are obtained from The Institute of Geology in Skopje (Gorgiev, written communication).

5. MINERAL EQUILIBRIA, CHEMICAL GEOTHERMOMETERS AND MIXING MODEL AS A BASE OF INTERPRETATION

The principal role of geochemistry and especially hydrochemistry in geothermal reconnaissance and exploration surveys involves estimation of subsurface temperature. During later stages in geothermal development hydrochemistry is involved in assessing in various reservoir characteristics such as solving scaling and corrosion problems and effluent disposals. For an estimation of the reservoir temperatures, knowledge about reservoir equilibrium conditions are necessary.

5.1 Mineral equilibria

What is equilibrium? By basic thermodynamic data one system is in equilibrium when free energy of the reaction (drives chemical reaction) is equal to zero, $G=0$, which means:

$$\Delta G^\circ r = \Sigma G^\circ f, \text{ prod.} - \Sigma G^\circ f, \text{ reac.} \text{ where,}$$

ΔG_r = free energy of reaction

ΣG_f , prod. = sum product free energy

ΣG_f , reac. = sum reaction free energy

$^\circ$ = reference temperature, 25°C

Equilibrium in geothermal systems involves geothermal fluid, reservoir rocks and conditions under which interaction takes place, pressure and temperature. It is believed that pressure is not an important factor because of relatively small changes in equilibrium with change of pressure within the geothermal field. For studying equilibrium the following phases are take into consideration: Water, dissolved constituents, precipitation and secondary minerals. But it is difficult to study equilibrium considering only concentration of the elements due to large distributions and inaccuracy. Therefore activity of aqueous species such as simple ions, complexes or ion pairs are used.

Equilibrium has been subject to different studies for many scientists and according to the phase rule, Arnórsson et al., (1983a) describe equilibrium by 12 phases. One of the phases is water and the remaining 11 are minerals. For basaltic magmatic environment equilibrium is controlled by 10 minerals, because of undersaturation of fluorite. The attainment of equilibrium in the reservoir depends on a number of

factors such as the kinetics of the particular reaction, the temperature in the reservoir, the activity of the wallrocks, the concentration of the elements in the fluids and the residual time of the water in the reservoir. Therefore in some cases, equilibrium in the reservoir may be reached for some reactions and elements but not for others and not for all. The minerals controlling the equilibrium in magmatic environments are:

1. Quartz and chalcedony,
2. Low albite (sodium feldspar),
3. Microcline (potassium feldspar),
4. Calcite,
5. Smectite-chlorite,
6. Pyrite-marcasite,
7. Iron hydroxides,
8. Pyrrhotite-anhydride,
9. Epidot at higher temperature and some other Al silicate at lower temperature,
10. Some Al silicates,
11. Fluorite.

In other geological environments other minerals may be involved. Among the first secondary minerals which approach equilibrium with the aqueous phase are calcite and amorphous silica then chalcedony. After studying the mineral equilibria in different geothermal waters in Iceland, using activity of aqueous species calculated by the WATCH computer program (Arnórsson et al., 1982; Arnórsson et al., 1983a; Arnórsson and Svavarsson, 1985) equations were reached which can be used as "equilibrium lines" for the elements. The equations are given in Tab. 2.

The following can be used as "rule of thumb" to determine equilibrium:

- # Geothermal waters are as a rule saturated with calcite and often saturated with anhydrite and fluoride. If degassing occurs in hot springs the water may become significantly supersaturated with respect to calcite.
- # Mineral solute equilibria fix the $\sqrt{\text{Ca}^{++}/\text{H}^+}$ ratio at a particular temperature.
- # Surface water and shallow groundwaters are typically calcite undersaturated and have very low $\sqrt{\text{Ca}^{++}/\text{H}^+}$ ratio. Relatively short underground resident time is needed for cold groundwater to attain equilibrium with calcite.
- # Mixed water as a role has low $\sqrt{\text{Ca}^{++}/\text{H}^+}$ ratio for their temperature but they are usually calcite saturated.

5.2. Chemical geothermometers

Determination of the subsurface equilibrium temperature in a geothermal field is a major goal in geothermal investigation. Both quantitative and qualitative methods are used to predict the temperature.

5.2.1. Qualitative geothermometers

Qualitative methods consist of looking for anomalous concentration of various elements called "indicator" or anomalous ions or complexes ratios in the water. Some of these indicators are listed in Tab. 3, taken from Koga (1988). Enrichment of B, NH₄, HCO₃, Hg and H₂S in near-surface water may result from boiling at depth. High concentration of volatile components often accumulate 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 indication of thermal water.

High Cl/F and Cl/SO₄ ratios in liquids of a geothermal area generally indicate high temperature in the system. Anomalously high concentrations of nonvolatile trace elements may sometimes be an indication of high subsurface temperature. This would be true if the element tended to be leached from rocks only at high temperatures. Often high concentration of chloride is an indication of high temperatures.

5.2.2. Quantitive geothermometers

Quantitive geothermometers can be divided into two groups, chemical and isotopic geothermometers. The latter group is mostly used for high temperature waters. Two geothermometers are sustained by the evidence of chemical equilibria between deep solution and mineral phases, respectively, the silica minerals and alkali felspars.

5.2.2.1. Silica geothermometers

The silica geothermometers are based on experimentally determined solubilities of chalcedony and quartz. The concentration of the silica in the geothermal water is correlated with the solubility of these minerals using experimentally obtained solubility curves to predict reservoir temperatures.

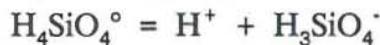
The first geothermometer ever used for temperature prediction was entirely empirical. Böðvarsson (1960) found that there was a good correlation between silica content and temperature. Nowadays many equations exist to compute the silica temperature.

Those used in this report are listed in Tab. 1. Good knowledge about the calibrations as well as geological knowledge is essential for the use of the silica geothermometers. In Iceland the chalcedony temperature is used up to 180°C and quartz at higher temperatures. In other countries quartz equilibrium seems to be attained at lower temperatures, in some cases down to 90-100°C and even all the temperature range.

An important fact to be considered when applying the silica geothermometer is that equilibrium between mineral and solution involves only the unionized silica in the solution. This is especially significant for dilute water with high pH. The analysed silica quoted as SiO_2 consists of different species:



The last two species are in very low concentration and can be omitted and we can say that $\text{H}_4\text{SiO}_4^\circ$ and H_3SiO_4^- concentration have to be computed from reaction:



assuming that the concentration is equal to activity. On the basis of this assumption, the concentration of unionized silica in the solution is found from the measured water pH and the analysed total silica using the dissociation constant for the reaction at the pH measured temperature as follows:

$$(\text{H}_3\text{SiO}_4^-) / (\text{H}_4\text{SiO}_4^\circ) = K_{\text{diss}} / (\text{H}^+) \quad \text{where}$$

$$\text{SiO}_2 \text{ (analysed)} = [\text{H}_4\text{SiO}_4^\circ] + [\text{H}_3\text{SiO}_4^-]$$

K_{diss} = dissociation constant expressed as $\log K = -2549/T - 15.36 \cdot 10^{-6}T^2$

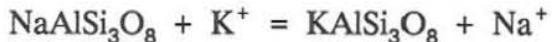
and T = temperature in °K. In cases where the pH is lower than 8.5, correction is not needed where all silica concentration calculates to the unionized state.

Knowing that the hot water has lost some steam during its passing up the surface, it becomes necessary to correct for steam lost or for the increasing of silica content in the residual solution. This is always related to an increase in water pH due to degassing associated with steam loss (loss of CO_2 and H_2S). Therefore it is necessary to calculate the deep water pH, taking into account the buffer action of various weak acids (silica, carbonic acid and hydrogen sulphide). This can be calculated using the WATCH computer program (Arnórsson et al., 1982). But for the first temperature calculation the assumption may be used that the pH change depends only on the buffer action of silica. For the silica geothermometer, equations are also available to deal with water where steam loss has occurred.

5.2.2.2. Cation geothermometers

There are many different cation geothermometers used to interpret the composition of geothermal water, such as Na/K, Na-K-Ca with CO₂ and Mg correction, Na/Li, K/Mg, etc. Equations for the geothermometers used in this report are given in Tab. 1.

Cation geothermometry is based on ion exchange reactions as for example



which have temperature dependent equilibrium constants. With the assumption that activities of the solid reactions are unity and activities of the dissolved species are about equal to their molal concentration in aqueous solution, the equilibrium constants K_{eq} is expressed in simple ratio as Na/K. If the reaction involves divalent and monovalent ions, for example Ca and Na, the equilibrium constant is approximately equal to √Ca/Na.

Some of the cation geothermometers are based on laboratory experiments where known minerals are controlling the equilibrium while others are based on the correlation between the measured temperature in boreholes and the cations content in the drillhole discharges. In this case the minerals controlling the equilibria are unknown.

Cation geothermometers give satisfactory results for samples from high temperature geothermal fields but it is more difficult to use them for low temperature waters because of relatively slow reaction rate.

The Na-K-Ca geothermometer (Fournier and Truesdell, 1973) is an empirical geothermometer based on more than one exchange reaction. This geothermometer works well for high temperature waters above 200°C but when applying it at low temperature waters the results are sometimes erratic. The erratic results appear from 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 degassing or boiling also affects the Na-K-Ca geothermometer. In this case the predicted temperature is too high. To avoid the influence of the partial pressure of CO₂ on the Na-K-Ca geothermometer, Paces (1975) suggested a correction, see Tab. 1. Corrections are also recommended for Mg when this geothermometer is applied to Mg rich waters (Fournier and Potter, 1979).

Equations for this correction are also given in Tab. 1. As a rule Mg concentration in geothermal waters decreases rapidly as the temperature increases and all Mg rich waters found in the nature have undergone water rock reaction at a relatively low temperature. It is believed that Mg correction to Na-K-Ca geothermometer gives satisfactorily results for low temperature waters but for high temperature waters predicted reservoir temperature may be too low.

In recent years new cation geothermometers have been proposed such as K/\sqrt{Mg} (Giggenbach, 1988) and Li/\sqrt{Mg} (Kharaka and Mariner, 1988). These are useful to indicate re-equilibrium because magnesium is an element which is included in the exchange reactions at lower temperatures. When there is good agreement between the temperature estimation using K/\sqrt{Mg} , Li/\sqrt{Mg} and other geothermometers, one can be fairly sure that water rock equilibrium has been reached at that temperature. Disagreement between geothermometers may indicate short time for re-equilibration and that equilibrium occur only in respect to the most reactive phases.

Many other cation geothermometers have been proposed for temperature estimations such as the Na/Li (Fouillac and Michard, 1981). This geothermometer is very sensitive to slight changes of Li that result from exchange involving other ions than Na. It is therefore recommended to use this geothermometer in combination with other geothermometers but not alone.

5.3. Mixing

Ascending hot water may undertake different changes such as adiabatical or conduction cooling, mixing with shallow waters or a combinations of these processes. Chemical analysis of spring waters may provide information about which of these processes are occurring. Water which is not in equilibrium with reservoir rocks is either a non-equilibrium water (cold water) or mixed water. Partial or complete chemical equilibrium may or may not occur after mixing. If equilibrium is reached after mixing, the chemical geothermometers indicate temperatures of the last equilibrium. Therefore the obtained temperature refers to the mixed water.

The chemical composition of the mixed water may be used for temperature estimation applying mixing models (Fournier and Truesdell, 1973). Mixing models should never be applied unless there is an independant evidence for mixing because when mixing

model is used for unmixed water, the predicted temperature will be too high. Some independant indications of mixing are:

1. Large discrepancy between the temperatures indicated by the silica and the cation geothermometers.
2. Systematic variation in temperature and in the compositions of water in springs from the same area.
3. Relatively cool spring with large mass flow, and much higher temperature indicated by the geothermometers.
4. Variation in oxygen and hydrogen isotopes, especially tritium.
5. Variation in elements that do not participate in alteration (Cl/B ratio).
6. Variation in chloride concentration, larger than could be explained by steam loss.

The silica mixing model is the most appropiate for low temperature waters. If silica mixing model are used to estimate the temperature it is necessary to know the silica content and the temperature of the local cold water. The silica enthalpy graph, Fig. 4, shows the procedure of the temperature estimation. Point A represents cold water, B thermal mixed water, C thermal water adiabatically cooled before mixing occurs, D boiling point at atmospheric pressure, E thermal water after maximum steam loss and F thermal water before steam loss. The concentration of silica may be read directly from the graph as well as the predicted temperature using enthalpy and steam tables.

5.4. Estimate of subsurface temperatures in Serbia and Macedonia.

In this report chemical geothermometers are used to predict subsurface temperatures in Serbia and Macedonia. As shown in previous chapters there are many different geothermometers and it is rare that they all give the same result, especially when they are applied to hot spring water. Mineral equilibria study is used here to strengthen or impair the result of the chemical geothermometers. If mineral equilibria is not attained, the calculated values from the chemical geothermometers are not reliable.

The equations listed in Table 2 have been used to describe mineral equilibria for geothermal water in Iceland (Arnórsson et al., 1983a). The activity of the chemical

species calculated by the WATCH computer program (Arnórsson et al., 1982) is compared to these equilibrium equations. This comparison can be done by plotting the equations and the water composition on activity/temperature graphs, example Fig. 6, where the activity of the water sample is calculated at the temperature obtained from some of the chemical geothermometers. When equilibrium is reached the chemical composition plots close to the theoretical equilibrium lines.

It is also possible to calculate the activity of the species for each sample at different temperatures and compare it with the equilibrium equations. An example of this method is shown in Fig. 11 (equilibrium temperature graph), where Q represents the water composition and K the equilibrium equation (theoretical equilibrium). When equilibrium is reached all the lines representing chemical composition cross the zero line ($\log Q/K = 0$) in a small temperature range. When equilibrium is not reached the lines representing the chemical composition cross the zero line in a large temperature range. Plot of both types were prepared during the interpretation of the samples but only a few are included in the report.

6. EQUILIBRIUM STATE AND CHEMICAL GEOTHERMOMETERS FOR THERMAL WATERS IN YUGOSLAVIA

6.1. Geothermal waters in Serbia

The chemical composition of thermal waters in Serbia are listed in Table 5 and the results of chemical the thermometers are listed in Table 6.

6.1.1. Samples from metamorphic environment

The equilibrium state for samples from metamorphic geological environment in Serbia at chalcedony geothermometer temperature is given in Fig. 7a and 7b.

SAMPLES: 181 89-10; 182 89-11; 183 89-12

Location: Josanicka banja

Geological environment: Schists, serpentinites, volcanic rocks.

Type of water: Na-Cl water with high pH

There are three samples from this area, two from springs 89-10 and 89-11, and one

from borehole 89-12. The calculated Na-K geothermometer and the silica temperature in equilibrium with chalcedony compare relatively well. The difference is 7-18°C. The Na-K-Ca geothermometer also predicts similar values but slightly higher. Closer study of equilibria indicates that all elements except $\sqrt{\text{Mg}/\text{H}}$ ratio is close to equilibrium at calcedony temperature, Fig. 7b. The concentration of magnesium is high in two of these samples and it is possible that some other minerals or reactions govern the Mg concentration. The samples are slightly supersaturated with respect to calcite at measured temperature but undersaturated with fluorite and anhydrite as is common for geothermal waters in volcanic terrains. The slight supersaturation of calcite can be explained by some degassing of carbonate. The results of the geothermometers in the range of 100-110°C can be expected.

SAMPLE: 188 89-29

Location: *Grocka, vicinity of Belgrade*

Geological environment: *The sample is from a 1800 m deep borehole located in the southeastern part of Panonian Tertiary basin. The basement consists of marbles and schists, but the main aquifer is in Tertiary sediments.*

Type of water: *Na-Cl water with high carbonate content.*

The Na-K geothermometer yields temperature of 36°C, silica temperature of 86°C and 114°C for chalcedony and quartz equilibrium, respectively. The Na-K-Ca-Mg and the K/Mg geothermometers yield similar results as the quartz temperature. Equilibrium graphs do not show overall equilibrium between water and rocks at silica temperature (Fig. 7a). Therefore the results of the geothermometers are uncertain for this field although temperatures up to 100-115°C may be expected.

SAMPLES: 185 89-34; 186 89-35

Location: *No. 89-34 is from Suva cesma and 89-35 from Vica in South Morava region*

Geological environment: *Marbles.*

Type of water: *Na-HCO₃*

The chalcedony temperature (112°C) and the Na-K geothermometer temperature (109°C) compare well for sample 89-34, difference 4°C, and relatively well for sample 89-35, difference 16°C. The K/Mg geothermometer yields slightly lower temperature. For sample 89-35 equilibrium seems to be reached for all cations/proton ratios except $\sqrt{\text{Ca}/\text{H}}$, and acid molecules of anions except H₂CO₃ and HF molecules at the

chalcedony temperature (112°C), see Fig. 7b. This water is also near calcite equilibrium at measured temperature but slightly supersaturated at higher temperatures, (T_{ch}). The supersaturation of calcite at chalcedony temperature can be explained by slight degassing. The geothermometry result of about 100 - 110°C is therefore strengthened by the mineral equilibria for this sample. For sample 89-34 the geothermometer result of about 110°C is more uncertain where equilibria is not reached for the acid molecules of anions and not either the $\sqrt{\text{Ca}/\text{H}}$ ratio. This sample is undersaturated with respect to calcite at measured temperature.

SAMPLE: 184 89-42

Location: *Tulare - South Serbia*

Geological environment: *Schists.*

Type of water: *$\text{Na}-\text{HCO}_3$ with high Mg content*

The Na-K and the silica geothermometers compare relatively well for this sample but anion equilibria do not seem to be reached. The water is slightly undersaturated with respect to calcite at measured temperature. The R value of the Na-K-Ca-Mg geothermometer is in excess of 50, indicating mixing (Tab. 6) and Mg content of this water is extremely high. The result of the geothermometers of 85 - 100°C are not certain for this sample due to lack of overall equilibria (Fig. 7b) and a high content of Mg which may disturb the silica geothermometers.

SAMPLE: 187 89-41

Location: *Cibutkovica- Vicinity of Valjevo*

Geological environment: *Schists and marbles.*

Type of water: *$\text{Na}-\text{HCO}_3$*

There is large discrepancy is between the silica geothermometers and the Na-K geothermometer. The $\sqrt{\text{Mg}/\text{K}}$ geothermometer yields similar temperature as the calcedony temperature. The water does not show equilibria (Fig. 7b). The base temperature of about 90°C is therefore not reliable. If this non-equilibria is due to mixing, the silica temperature should be minimum temperature.

SAMPLE: 189 89-02

Location: *Prološka banja*

Geological environment: *Schists and andesites.*

Type of water: *Na-HCO₃-Cl*

The Na-K temperature is extremely low and the potassium proton ratio seems to be out of equilibrium. By studying geothermometer results for this sample it seems that minimum temperature is about 60°C, calculated from chalcedony and Na/Li geothermometer. But from equilibrium graphs it seems that this sample is close to equilibrium at quartz temperature (Fig. 7a). Higher temperatures than silica temperature should not be expected. The predicted temperature is therefore in the range 60-85°C.

SAMPLE: 190 89-33

Location: *Lukovska banja*

Geological environment: *Schists and diabases.*

Type of water: *Na-Cl*

Geothermometers for this sample give three different temperature ranges. Chalcedony temperature corresponds well with K/Mg temperature, quartz temperature corresponds relatively well with Na-K-Ca temperature, difference 4°C, and Na-K geothermometer gives 139°C. Difference between the geothermometers may be caused by mixing. Assuming mixing with cold water at 10°C with 20 ppm SiO₂ silica mixing model indicate temperature near Na-K geothermometer temperature if chalcedony equilibrium is assumed to control the silica concentration. Much higher temperature would be obtained if quartz is assumed to control the silica concentration. Carbonate is not in equilibrium and the water is calcite saturated at measured temperature. Equilibrium graphs for this sample indicate approach to equilibrium at Na-K temperature. According to equilibrium graphs the predicted temperature for this area seems to be about 130°C.

SAMPLE: 191 89-47

Location: *Kursumliska banja*

Geological environment: *Schists and diabases.*

Type of water: *Na-HCO₃*

According to the R value of the Na-Ca-Mg geothermometer (Tab. 6) this sample

represents mixed water. Both Na-K and quartz geothermometers yield high temperatures but with 30°C difference. Slight mixing with cold water might explain the difference. High flow rate is also in favour of this explanation. For this reason it is difficult to predict the underground temperature. If quartz equilibrium is assumed as for many waters from metamorphic environments, temperatures up to 124°C could be expected. The water is supersaturated by calcite at measured temperature indicating that re-equilibrium has not been attained (Fig. 7a).

SAMPLE: 192 89-48

Location: *Avala, vicinity of Belgrade*

Geological environment: *Metamorphic andesites.*

Type of water: *Na-Mg-Cl*

Sample 89-48 shows relatively low reservoir temperature compared with other samples from Serbia. Concentration of silica is very low similar to cold water. Large difference is between silica and Na-K geothermometer and the water is calcite supersaturated. All this is in favour of non-equilibria and so is the high flow rate. Therefore chemical geothermometers should not be applied and temperature much higher than measured should not be expected. The sample is from a borehole and is truly mainly cold water. More information about the borehole, such as depth, depth of casing and location of main aquifers could help to interpret the sample.

6.1.2. Samples from magmatic environment

The equilibrium state for these samples at chalcedony temperature is given in Fig. 8.

SAMPLE: 163 89-13

Location: *Vranska banja-Vranje valley*

Geological environment: *Granites and granite-gneisses.*

Type of water: *Na-Cl*

Water from this location is the hottest geothermal water known in Yugoslavia. Last year a new 1000 m deep well was drilled, yielding water and steam at 111°C. According to equilibrium with most elements and minerals, reservoir temperature in Vranska banja area is in the range 120-130°C or slightly higher (Fig. 5). By using silica mixing model for one water sample from the same area with temperature of 23°C and silica content 40 ppm, reservoir temperature of 150°C was obtained.

SAMPLE: 161 89-38

Location: *Bukovacka banja*

Geological environment: *Volcanic rocks and granitoid pluton in the vicinity.*

Type of water: *Na-HCO₃*

There is a big difference between TSiO₂ and TNa-K which often is the case for mixed water. The √Ca/H ratio is not in equilibrium but some other elements show equilibrium between Tch and TNa-K (Fig. 8). Slight mixing could explain the difference between the silica and the cation geothermometers. Temperatures of 100°C can be expected or even higher. The water is supersaturated with calcite at higher temperature which causes non-equilibrium with calcium and carbonates at all temperatures (Fig. 13).

SAMPLE: 162 89-40

Location: *Metkovic-Macva*

Geological environment: *Tertiary sediments with marble bedrock. The sample is from a 700 m deep borehole.*

Type of water: *Na-Cl*

There is big difference between the silica and sodium potassium geothermometers. Equilibrium with minerals and ions is not reached at any temperature (Fig. 8). This suggests mixing or non-equilibrium water. The water is in equilibrium with calcite at the measured temperature but supersaturated at higher temperatures. Only one analysis with low silica content and temperature close to chalcedony temperature is available, making the mixing model inaccurate. If mixing is taking place the silica temperature is a minimum temperature.

SAMPLE: 164 89-44

Location: *Sierinska banja-Vranje valley*

Geological environment: *Andesites.*

Type of water: *Na-HCO₃*

Geothermometers compare well for this sample, yielding a temperature in the range 130-140°C. The water is close to equilibrium in this temperature range (Fig. 8 and Fig. 15), strengthening the geothermometer results.

6.1.3. Samples from flysch sediments

The equilibrium state for these samples at chalcedony temperature is shown in Figure 9.

SAMPLE: 141 89-19

Location: *Ljig*

Type of water: *Na-HCO₃*

Sample 89-19 is taken from 850 m deep borehole. The silica concentration is similar as in cold water. If the drillhole has short casing, silica may be low due to mixing with cold water. Equilibrium is not seen on the equilibrium graphs but water seems to approach equilibrium at higher temperatures. The water is saturated with calcite at measured temperature (Fig. 9). For one sample it is difficult to apply mixing model. But temperatures in range 40-100°C can be expected if mixing is taking place. If the borehole is well cased and mixing not probable, higher temperatures than measured should not be expected were equilibrium is not attained at the geothermometry result.

SAMPLE: 142 89-20.

Location: *Vrujci*

Type of water: *Ca-Mg-HCO₃-Cl*

The sample is from a 450 m deep borehole, drilled in Cretaceous flysch. The water is probably a mixed water or non-equilibrium water according to unexisting equilibrium at all temperatures and big difference between silica and sodium/potassium geothermometer temperatures (Tab. 6). Silica content is very low similar to cold water, probably outcome of dilution. High flow rate is in favour of a mixing or non-equilibrium water. If the drillhole is with short casing and the main aquifer is near the surface then this is mainly non-equilibrium water. Subsurface temperature is a possibility for this sample.

SAMPLE: 143 89-09

Location: *Ribarska banja*

Type of water: *Na-Cl*

The water is from a borehole drilled in flysch. The water is close to equilibrium with most elements at chalcedony temperature (Fig. 9). The Na-K geothermometer yields slightly lower temperature compared to silica temperatures. Water is slightly

supersaturated with calcite at all temperatures which means that calcite deposits may form. Temperature close to 100°C can be expected.

6.1.4. Samples from boreholes in Tertiary sediments with carbonates or metamorphic rocks in the basement

The equilibrium state for these samples at chalcedony geothermometer temperature is given in Fig. 12b.

SAMPLES: 121 89-14 and 122 89-16

Location: *Sample 14 is from Dublje and 16 from Bogatic - Macva region.*

Geological environment: *Tertiary sediments with carbonate bedrock.*

Type of water: *Na-Cl water with high CO₂ content*

For these two samples there is a big discrepancy between silica and Na-K geothermometers (77-100°C), but chalcedony temperature and T K/Mg compare relatively well, difference 10°C, for sample 89-14, and also Tch and T Na-K-Ca, difference 7°C, for sample 89-16. Equilibrium graphs for sample 89-14 do not show equilibrium at the geothermometer results, and mixing is probable. Assuming that cold water in this field is 10°C with 20 ppm SiO₂, the mixing model predicts a temperature of about 60°C (Fig. 16). For sample 89-16 water is not in equilibrium at the geothermometry temperatures. Mixing is also possible in this case. Assuming similar cold water as for sample 89-14, the silica mixing model predicts a temperature of about 95°C (Fig. 16). Temperature of 90-100°C could be expected. These two samples are slightly supersaturated with calcite at the predicted temperatures (Fig. 12b).

SAMPLES: 123 89-18 and 124 89-17

Location: *Sample 89-18 is from Salters and sample 89-17 from Smederevska palanka.*

Geological environment: *Tertiary sediments with bedrock of shales.*

Type of water: *Na-Cl water with high content of carbonates*

Chalcedony temperature for sample 89-18 is lower than the measured temperature but quartz temperature and sodium/potassium temperature compared very well. By studying the equilibrium graphs it is evident that equilibrium is almost reached at Tq with all cations except calcium. Equilibrium is not attained for H₂CO₃ and HF at any temperature but sulphate and hydrogen sulphide are not determined. Silica

concentration is low but higher temperature than quartz geothermometer temperature should not been expected, so the predicting temperature is in range 70-75°C. The water is calcite saturated at measured temperature but slightly supersaturated at T_{QZ}. For sample 89-17 there is a big difference between the quartz and the Na-K geothermometers, difference 50-79°C. All cation geothermometers show temperatures higher than 100°C, 108-139. From the equilibrium graphs it is obvious that equilibrium is not reach at any particular temperature, but some elements (H_2SO_4 , H_2S , Mg/K and Na/K) are near equilibrium at temperatures close to 125°C (Fig. 10). The \sqrt{Ca}/H ratio suggests some mixing, and also the discrepancy between chemical geothermometers. The silica concentration is low and therefore it is difficult to apply mixing model for this sample but supposing cold water at 10°C with 20 ppm SiO₂, the silica mixing model yield temperature of about 100°C. Reservoir temperature about 80-90°C is possible.

SAMPLE: 125 89-45

Location: *Bujanovac, Vranje valley*

Type of water: *Na-HCO₃*

The chalcedony and the Na-K geothermometer temperatures compare relatively well, difference 11°C, and also Na-K-Ca with CO₂ correction and K/Mg, difference 2°C. The sample is near equilibrium at Na-K temperature with all ions and minerals (Fig. 13) except calcium probably due to loss of some CO₂ at higher temperatures. Predicting temperature in this area is between 125 and 136°C.

6.1.5. Samples from Tertiary sediment environment

Equilibrium state for samples from this geological environment at chalcedony temperature is given in Fig. 12a.

SAMPLE: 104 89-30

Location: *Ovcar banja*

Geological environment: *Tertiary sediments with underling carbonate rocks.*

Type of water: *Ca-HCO₃ with high content of Mg*

The silica concentration for this sample is very low, similar or slightly higher than in cold groundwater. The chalcedony temperature is close to measured temperature. The Na-K geothermometer gives very high temperature. At measured and chalcedony

geothermometer temperature the sample does not show equilibrium with any ions and molecules except with magnesium. Equilibrium is not reached at quartz temperature (Fig. 12a). The water is slightly supersaturated with calcite at measured and higher temperatures. The big difference between silica and the Na-K geothermometer is an indication of some mixing or non-equilibrium water. Temperature much higher than measured should not be expected. But if mixing occurs the silica temperature same as measured is a minimum reservoir temperature. There is not enough data for using mixing model.

SAMPLE: 105 89-46

Location: Vrnici - Vrnacka banja

Geological environment: *Tertiary sediments with andesites and serpentinites in the basement.*

Type of water: *Na-HCO₃ with high Mg content.*

The geothermometers give different temperatures with large discrepancy between silica and the Na-K temperature. By studying the equilibria graphs, one may conclude that there exists equilibrium with all ions except H₂CO₃ at quartz geothermometer temperature (Fig. 12a). At chalcedony temperature equilibrium is almost reached with √Mg/H, K/H, H₂S and H₂SO₄. The measured temperature is near amorphous silica temperature. Because of serpentinites in the vicinity the high content of magnesium may probably by a result of leaching from these rocks and this may be the reason for the high content of silica. That means that silica geothermometers are uncertain. Mixing is indicated by the R value of Na-K-Ca-Mg geothermometer (Tab. 6) but the reason is the high content of Mg. Scattering cross point at equilibrium temperature graph indicates also mixing or non-equilibrium. According to equilibria state, temperatures about 100°C may be expected by this sample but all interpretation for this sample is uncertain as explained above.

SAMPLE: 106 89-49

Location: Mataruska banja

Geological environment: *Tertiary sediments with serpentinites in the basement.*

Type of water: *Na-Cl with high Mg.*

It is very difficult to interpret this sample because geothermometers may be disturbed by a high content of magnesium possible outcome of leaching from serpentinites.

Therefore the mixing, noted by Na-K-Ca-Mg geothermometer is also uncertain. The sample is near equilibrium with Mg and K at measured temperature. The water is near equilibrium at silica temperature especially at quartz temperature for all ions and molecules except with H_2CO_3 and magnesium and magnesium/proton ratio (Fig. 12a). According to equilibrium graphs, equilibrium is best achieved at T_{QZ} temperature. Temperatures slightly higher than 100°C are therefore predicted but the result is uncertain as explained above. The water is supersaturated by calcite at measured and higher temperature. Therefore some calcite scaling is to be expected. The water is also supersaturated with fluorite.

SAMPLE: 101 89-01

Location: Svrackovci

Geological environment: Tertiary sediments.

Type of water: $\text{Na}-\text{HCO}_3$ with high pH

The geothermometers for this water sample give slightly higher temperature than measured. The Na-K geothermometer temperature is lower than calculated quartz temperature and slightly higher than the measured temperature, difference 4°C. The Na-K-Ca and K/Na geothermometers give lower temperature than measured. At measured temperature (28°C) the sample is in equilibrium with $\sqrt{\text{Mg}/\text{H}}$ and Na/H and near equilibrium with $\sqrt{\text{Ca}/\text{H}}$, H_2SO_4 and H_4SiO_4 . Temperature much higher than 30-40°C should not be expected although temperature up to 60-65°C is possible if the water has reached equilibrium with quartz. The water is supersaturated with calcite at measured temperature (Fig. 12a).

SAMPLE: 103 89-27

Location: Gorna Trepca

Geological environment: Tertiary sediments.

Type of water: $\text{Mg}-\text{HCO}_3$

The chalcedony temperature is the same as the measured temperature, difference 1°C, the Na-K temperature is extremely high and Na-K-Ca and K/Na geothermometers give lower temperature than measured. Overall equilibrium between water and rock is not attained at any of the geothermometer temperatures. The silica concentration is low, similar as in cold water. The water is also supersaturated with calcite at measured temperature. All these and high flow rate is in favour of non-equilibrium

water. From this data temperature much higher than measured should not be expected.

SAMPLE: 102 89-28

Location: *Mlakovac*

Geological environment: *Tertiary sediments.*

Type of water: *Mg-Ca-HCO₃*

The chalcedony temperature, Na-K-Ca and K/Na geothermometer temperatures compare very well for this sample, difference 2-6°C but the Na-K geothermometer temperature is extremely high. The silica concentration is low similar or slightly higher than in cold water. The water has not reach equilibrium at any of the geothermometer temperatures. The water is slightly supersaturated with calcite at measured temperature. This sample represents non-equilibrium water or mixed water. Temperature much higher than measured should not be expected.

6.2. Samples from Macedonia

6.2.1. Samples from Tertiary sediments with basement of metamorphic rocks

The equilibrium state for these samples is given in Figure 17 and Figure 18.

SAMPLES: 201 89-59 and 202 89-60

Location: *Volkovo - Skopje valley, sample 89-59 is from borehole D/75 and sample 89-60 from borehole GTD 1/86*

Geological environment: *Tertiary sediments, bedrock marbles or serpentinites.*

Type of water: *Sample 89-59 Ca-Mg-HCO₃ and sample 89-60 Ca-Mg-Cl.*

The silica and Na-K geothermometers give similar temperatures for sample 89-59, difference 8-28°C. For sample 89-60 the silica geothermometer temperatures are similar but slightly lower than for sample 89-59. The Na-K geothermometer temperature for sample 89-60 is much higher and probably indicate some mixing. Flowrate is also much larger from borehole GTD 1/86 than from borehole D/75. At measured, chalcedony and quartz temperature the samples are only near equilibrium with Mg. At Na-K temperature equilibrium is not reach for sample 89-60 with any ions but sample 89-59 is near equilibrium with HF, √Mg/H and H₄SiO₄. So entire equilibrium is not reach at any geothermometer temperature which means

that these two samples represent mixed water or water not in equilibrium with reservoir rocks. The water is supersaturated with calcite so calcite scaling can be expected (Fig. 17). The silica geothermometer temperatures are uncertain because of a high content of magnesium possibly coming from serpentinites in the bedrock. A temperature in the range 80-90°C can be expected, or even higher if mixing occurs.

SAMPLE: 203 89-61

Location: *Kumanovo-Proevci*

Geological environment: *Tertiary sediments, bedrock metamorphosed magmatic rocks.*

Type of water: *Ca-Na-HCO₃*

There is a good correlation between quartz, Na-K-Ca, and K/Mg geothermometer temperatures, difference 6-9°C. The Na-K geothermometer on the other hand yields much higher temperature, 168°C. The sample is not near equilibrium at silica and the measured temperature, but at Na-K temperature sample is near equilibrium with some ions and molecules except H₂CO₃ and H₄SiO₄. The equilibrium temperature graph shows equilibrium temperature with some ions and molecules between 145-165°C. The silica concentration is low, slightly higher than in cold water. The water is supersaturated with calcite at all temperatures so calcite scaling is possible (Fig. 17).

All this is an indication of that this sample may represent mixed water. It is difficult to predict high reservoir temperature because of low content of silica and not having enough data to apply mixing model.

SAMPLE: 204 89-62

Location: *Sabota voda - Titov Veles*

Geological environment: *Tertiary sediments, the bedrock consists mainly of marbles.*

Type of water: *Ca-Cl*

The chalcedony, Na-K-Ca and K/Na geothermometers give similar temperatures, difference 1-4°C, and so do T_{Qz} and T_{Na-K} with difference 20°C. The water is not in equilibrium at measured or chalcedony temperature but not so far from equilibrium at quartz (Fig. 18) and Na-K geothermometer temperature. Therefore it is probable that quartz is controlling the silica content. The water is supersaturated with calcite and slightly saturated with fluorite at the measured temperature. On equilibrium temperature graph most elements cross the zero line between 110-175°C but the main

cations are in equilibrium at about 115°C. Predicting temperature about 80-110°C is confirmed with near equilibrium in that temperature range.

SAMPLES: 205 89-65 ; 206 89-66 and 207 89-67

Location: *Kocani valley, sample 89-65 is from Podlog, sample 89-66 from Banja and sample 89-67 from Istibanja.*

Geological environment: *Tertiary sediments with bedrock consisting mainly of carbonate schists.*

Type of water: $\text{Na}-\text{HCO}_3$

These three samples represent three geothermal fields in the Kocani valley which all may be connected. It is known that Podlog and Banja geothermal fields are connected. These fields extend over 30 km², and are widely used for greenhouse farming. The equilibrium state for samples from this valley at quartz geothermometer temperature is shown in Fig. 18. From a geological point of view the silica concentration is truly controlled by the solubility of quartz. For the Podlog sample, 89-65, there is a difference of about 80°C between quartz and the Na-K temperature and equilibria are not reached between water and minerals. This may indicate that mixing is taking place. If so the quartz temperature is minimum temperature and the subsurface temperature is expected to be between quartz and Na-K geothermometer temperature (100-180°C). For the Banja sample, 89-66, the difference between the quartz and the Na-K geothermometer temperature is 69°C. The water is not far from equilibrium at the quartz temperature. Slight mixing could explain the difference between the geothermometers. Temperature of 90-120°C can be expected. The geothermometers for sample from Istibanja, 89-67, yield similar results as in Banja field, 98-126. The water is not far from equilibrium at this temperature, strengthening the results of the chemical geothermometers. The samples 89-65 and 89-66 are slightly supersaturated with calcite at measured temperature and undersaturated with anhydrite and fluorite but sample 89-67 is extremely supersaturated by calcite and fluorite at measured and higher temperatures.

In the Kocani valley geothermal energy is widely used. Detailed geochemical study is recommended. The chemistry should be interpreted with other data to locate upflow zones and mixing. This study could also be used as base for regular chemical monitoring of the field which is also recommended.

SAMPLE: 208 89-68

Location: Rakles - Radovis valley

Geological environment: Tertiary sediments with bedrock of schists.

Type of water: Mg-HCO₃

The chalcedony geothermometer gives lower temperature than measured. The difference between quartz temperature (53°C) and Na-K temperature (180°C) is very high. The difference between T_{Qz} and T_{Na-K-Ca} is 16°C. At measured temperature the water is undersaturated with calcite but supersaturated at higher temperatures. From equilibrium temperature graph it is obvious that equilibrium is not reached at a definite temperature, therefore sample 89-68 represents non-equilibrium water or mixed water where temperature slightly higher than measured may be expected.

SAMPLE: 209 89-69

Location: Bansko - Strumica valley

Geological environment: Tertiary sediments, the bedrock consists of granite-gneisses.

Type of water: Na-SO₄

The quartz and the Na-K geothermometer give almost the same result, 117 and 118°C, respectively. The water is close to equilibrium at this temperature (Fig. 18). The sample is saturated with calcite at measured temperature but supersaturated at higher temperatures. Equilibrium with all main ions is reached at 115-120°C which is the predicted temperature.

SAMPLES: 221 89-55; 222 89-56; 223 89-57 and 224 89-58.

Location: Katlanovo - Skopje valley

Geological environment: Tertiary sediments with bedrock of marbles and schistes.

Type of water: Sample 89-55 is Ca-Na-HCO₃ type, 89-56 is Ca-HCO₃, 89-57 Na-Cl and 89-58 is Na-HCO₃ type.

The geothermometers give relatively similar results except the Na-K geothermometer. The chalcedony temperatures are in range 73-90°C, the quartz temperature 102-119, the Na-K-Ca temperature 79-93 and the K/Mg temperature 72-85°C. The Na-K temperatures yield extremely high values and might indicate mixing. Equilibrium is not reached at silica temperature except with magnesium. All samples, except 89-58, are saturated with calcite at measured temperature and supersaturated at higher temperatures. From the equilibrium temperature graphs it is obvious that there are

three equilibrium states. These are at temperature 60-80°C with Mg/K and H_4SiO_4 , the second at 150-175°C with \sqrt{Ca}/H , H_2S and H_2SO_4 and the third equilibrium state is with HF, H_2CO_3 and Na/K at very high temperatures. This suggest that the samples from Katlanovo represent mixed water. Further study should be carried out taking samples from all thermal springs and wells and apply mixing model to predict subsurface temperature. In Katlanova area the bedrock is metamorphic. Therefore it is likely that the quartz geothermometer is controlling the silica concentration and quartz temperatures in excess of 100°C is minimum temperature if mixing occurs.

6.2.2. Samples from magmatic environment

The equilibrium state for these samples is given in Figure 19.

SAMPLES: 241 89-63 and 242 89-64

Location: *Sample 89-63 is from the spring Ldji and sample 89-64 from the borehole in Kezovica spa in Stip*

Geological environment: *Granites.*

Type of water: *Na-Cl*

The geothermometers for these two samples give similar values (104-115°C). The difference between Tch and TNa-K is 10-11°C. The T K/Mg compare well with Tch, difference 3-5°C. The T Na-K-Ca compare also well with Tqz, difference 1-2°C. The water samples are near equilibrium with minerals at silica and Na-K geothermometer temperature. The waters are saturated with calcite at measured temperature and supersaturated at higher. The concentration of fluorite is extremely high which is a common case with water from acid magmatic rocks. A temperature of about 100-115°C is strengthened by mineral equilibria.

SAMPLE: 243 89-70

Location: *Smokvica-Gevgelia valley*

Geological environment: *Diabases and spilites.*

Type of water: *Na-Cl*

The geothermometers give similar values slightly higher than 70°C. The difference between Tch and TNa-K is 4°C. This water is near equilibrium with all the main elements at this temperature, strengthening the results of the geothermometers.

SAMPLES: 244 89-71 and 245 89-72

Location: Negorska banja - Gevgelia valley

Geological environment: Diabases and spilites.

Type of water: Na-Cl

The chalcedony temperature for sample 89-71 is almost the same as the Na-K temperature (75°C), difference 2°C. It is different for sample 89-72. The Na-K geothermometer temperature is lower than the silica temperatures, difference 31-61°C, but the T K/Na is similar to the chalcedony temperature, difference 4°C. From the equilibrium graphs it is obvious that equilibrium for these samples is between quartz and Na-K (almost same as Tch) geothermometer temperature. According to the chemical composition of those two samples from Negorska banja, temperatures in the range of 75-100°C can be expected.

SAMPLE: 246 89-73

Location: Gornicet - vicinity of Gevgelia city

Geological environment: Granites and serpentinites.

Type of water: Mg-HCO₃

For this sample geothermometers do not give definite results, probable outcome of some mixing indicated by the R value of the Na-K-Ca-Mg geothermometer. Big difference between the silica and the Na-K temperatures for this sample could also be an indication of mixing. The sample is near equilibrium with all cations and molecules except H₂CO₃ and Mg/K at the quartz temperature. The geothermometers for this sample are uncertain because of high content of magnesium which may disturb the silica and Na-K-Ca-Mg geothermometer, respectively. According to the above it is difficult to predict any temperature.

SAMPLES: 247 89-76 and 248 89-77

Location: Sample 89-76 is from mine Zletovo and sample 89-77 from a borehole in Kratovo, Kratovo-Zletovo volcanic area.

Geological environment: Volcanic rocks, andesites.

Type of water: Sample 89-76 is Ca-SO₄ type and sample 89-77 Ca-HCO₃-SO₄ type.

The geothermometers for these two samples give different temperatures. The Na-K geothermometer gives very high value for both samples. The silica, Na-K-Ca and K/Na geothermometers give similar results with difference 15-28°C for sample 89-76 and 5-

29°C for sample 89-77. According to geothermometers and equilibrium temperature graph, subsurface temperature for sample 89-77 could be 60-65°C but the result is uncertain due to lack of equilibrium (Fig. 21). Sample 89-76 represents non-equilibrium water (Fig. 20) with silica concentration similar to cold water. Temperatures higher than measured should not be expected.

6.3 Discussion

During the interpretation of chemical analysis from Vardar zone and Serbo-macedonian mass many problems have risen. When the geothermometers gave different results it has often been explained by mixing or in some cases that the sample represents non-equilibrium waters. In other cases mineral equilibria was disturbed by degassing followed by precipitation of calcite.

The silica geothermometer is controlled by two minerals, quartz and chalcedony. It seems that quartz equilibrium controls the silica concentration if the water issues through metamorphic rocks but chalcedony equilibrium if the rock is magmatic. A great deal of the waters contain high content of magnesium disturbing chemical geothermometers. In some cases high magnesium can be a result of serpentinization if the water flows through serpentine. In such cases silica concentration can be high and in equilibrium with amorphous silica and the water is often showing non-equilibrium and the result of the chemical geothermometers are taken with mistrust. High magnesium content as well as high content of CO₂ affects Na-K-Ca geothermometer. For this reason this geothermometer was not often taking into consideration. The available data is not sufficient to apply silica mixing models. In a few cases mixing model was used, taking arbitrary selected values for cold water. Therefore the result of the mixing models have to be taken with care.

7. CONCLUSION AND RECOMMENDATIONS

The chemical composition of thermal waters from Vardar zone and Serbo-macedonian mass were interpreted by chemical geothermometers and mineral equilibria to obtain subsurface temperatures. When the chemical geothermometers are applied it is necessary to take into consideration all the available data such as the geology of the fields, present and former processes and conditions. In this report the geology of the fields was used to group the water samples and also to distinguish which minerals were most likely describing equilibrium.

The main results of this report are listed in Table 7 and shown in Figure 22. All the thermal fields are of low-temperature type with reservoir temperature below 150°C. The highest predicted temperature in Serbia (120-140°C) is in the middle and southern part at Sierinska banja, Vranska banja, Bujanovacka banja and Lukovska banja. In Macedonia the highest predicted temperature is in Bansko in the range 115-120°C.

It was not always possible to predict temperature due to inaccurate analysis or lack of mineral equilibrium. In cases where equilibrium was not attained the samples represent mixed water or non-equilibrium waters.

Geochemical survey is a relatively fast and inexpensive investigation method and should be an integral part of all geothermal exploration. The interpretation depends on many different factors and the most important ones are the chemical analysis. Good chemical analysis also depends on the collection and the storage of samples. Some elements change with storage and have to be analysed soon after collection. Table 8 shows analytical methods used by the writer in her training at the UNU. It is recommended that chemical analysis and collection should be revised in order to obtain most reliable analysis.

The interpretation for many samples is that the analysis represent mixture of thermal water and cold water. But the data is not sufficient to apply mixing models. In a few cases mixing model has been used and then the silica content of the cold water has been estimated. For all the fields where there is an indication of mixing further

study is necessary. Then water samples from all thermal springs should be collected and mixing models applied if sufficient indication for mixing are found.

Detailed geochemical study is recommended in all the geothermal fields where utilization on a large scale has started, such as in the Kocani valley, Katlanova area, Smokvica and Negorci in Macedonia. This study can give useful information on flow directions, mixing and upflow zones if the data is interpreted together with all available data.

Changes of chemistry with time can give useful information on cooling and mixing. Changes in the chemical composition of water are often seen before changes in temperature are measured. Therefore chemical monitoring is recommended for the fields where utilization has started. The data obtained in detailed chemical study can be used as a base for monitoring chemical changes.

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TABLE 1. Equations for chemical geothermometers used in the report.
Concentrations in ppm.

$t_{\text{ch}} = 1112/(4.91 \cdot \log \text{H}_4\text{SiO}_4) - 273.15$	(Arnórsson et al. 1983b)
$t_{\text{qz}} = 1309/(5.19 \cdot \log \text{H}_4\text{SiO}_4) - 273.15$	(Fournier, 1977)
$t_{\text{qz-ad}} = 1522/(5.75 \cdot \log \text{H}_4\text{SiO}_4) - 273.15$	(Fournier, 1977)
$t_{\text{am}} = 731/(4.52 \cdot \log \text{H}_4\text{SiO}_4) - 273.15$	(Fournier, 1977)
$t_{\text{Na-K}} = 933/(\log \text{Na}/\text{K} + 0.993) - 273.15$	(Arnórsson et al. 1983b)
$t_{\text{K-Na}} = 1390/(1.75 - \log \text{K}/\text{Na}) - 273.15$	(Giggenbach, 1988)
$t_{\text{Na-Li}} = 1000/(\log \text{Na}/\text{Li} + 0.389) - 273.15$	(Foulliac & Michard, 1981)
$t_{\text{Na-Li}} = 1195/(\log \text{Na}/\text{Li} - 0.13) - 273.15$	(Foulliac & Michard, 1981)
$t_{\text{Na-K-Ca}} = 1647/(\log(\text{Na}/\text{K}) + \beta(\log(\sqrt{\text{Ca}/\text{Na}}) + 2.06) + 2.47) - 273.15$	
concentrations in moles	(Fournier & Truesdell, 1973)
$\beta = 4/3$ for $t < 100^\circ\text{C}$; $1/3$ for $> 100^\circ\text{C}$	
$t_{\text{Na-K-Ca-CO}_2\text{-corr.}} = 1647/(\log(\text{Na}/\text{K}) + \beta(\log(\sqrt{\text{Ca}/\text{Na}}) + 2.06) + 2.47 - I) - 273.15$	
where $I = -1.36 - 0.253 \log P_{\text{CO}_2}$	(Paces, 1975)
$t_{\text{Na-K-Ca-Mg}} = T_{\text{Na-K-Ca}} - \Delta t_{\text{Mg}}$	
For R between 5 and 50	
$\Delta t_{\text{Mg}} = 10.66 - 4.7415R + 325.87(\log R)^2 - 1.032 \cdot 10^5(\log R)^2/T$	
$- 1.968 \cdot 10^7(\log R)^2/T^2 + 1.605 \cdot 10^7(\log R)^3/T^2$	
and for $R < 5$	
$\Delta t_{\text{Mg}} = -1.03 + 59.971 \cdot \log R + 145.05(\log R)^2$	
$- 36711(\log R)^2/T - 1.67 \cdot 10^7 \cdot \log R/T^2$	
where $R = [\text{Mg}/(\text{Mg} + \text{Ca} + \text{K})] * 100$ (in equivalents).	
	(Fournier & Potter 1979)

TABLE 2. Equations describing the temperature dependence of cation/proton ratios and undissociated weak acid concentrations. From Arnórsson et al. 1983a.

$\log \text{H}_4\text{SiO}_4^0$	$= -0.588 - 0.00441 * T - 1515.21/T + 1.3470 * \log T$
$\log \text{H}_2\text{CO}_3^0$	$= -1.794 - 0.00510 * T - 4469.63/T + 4.1414 * \log T$
$\log \text{H}_2\text{S}^0$	$= -1.678 - 0.00355 * T - 5071.05/T + 3.8889 * \log T$
$\log \text{H}_2\text{SO}_4^0$	$= -6.436 - 0.03906 * T - 13335.68/T + 14.7958 * \log T$
$\log \text{HF}^0$	$= -5.262 - 0.03511 * T - 7964.11/T + 12.1022 * \log T$
$\log \text{Na}^+/\text{H}^+$	$= 2.694 + 0.02023 * T + 4243.47/T - 6.2069 * \log T$
$\log \text{K}^+/\text{H}^+$	$= 2.505 + 0.01917 * T + 3325.71/T - 5.7814 * \log T$
$\log \sqrt{\text{Ca}}^{+2}/\text{H}^+$	$= 1.733 + 0.01117 * T + 3890.51/T - 3.9977 * \log T$
$\log \sqrt{\text{Mg}}^{+2}/\text{H}^+$	$= 1.816 + 0.01078 * T + 3727.48/T - 4.1640 * \log T$

TABLE 3. Chemical indicators of underground temperature in hot water system

Indicator	Comments
1. SiO_2	Best of indicators; assumes quartz equilibrium at high temperature, with no dilution or precipitation after cooling.
2. Na/K	Generally significant for ratios between 20/1 to 8/1 and for some systems outside these limits.
3. Ca and HCO_3 contents	Qualitatively useful for near neutral waters; solubility of calcium carbonate inversely related to underground temperature.
4. Mg ; Mg/Ca	Low values indicate high underground temperature.
5. Cl dilution	Assumes dilution of lower Cl springs by cold water, permitting calculation of underground temperatures from required mixing ratios with highest Cl waters.
6. Na/Ca	High ratios may indicate high temperatures.
7. $\text{Cl}/\text{HCO}_3 + \text{CO}_3$	Highest ratios in related waters indicate highest underground temperatures.
8. Cl/F	High ratios may indicate high temperatures but Ca content (as controlled by pH and CO_3 contents) prevents quantitative application.
9. Silica sinter deposits	Reliable indicator of underground temperatures (now or formerly) 180 °C.
10. Travertine deposits	Strong indication of low underground temperatures unless bicarbonate water have contacted limestone after cooling.

Table 4. List of samples from Yugoslavia taken into consideration in the report.

SERBIA	Tertiary sediments	
101	10-89-01 Svrackovci,	s, VZ
102	74-89-28 Mlakovac,	s, VZ
103	68-89-27 Gorna Trepca,	s, VZ
104	78-89-30 Ovcar banja,	w, VZ
105	110-89-46 Vrnici (Vrnacka banja),	w, VZ
106	116-89-49 Mataruska banja	w, VZ
	Tertiary sediments, basement carbonates or metamorphic rocks.	
121	30-89-14 Dublje,	w, VZ
122	32-89-16 Bogatic,	w, VZ
123	34-89-18 Salters,	w, VZ
124	33-89-17 Smederevska palanka,	w, SMM
125	109-89-45 Bujanovac, Heba,	w, SMM
	Flysch sediments	
141	35-89-19 Ljig,	w, VZ
142	36-89-20 Vrujci,	w, VZ
143	19-89-09 Ribarska banja,	w, SMM
	Magmatic environment	
161	95-89-38 Bukovacka banja,	w, VZ
162	97-89-40 Metkovic,	w, VZ
163	28-89-13 Vranjska banja,	w, SMM
164	108-89-44 Sierinska banja,	w, SMM
	Metamorphic environment	
181	20-89-10 Slanaca,	s, VZ
182	21-89-11 Josanicka banja,	s, VZ
183	22-89-12 Josanicka banja,	w, VZ
184	99-89-42 Tulare,	w, SMM
185	84-89-34 Suva cesma,	s, SMM
186	85-89-35 Vica,	s, SMM
187	98-89-41 Cibutkovica,	w, VZ
188	75-89-29 Grocka,	w, VZ
189	12-89-02 Prolom banja,	w, SMM
190	83-89-33 Lukovska banja,	w, VZ
191	112-89-47 Kursumliska banja,	w, VZ
192	115-89-48 Avala,	w, VZ
MACEDONIA	Tertiary sediments, basement metamorphic rocks	
201	89-59 Volkovo, D/75	w, VZ
202	89-60 Volkovo, GTD 1/86	w, VZ
203	89-61 Proevci, Kumanovo,	s, VZ
204	89-62 Sabota voda,	w, VZ
205	89-65 Podlog,	w, SMM
206	89-66 Banja, Kocani,	w, SMM
207	89-67 Istibanja,	w, SMM
208	89-68 Rakles,	w, SMM
209	89-69 Bansko,	w, SMM
	Metamorphic environment	
221	89-55 Katlanovo, B-1	w, VZ
222	89-56 Katlanovo, Nervna voda	s, VZ
223	89-57 Katlanovo, D 1/78	w, VZ
224	89-58 Katlanovo, Fontana	s, VZ
	Magmatic environment	
241	89-63 Ldzi,	s, VZ
242	89-64 Kezovica,	w, VZ
143	89-70 Smokvica, SIED 7,	w, VZ
244	89-71 Negorska banja, NB-3	w, VZ
245	89-72 Negorska banja, NB-4	w, VZ
246	89-73 Gornicet,	s, VZ
247	89-76 Zletovo,	w, VZ
248	89-77 Kratovo,	w, VZ

s - spring
w - borhole
VZ - Vardar zone tectonic unit
SMM - Serbo-macedonian tectonic unit

Table 5. Chemical composition of water samples from Vardar zone and Serbo-macedonian mass, Yugoslavia.

Sample	°C	l/sec	pH/°C	SiO ₂	Li	Na	K	Ca	Mg	CO ₂	SO ₄	H ₂ S	Cl	F	Dis.solid	OHMM.
10-89-1	28.0	1.0	9.48/22.	30.0	.10	35.0	.3	4.0	1.00	103.0	6.0		7.0	2.5	138.0	275.00
12-89-2	30.0	6.0	9.00/20.	40.0	.01	49.4	.2	3.5		88.0	5.0		7.1	.2	2000.0	
19-89-09	51.3	12.0	9.18/22.	107.0	.05	84.2	1.8	5.8	.20	117.5	59.0	2.0	66.0	2.0	330.0	600.00
20-89-10	37.0	1.0	9.44/22.	97.0	.20	81.0	2.0	5.4	2.91	93.0	26.0	1.4	24.0	5.4	250.0	500.00
21-89-11	78.0	18.0	9.41/22.	132.0	.18	70.0	2.1	3.0	.10	128.5	27.4	.7	22.3	4.6	214.0	575.00
22-89-12	63.0	5.0	9.44/22.	125.0	.10	61.6	1.6	4.0	8.02	132.4	10.8	1.4	17.7	3.9	197.5	340.00
28-89-13	94.0	2.0	7.40/22.	129.0	.21	266.0	13.8	20.0	3.40	324.0	235.0	.4	46.0	8.2	740.0	*****
30-89-14	50.0	15.0	7.00/22.	34.0	.14	174.0	11.5	30.0	11.00	505.0	2.5	.2	55.0	2.6	568.0	*****
32-89-16	75.0	38.0	7.09/22.	64.0	.15	150.0	10.6	37.0	10.20	354.0	3.0	1.3	105.0	1.5	641.0	*****
33-89-17	48.0	12.0	7.20/22.	37.4	1.42	2000.0	107.3	6.0	19.60	4177.0	10.6	.3	452.3	8.1	5341.0	*****
34-89-18	50.0	12.0	7.17/22.	28.7	1.54	2100.0	43.8	13.2	20.10	2446.0			1971.0	2.7	5106.0	*****
35-89-19	32.0	5.0	7.28/22.	25.0	.83	261.0	8.5	22.4	21.80	681.0	2.2	.0	37.6	2.2	761.0	*****
36-89-20	26.0	200.0	7.36/22.	17.3	.06	16.0	1.7	39.3	17.90	178.2	.9	.1	14.2	.4	211.0	580.00
68-89-27	31.0	20.0	7.75/22.	18.8	.01	5.6	1.8	39.7	58.40	1175.0	4.8		10.6	.2	322.0	630.00
74-89-28	28.0	4.0	7.50/22.	24.6	.07	24.7	5.7	57.9	44.60	348.0	17.5		16.5	.6	402.0	730.00
75-89-29	19.0	.1	7.11/19.	65.0	1.20	3970.0	37.7	22.8	5.90	4027.0	363.0	8.5	3190.0	5.2	10120.0	*****
78-89-30	39.0	50.0	7.00/22.	22.0	.08	20.0	3.5	98.0	40.00	339.0	18.0		14.0	.8		
83-89-33	63.0	20.0	6.70/22.	50.0	1.10	355.0	19.0	105.0	18.05	793.4	117.0		85.0			
84-89-34	22.0	25.0	6.66/22.	106.0	1.30	958.0	34.0	10.6	27.40	2753.0	52.3	4.4	124.8	7.0	2727.0	*****
85-89-35	21.4	5.0	7.04/22.	76.5	.72	947.0	34.0	16.2	13.20	2698.0	3.1	.0	123.4	15.6	2650.0	*****
95-89-38	31.0	10.0	6.56/22.	94.3	4.47	925.0	67.0	18.8	13.00	3538.0	1.7	.7	24.1	4.6	2704.0	*****
97-89-40	55.4	13.0	7.09/20.	31.0	.35	268.0	16.8	27.9	8.51	611.0		.0	141.8	2.4	1082.0	*****
98-89-41	20.8	5.0	6.29/20.	69.0	2.40	442.0	81.2	32.3	70.30	2798.0	2.9	.2	22.3	.8	1756.0	*****
99-89-42	17.0	5.0	6.55/17.	78.0	2.00	1263.0	48.3	21.8	40.00	3401.0	261.0		254.0	3.6		
108-89-44	68.0	15.0	7.17/22.	137.0	1.18	1210.0	66.7	9.8	19.40	2852.0	44.4	.5	99.9	2.5	2907.0	*****
109-89-45	45.3	10.0	6.65/20.	130.0	.92	1158.8	60.0	9.0	12.70	3186.0	90.0		61.0	6.0	3019.0	*****
110-89-46	35.0	6.0	6.29/22.	124.0	1.03	490.0	74.8	70.5	66.70	3160.0		.4	42.5	1.9	1792.0	
112-89-47	65.0	20.0	8.12/22.	80.0	2.75	713.0	46.0	30.0	33.00	1669.8	20.0		35.5	3.7	1680.0	
115-89-48	26.0	70.0	8.50/20.	22.0	.07	50.0	3.4	20.0	27.20	193.4	18.0		35.5	.3		
116-89-49	43.0	34.0	7.50/20.	70.0	1.45	240.0	13.7	42.0	54.90	624.6	43.0		71.0	5.6	1400.0	
000-89-55	26.0	.2	6.29/18.	70.6		378.0	52.8	343.6	59.20	2401.8	.1	.1	166.8	2.9		
000-89-56	23.0	.2	6.16/19.	50.2		257.4	34.2	501.0	72.30	2619.4	36.0		106.5	1.8		
000-89-57	53.0	7.0	6.37/22.	53.2		375.2	45.1	268.5	47.00	1631.8	12.3	1.0	177.5	3.2		
000-89-58	35.5	.2	6.06/22.	53.2	.70	358.4	46.6	239.5	54.00	2156.0	4.1	.5	156.2	3.3		
000-89-59	24.0	7.5	6.56/24.	61.1	.13	277.0	7.5	472.0	221.00	2776.0	350.0	.2	183.9	.2		
000-89-60	25.0	36.0	6.95/22.	50.0		201.3	16.6	342.1	186.30	2156.0	201.0		191.0		2989.0	
000-89-61	31.0	2.0	6.60/25.	23.4		287.0	21.7	276.1	61.40	2068.8	27.5	.6	46.2	.8		
000-89-62	20.0	1.0	7.20/19.	36.4		397.7	14.0	529.6	40.10	390.7	37.7	.2	440.1	1.0		
000-89-63	56.0	1.5	7.75/19.	92.7		509.9	19.6	36.0	2.70	125.3	166.9	.1	480.0	16.4		
000-89-64	63.0	3.0	7.41/19.	92.4		507.1	19.6	37.2	1.48	140.6	161.1	.1	479.2	16.4		
000-89-65	78.0	100.0	6.85/19.	48.2	.18	189.4	16.3	100.2	15.80	444.3	50.0	.1	21.2	1.3	569.0	
000-89-66	42.4	6.0	7.40/25.	72.0	2.40	118.0	11.0	43.0	28.90	402.3	49.6	.1	14.7	.9	649.0	
000-89-67	67.5	20.0	6.98/19.	82.2	.45	756.1	51.3	229.1	9.40	1281.5	101.3	.1	60.3	5.7	1757.0	
000-89-68	26.5	.5	7.40/25.	15.0		28.0	2.4	26.4	80.00	313.3	18.4		15.9	.1		
000-89-69	68.0	55.0	7.30/20.	68.0		210.0	8.5	74.8	2.60	105.7	491.0	.1	20.5	5.9		
000-89-70	54.0	35.0	7.53/19.	43.3		273.5	5.1	141.0	1.26	73.8	597.7	.1	92.3	1.4		
000-89-71	47.4	7.0	8.50/19.	50.9		189.4	3.9	32.3	.34	29.4	213.6	.1	106.5	3.7		
000-89-72	52.7	4.5	8.74/19.	92.7		217.4	4.0	34.3	.12	24.2	237.0	.1	113.6	4.3		
000-89-73	23.8	.5	6.34/19.	131.3		284.8	32.6	202.0	345.00	3094.0	29.5	.1	44.4	.1		
000-89-76	29.0	.5	4.00/25.	24.0		85.0	11.0	130.3	27.20	221.0	389.5		5.5	1.6	801.0	
000-89-77	31.0	2.0	6.30/22.	40.0		184.0	25.4	450.0	23.80	800.5	848.5	53.7			2330.0	

Table 6. Results of chemical geothermometers for thermal water from Vardar zone and Serbo-macedonian mass, Yugoslavia.

Sample	l/s	Tme	T ch	T qz	T qz adiab.	T am	T NaK	T NaKCa	T CO ₂	corr.	T NaKCaMg	Na/Li	K/Na	K/Mg
							4/3	1/3	4/3	1/3	4/3	(1)	(2)	
10-89-1	1	28	40	68	73	0	32	20	69		68	222	91	20
12-89-2	6	30	59	88	90	0	2	15	51			62	62	
19-89-09	12	51	104	133	129	13	77	68	109		3	113	133	72
20-89-10	1	37	93	122	120	3	86	72	114		58	44	61	209
21-89-11	18	78	111	139	134	19	98	85	124		85	124	63	213
22-89-12	5	63	107	135	131	15	89	69	115			41	176	144
28-89-13	2	94	124	152	145	30	136	125	155	55	75	104	106	13
30-89-14	15	50	56	85	88	0	156	102	156	31	66	63	56	14
32-89-16	38	75	85	114	113	0	162	92	155	28	69	78	69	22
33-89-17	12	48	60	89	91	0	139	359	203	161	81	108	56	10
34-89-18	12	50	49	78	81	0	76	239	147	105	53	36	31	11
35-89-19	5	32	43	72	76	0	103	103	132	33	53	MIXED WATER	?	73
36-89-20	200	26	30	58	64	0	201	18	139		68	82	247	237
68-89-27	20	31	32	61	67	0	355	12	176		84	46	183	347
74-89-28	4	28	43	71	76	0	299	45	181	0	94	67	221	309
75-89-29	0	19	86	114	113	0	36	219	118	90	32	115	98	79
78-89-30	50	39	39	67	72	0	260	23	159		71	86	254	281
83-89-33	20	63	73	102	103	0	139	98	147	23	54	96	92	72
84-89-34	25	22	112	140	135	20	109	215	162	82	53	MIXED WATER	?	34
85-89-35	5	21	94	123	120	4	110	197	159	78	57	45	44	12
95-89-38	10	31	106	134	130	14	164	233	195	88	68	79	71	97
97-89-40	13	55	52	81	84	0	152	124	161	46	70	72	70	32
98-89-41	5	21	89	117	116	0	267	207	232	73	86	MIXED WATER	?	104
99-89-42	5	17	95	124	121	5	114	212	164	79	53	MIXED WATER	?	40
108-89-44	15	68	128	155	148	33	141	271	190	120	76	54	39	21
109-89-45	10	45	125	152	145	31	136	266	187	107	66	71	54	13
110-89-46	6	35	122	150	143	28	243	175	213	55	76	MIXED WATER	?	53
112-89-47	20	65	96	124	122	6	154	186	179			MIXED WATER	?	84
115-89-48	70	26	37	66	71	0	159	57	141			35	166	203
116-89-49	34	43	90	118	116	0	144	104	152	38	70	MIXED WATER	?	110
000-89-55	0	26	90	119	117	1	232	108	187	20	65	93	97	
000-89-56	0	23	73	102	103	0	226	79	174	1	56	79	103	
000-89-57	7	53	76	105	105	0	215	108	181	22	65	93	95	
000-89-58	0	36	76	105	105	0	223	111	186	21	62	80	81	50
000-89-59	8	24	83	111	111	0	91	37	105		19		100	146
000-89-60	36	25	73	102	103	0	176	62	150		52		217	46
000-89-61	2	31	41	69	74	0	168	78	153	4	49	78	75	
000-89-62	1	20	59	88	90	0	108	55	119	4	49		161	58
000-89-63	2	56	104	133	129	13	114	132	146	75	84	132	140	
000-89-64	3	63	104	133	129	13	115	131	146	67	77	131	144	
000-89-65	100	78	71	100	101	0	180	86	161	21	69	86	98	20
000-89-66	6	42	91	119	118	1	188	87	164	27	79	42	28	207
000-89-67	20	68	98	126	124	7	159	126	165	42	66	126	163	4
000-89-68	1	27	25	53	60	0	180	37	141		65		220	18
000-89-69	55	68	88	117	115	0	118	73	130	24	66	73	130	
000-89-70	35	54	66	95	97	0	70	48	98	11	50		126	74
000-89-71	7	47	73	101	102	0	75	65	107				131	84
000-89-72	5	53	102	130	127	11	69	66	104				126	98
000-89-73	1	24	125	153	146	31	209	99	176	14	58	MIXED WATER	?	243
000-89-76	1	29	42	70	75	0	223	60	165		63		254	57
000-89-77	2	31	63	92	94	0	230	68	171	1	64		259	78

TABLE 7. Predicted temperature for water samples from Vardar zone and Serbo-macedonian mass in Yugoslavia.

SAMPLE	LOCATION	RANGE OF TEMP., °C	REMARK
101	10-89-01	30 - 40 (60-65)	
102	74-89-29	slightly higher than Tmeas.	
103	68-89-27	slightly higher than Tmeas.	
104	78-89-30	slightly higher than Tmeas.	
105	110-89-46	ca. 100	
106	116-89-49	ca. 100	
121	30-89-14	60 - 70	
122	32-89-16	90 - 100	
123	34-89-18	70 - 75	
124	33-89-17	80 - 90	
125	109-89-45	125 - 135	
141	35-89-19	40 - 100	
142	36-89-20	?	
143	19-89-09	near 100	
161	95-89-38	near 100	
162	97-89-40	slightly higher than Tmeas.	
163	28-89-13	120 - 130	
164	108-89-44	120 - 130	
181	20-89-10	100 - 110	
182	21-89-11	100 - 110	
183	22-89-12	100 - 110	
184	99-89-42	85 - 100	in doubt
185	84-89-34	100 - 110	in doubt
186	85-89-35	110	in doubt
187	98-89-41	90	
188	75-89-29	110 - 110	in doupt
189	12-89-02	60 - 85	
190	83-89-33	near 130	
191	112-89-47	about 120	mixing?
192	115-89-48	slightly higher than Tmeas	
201	89-59	80 - 90	
202	89-60	80 - 90	
203	89-61	?	non-equil.
204	89-62	80 - 100	
205	89-65	100	
206	89-66	100	
207	89-67	100	
208	89-68	slightly higher than Tmeas.	
209	89-69	115 - 120	
221	89-55	80 - 115	
222	89-56	80 - 115	
223	89-57	80 - 115	
224	89-58	80 - 115	
241	89-63	100 - 115	
242	89-64	100 - 115	
243	89-70	70	
244	89-71	75 - 100	
245	89-72	75 - 100	
246	89-73	?	non-equil.
247	89-76	?	non-equil.
248	89-77	?	non-equil.

TABLE 8. Analytical methods used in the UNU training.

ELEMENT	ANALYTICAL METHOD
pH	pH meter after storage in gas sampling bulb. Analysed within 24 hours from collection.
SiO ₂	Spectrophotometric, yellow silico-molybdic acid
Na	Atomic absorption spectrophotometry
K	Atomic absorption spectrophotometry
Ca	Atomic absorption spectrophotometry
Mg	Atomic absorption spectrophotometry
total CO ₂	Titration with 0.1 N HCl using pH-meter. Analysed within 24 hours from collection.
SO ₄	Titration with BaClO ₄ using thorin as indicator.
total H ₂ S	Ion chromatograph
	Titration with Hg(CH ₃ COO) ₂ using dithizone as indicator. Analysed within 24 hours from collection.
Cl	Mohr titration
	Ion chromatograph
F	Ion sensitive electrode

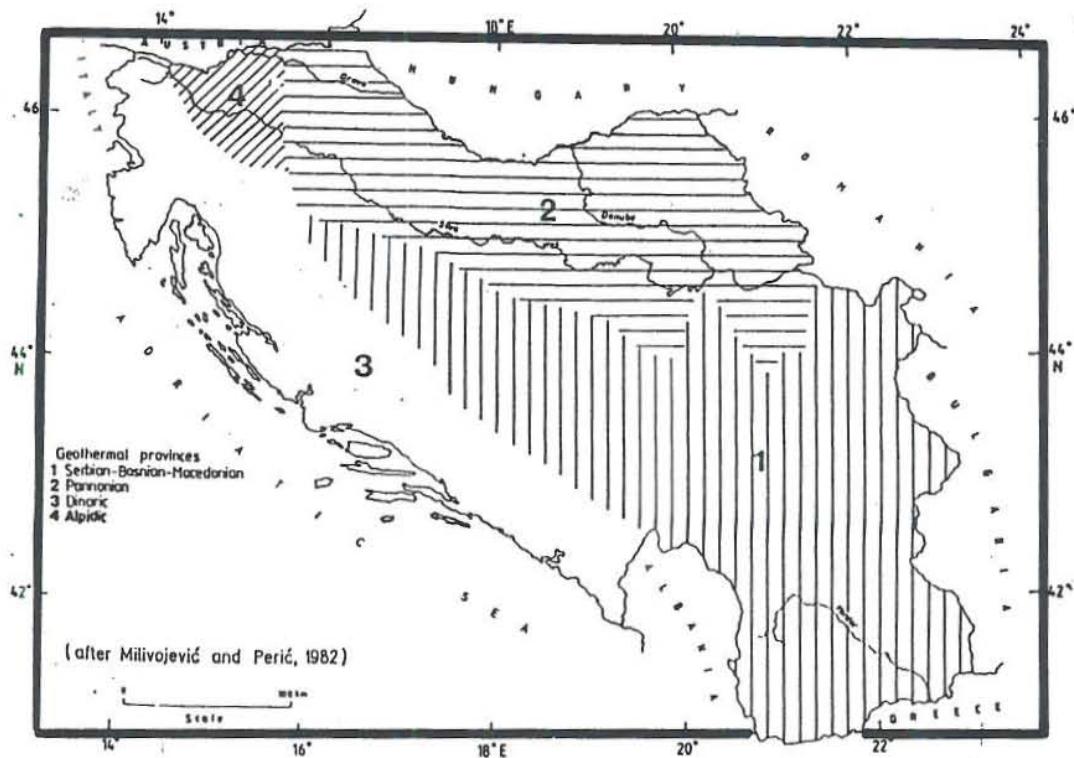


Figure 1. Geothermal provinces in Yugoslavia

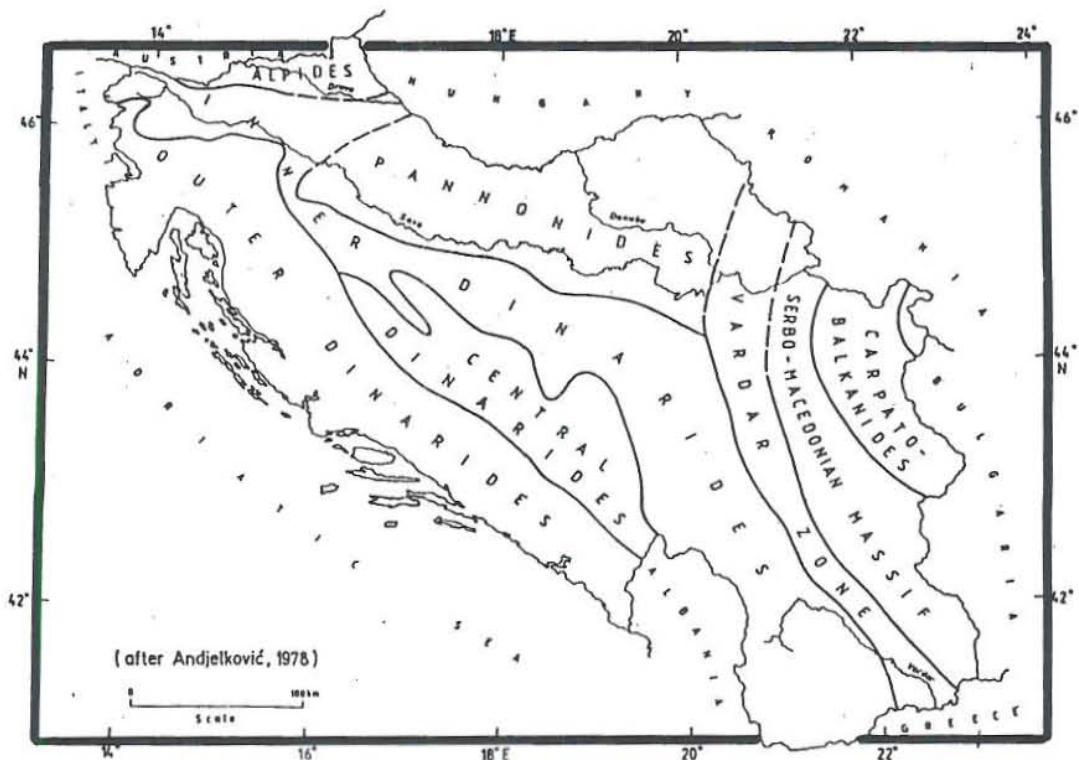


Figure 2. General tectonic setting of Yugoslavia

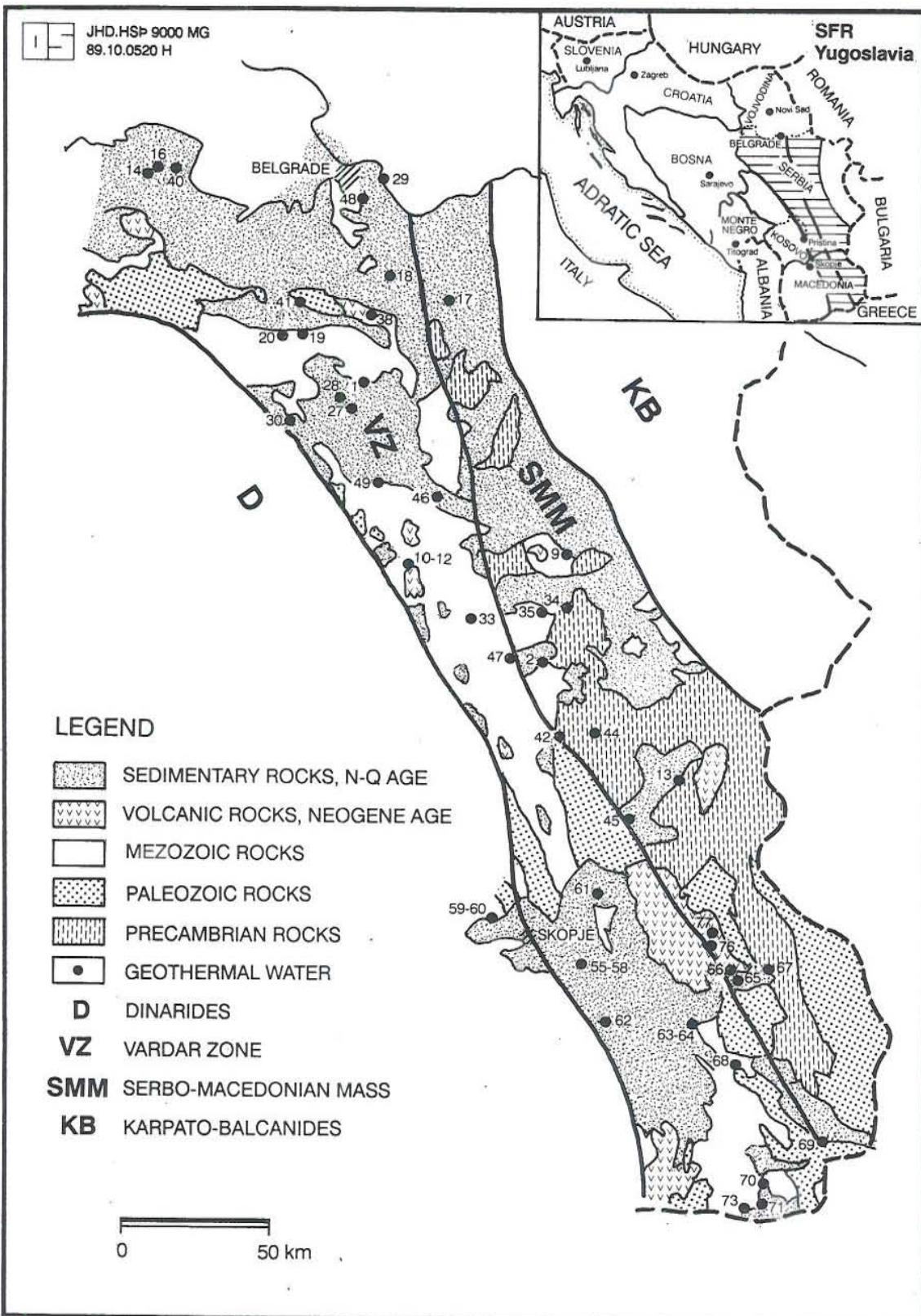


Figure 3. Geological map with main thermal waters in Vardar zone and Serbo-macedonian mass, Yugoslavia

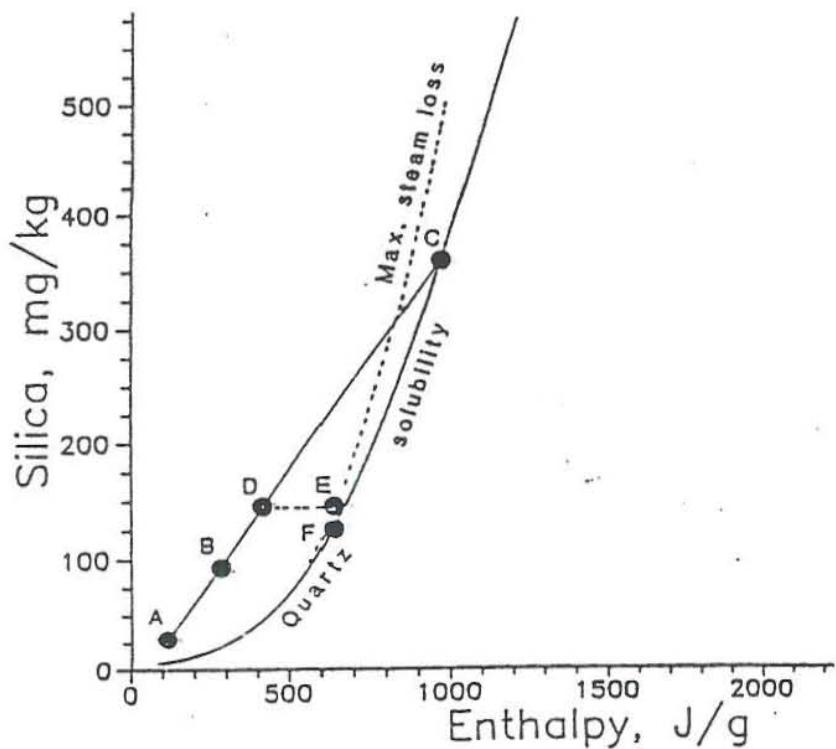


Figure 4. Enthalpy - silica graph illustrating use in calculating silica mixing model temperatures

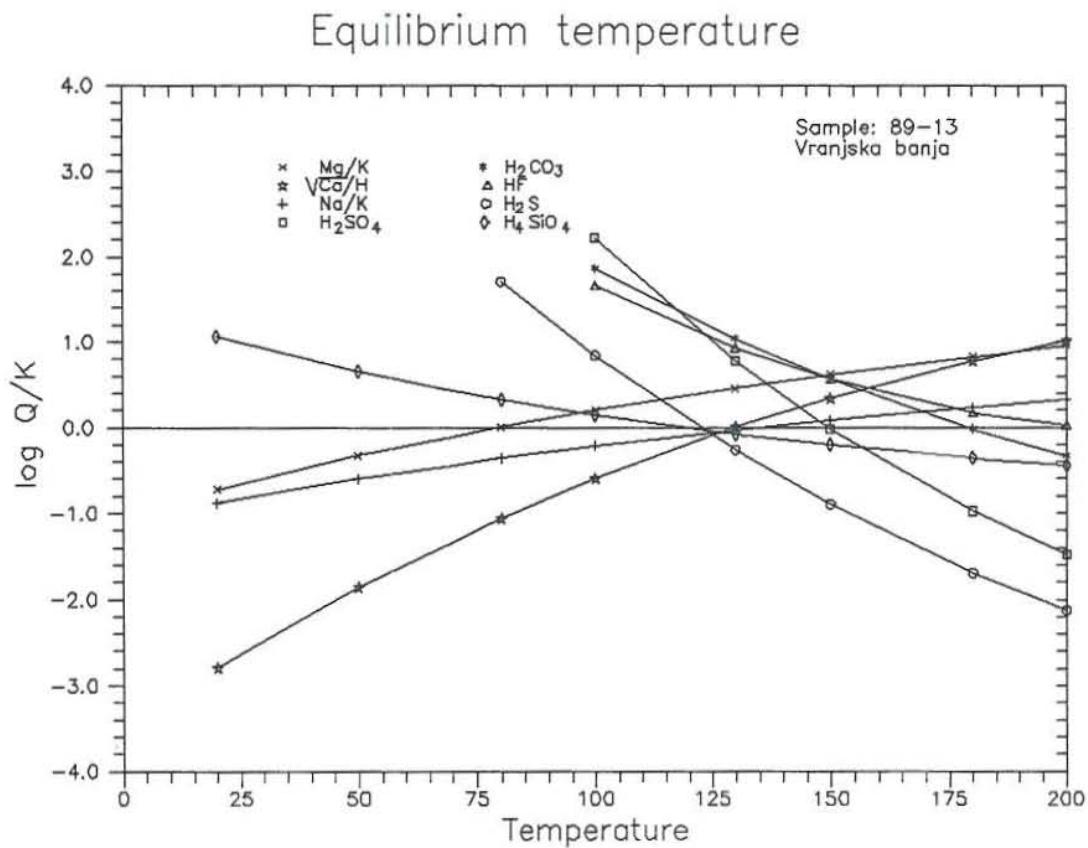


Figure 5. Equilibrium temperature graph for sample 89-13, Vranksa banja

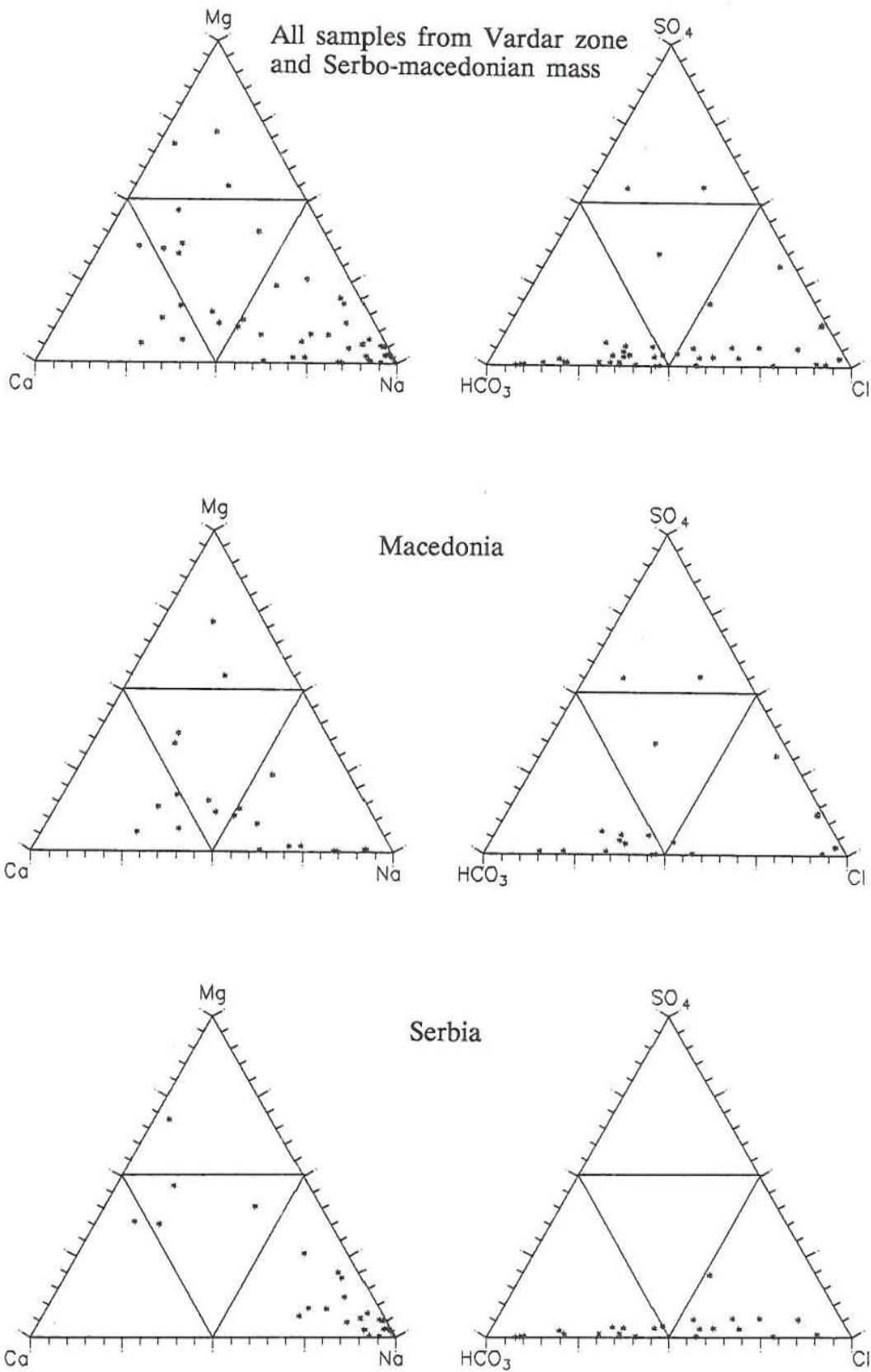


Figure 6. Triangle diagrams for thermal waters from Vardar zone and Serbo-macedonian mass in Yugoslavia

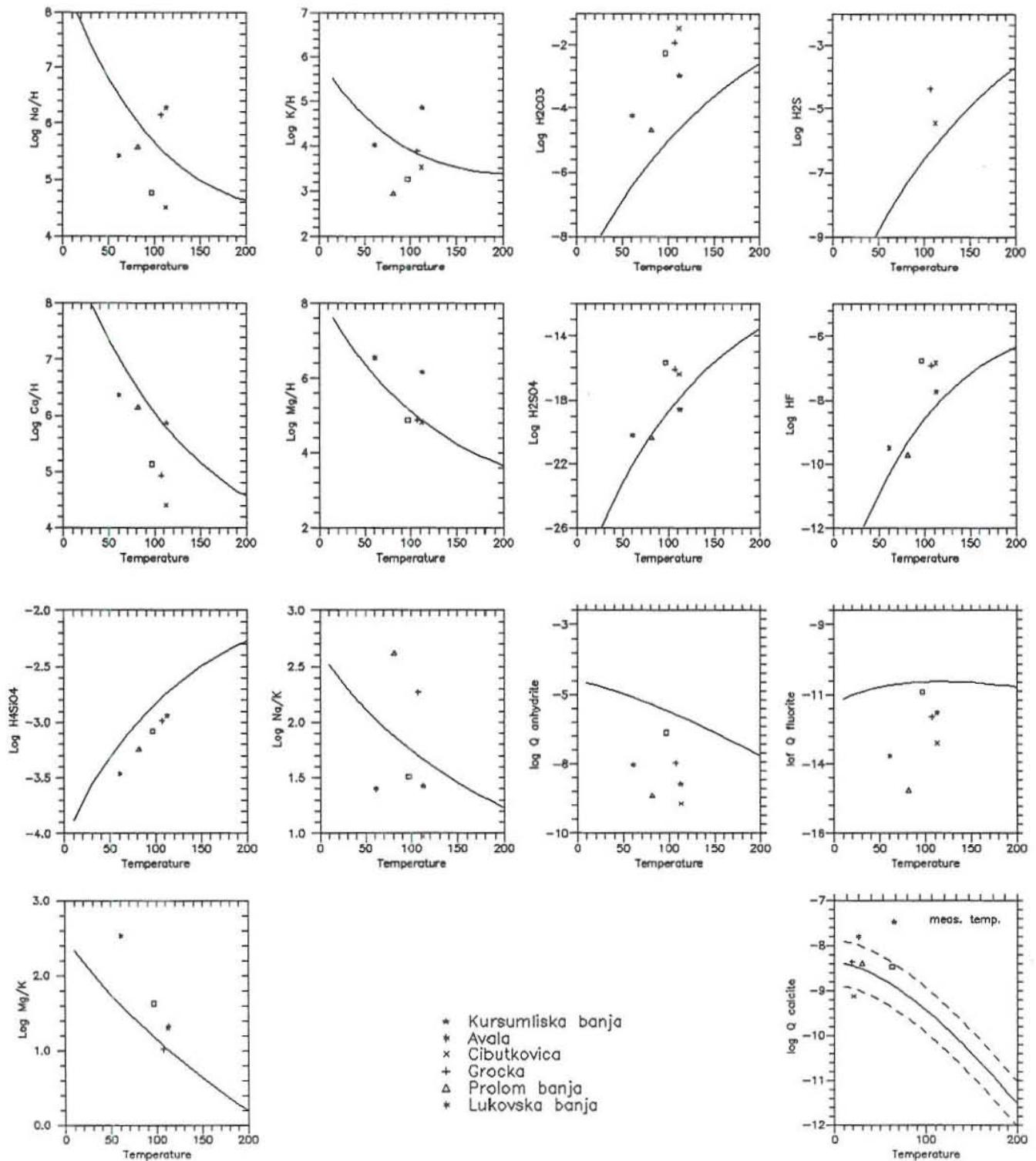


Figure 7a. Equilibrium state for water samples from metamorphic environment in Serbia at quartz geothermometer temperature

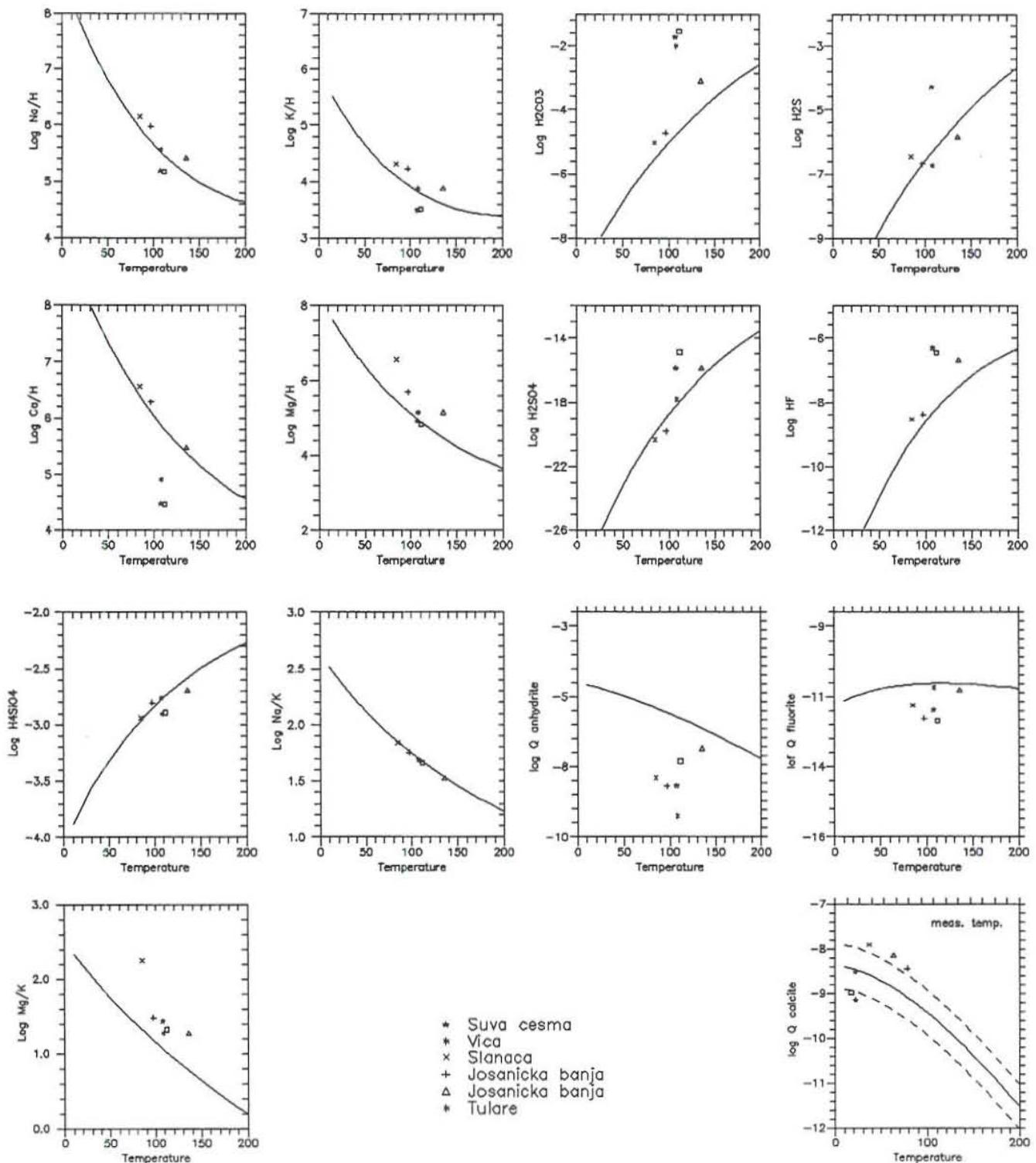


Figure 7b. Equilibrium state for water samples from metamorphic environment in Serbia at chalcedony geothermometer temperature

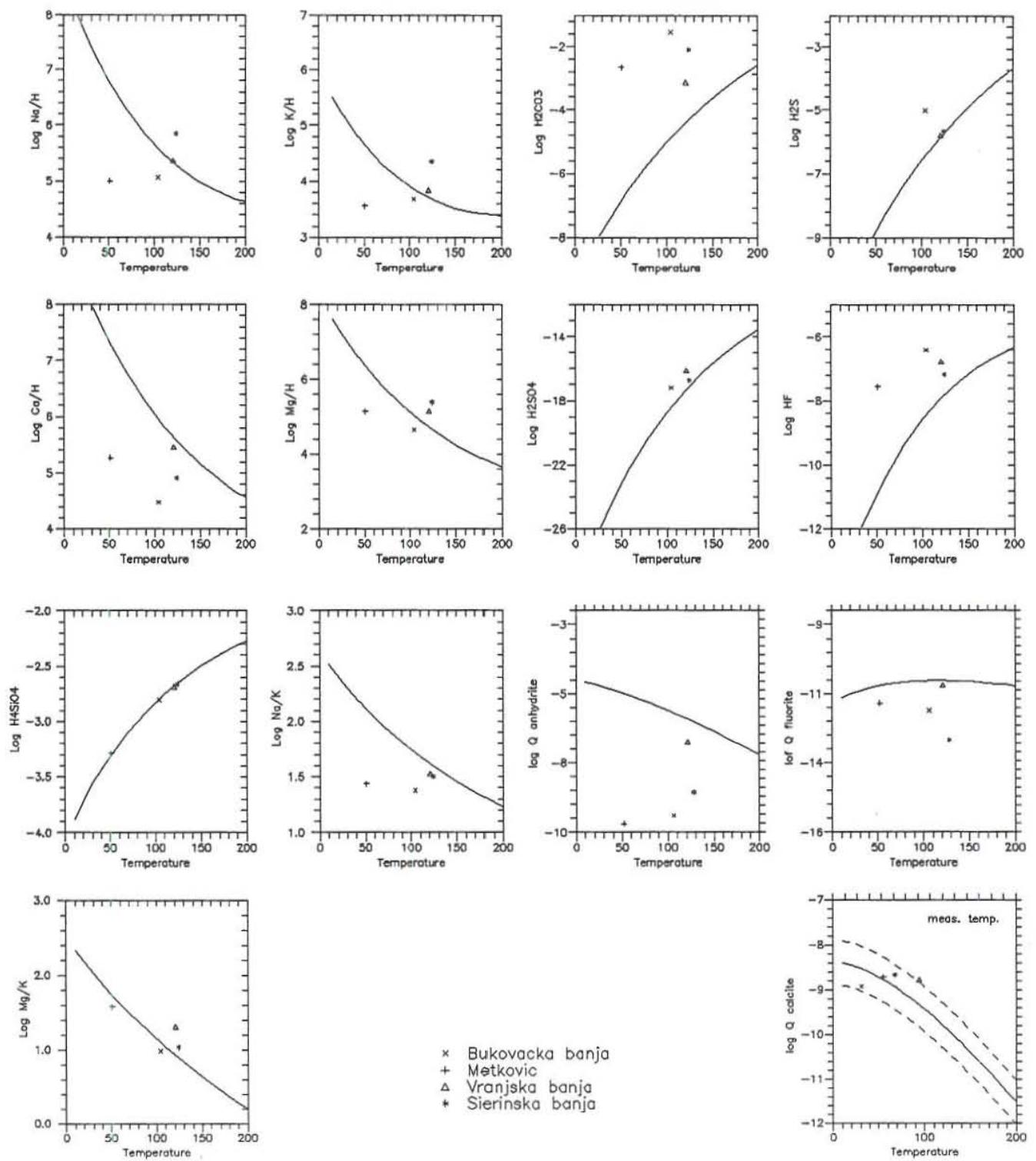


Figure 8. Equilibrium state for water samples from magmatic environment in Serbia at chalcedony geothermometer temperature

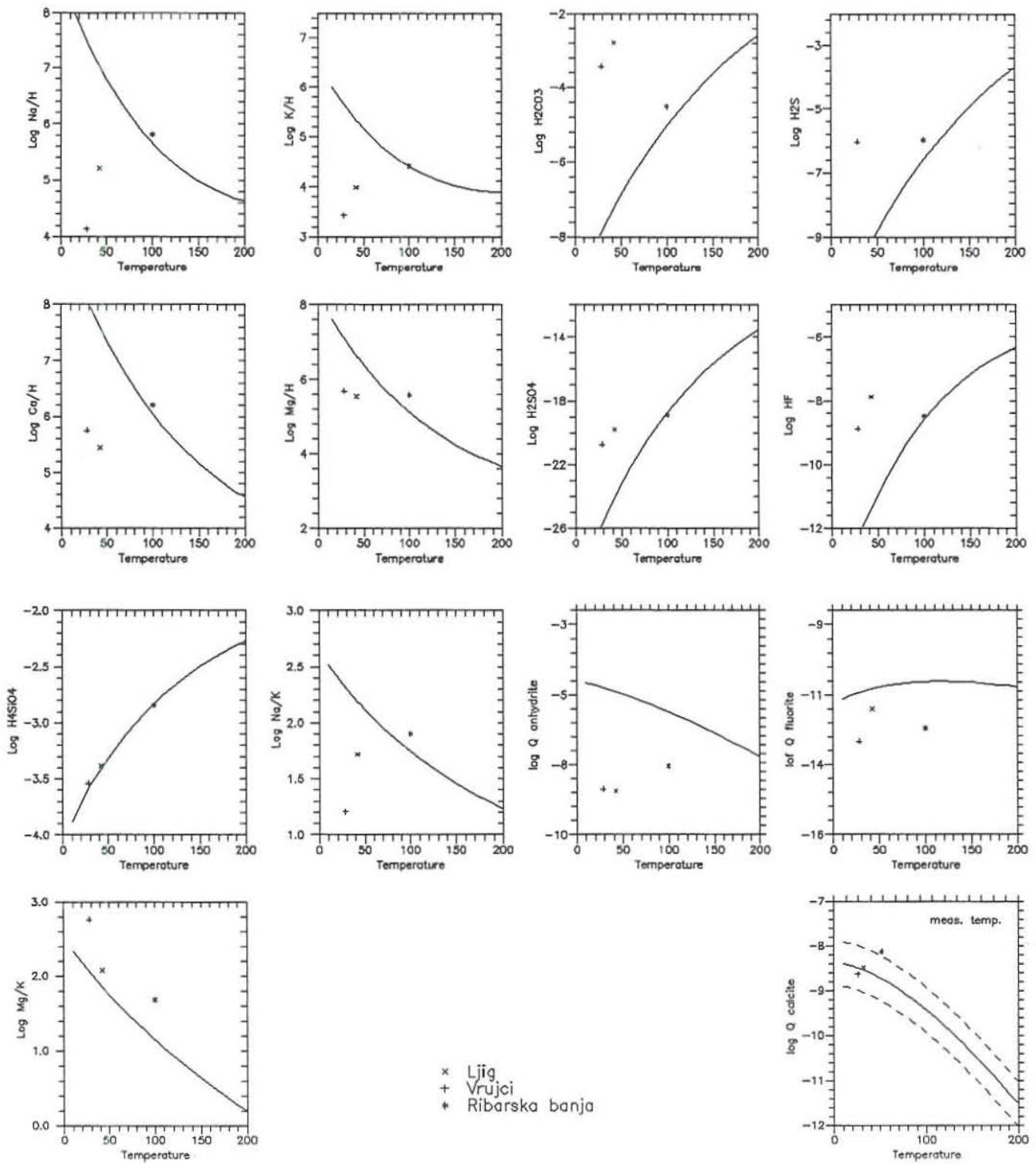


Figure 9. Equilibrium state for water samples from flysch sediments in Serbia at chalcedony geothermometer temperature

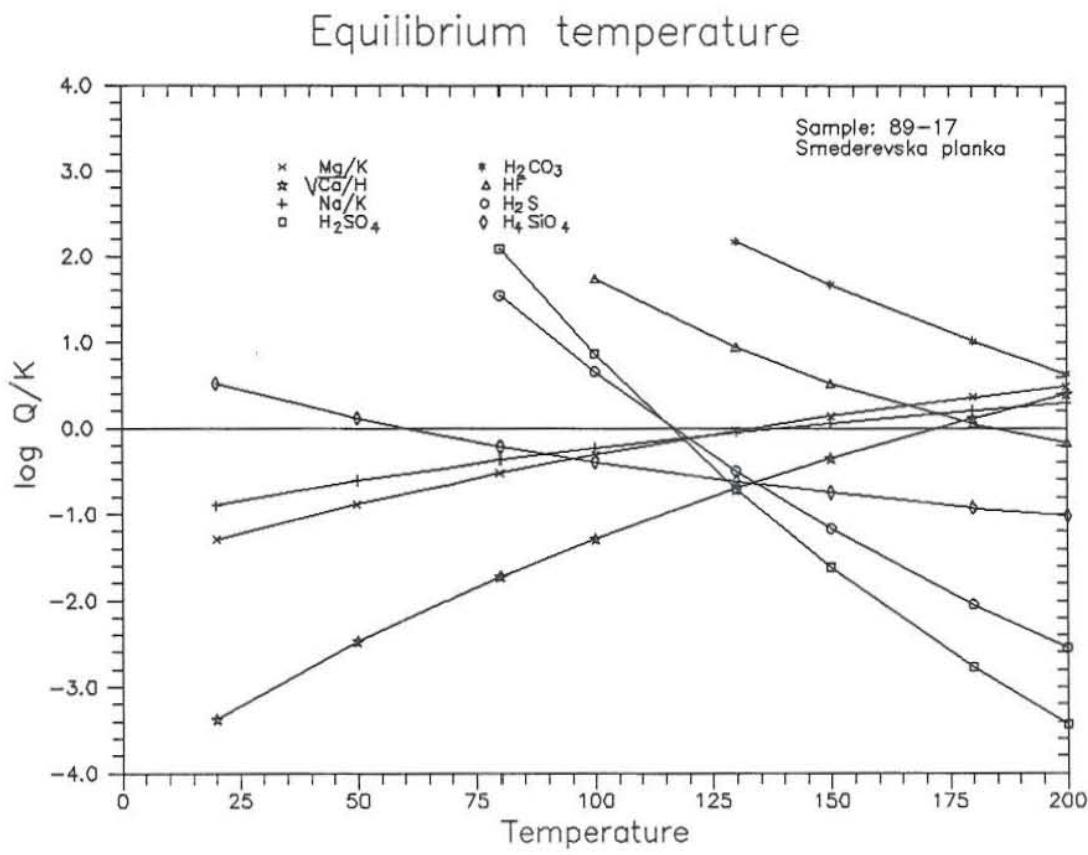


Figure 10. Equilibrium temperature graph for sample 89-17, Smederevska Palanka

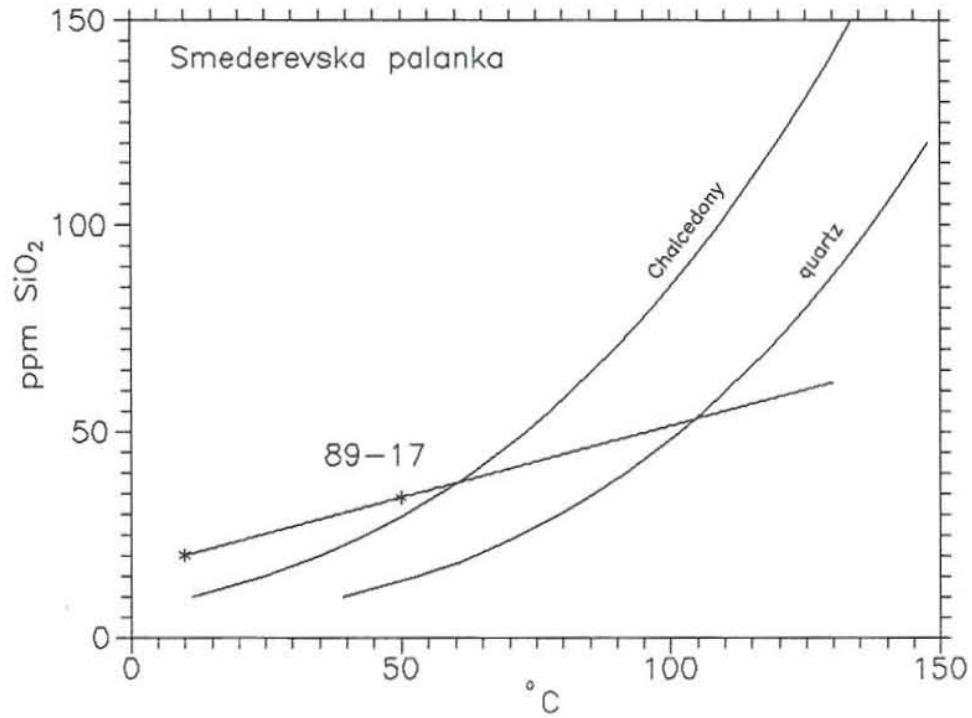


Figure 11. Enthalpy - silica mixing model for sample 89-17, Smederevska Palanka

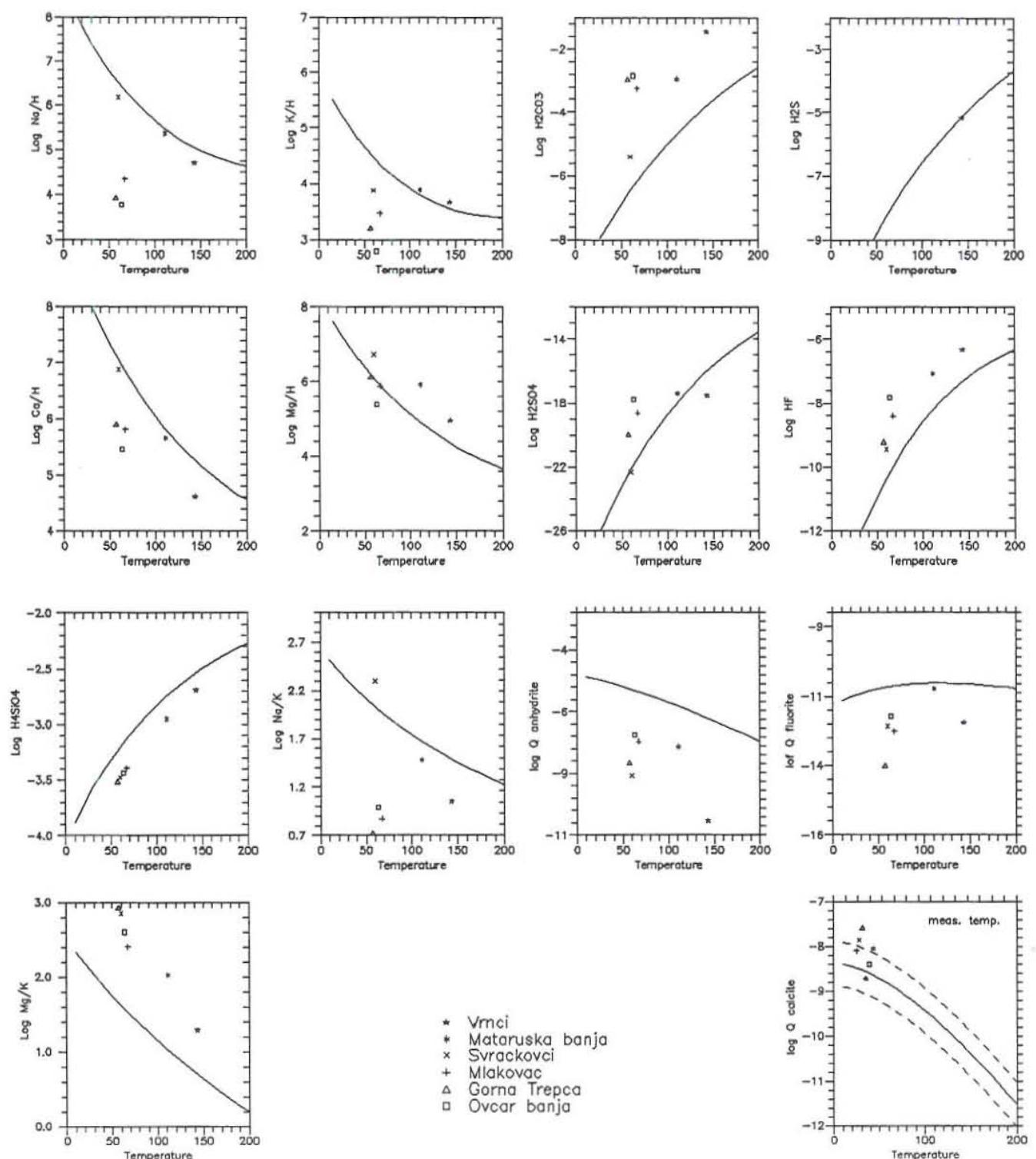


Figure 12a. Equilibrium state for water samples from Tertiary sediments in Serbia at chalcedony geothermometer temperature

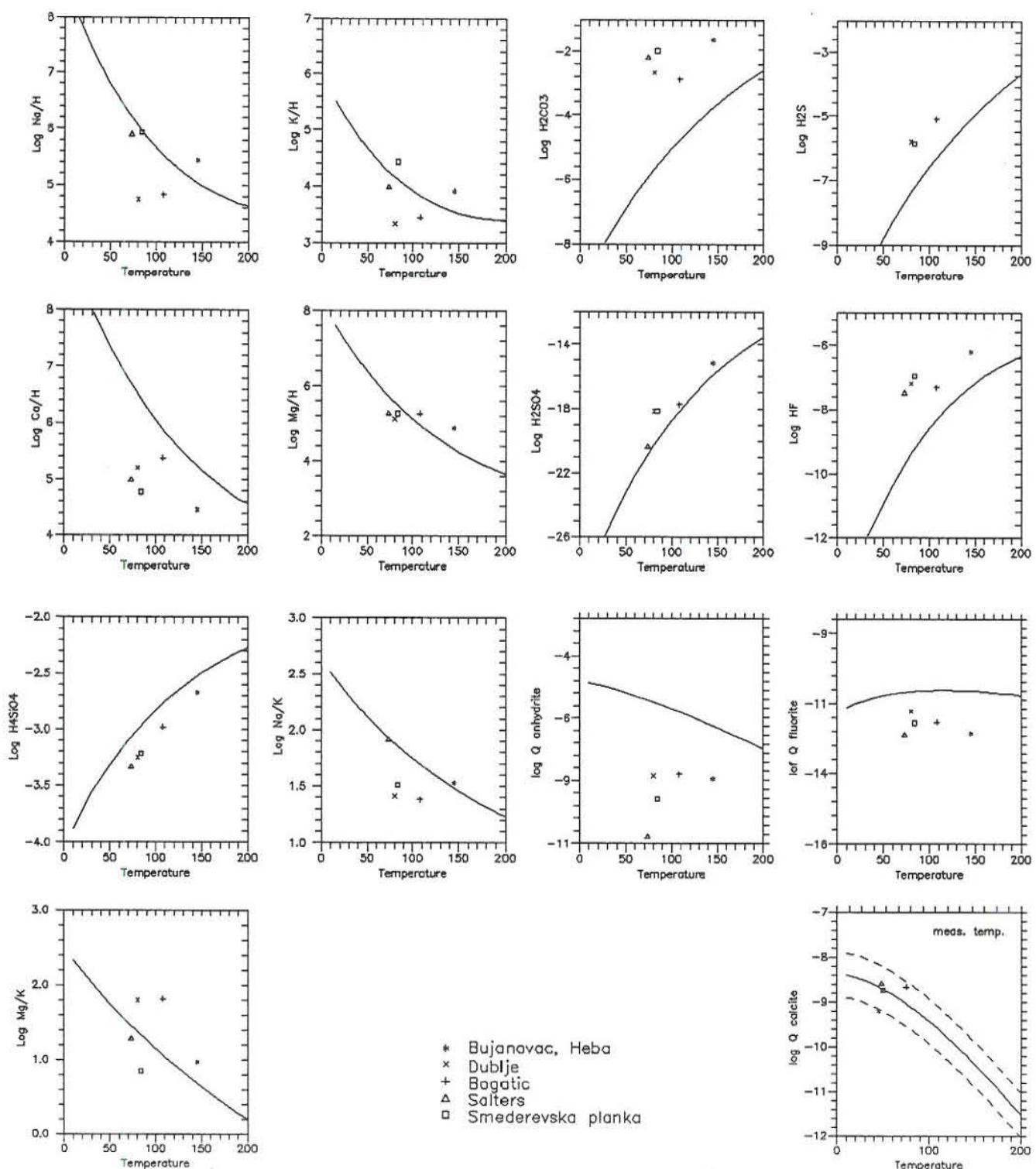


Figure 12b. Equilibrium state for water samples from Tertiary sediments in Serbia at chalcedony geothermometer temperature

Equilibrium temperature

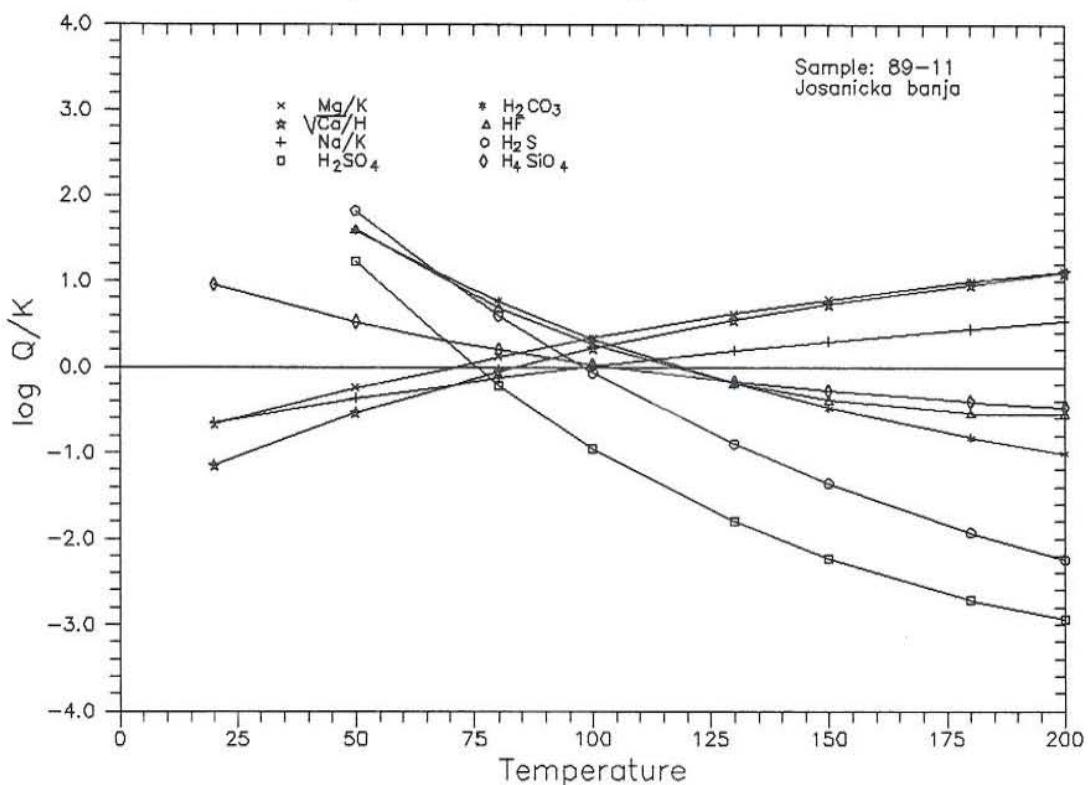


Figure 13. Equilibrium temperature graph for sample 89-45, Bujanovac

Equilibrium temperature

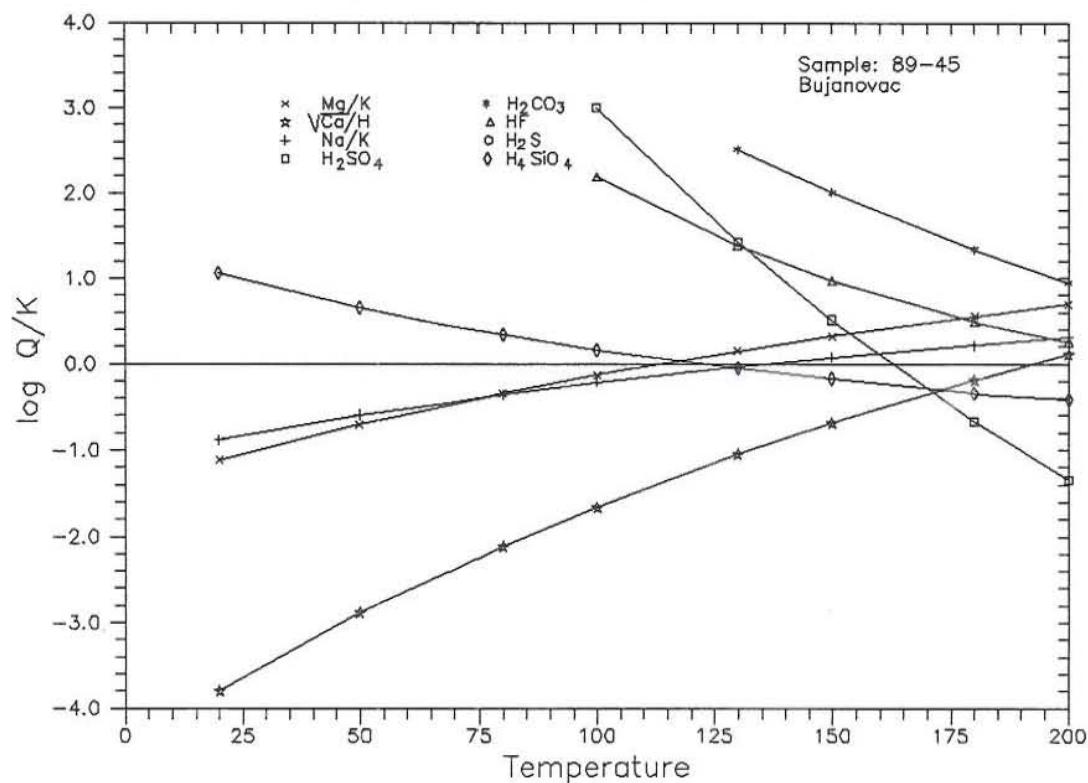


Figure 14. Equilibrium temperature graph for sample 89-11, Josanicka banja

Equilibrium temperature

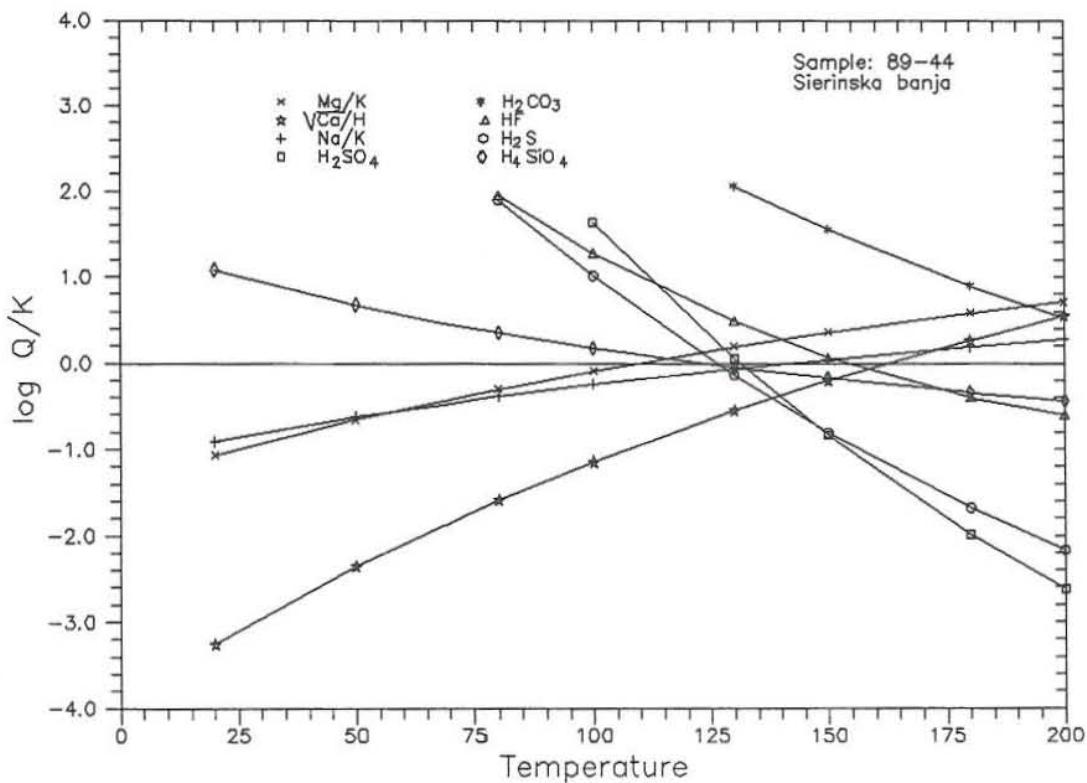


Figure 15. Equilibrium temperature graph for sample 89-44, Sierinska banja

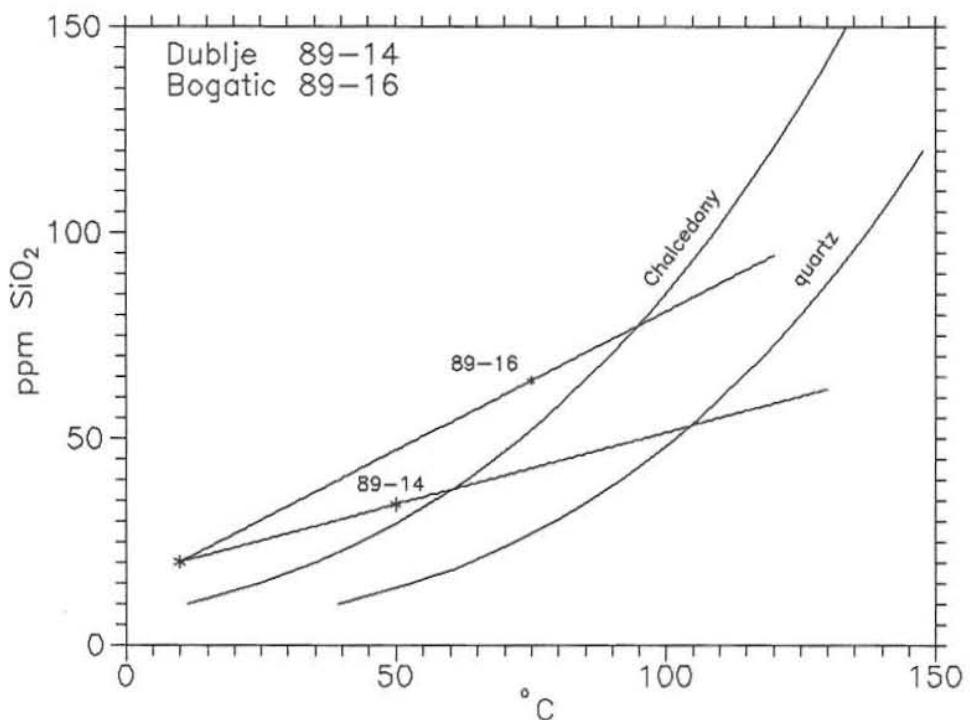


Figure 16. Enthalpy - silica mixing model for samples 89-14, Dublje and 89-16, Bogatic

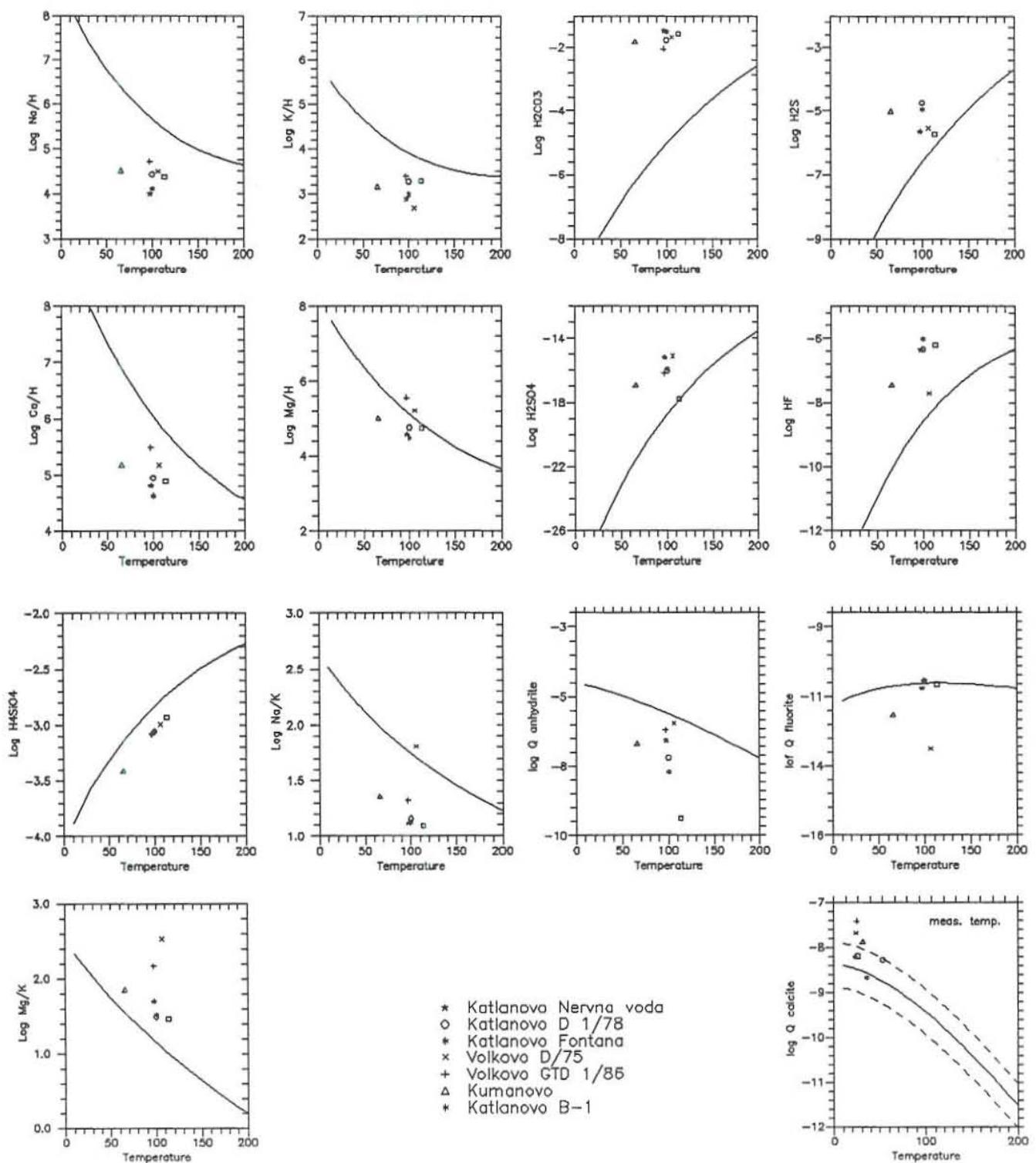


Figure 17. Equilibrium state for water samples from Skopje - Kumanovo valley in Macedonia at quartz geothermometer temperature

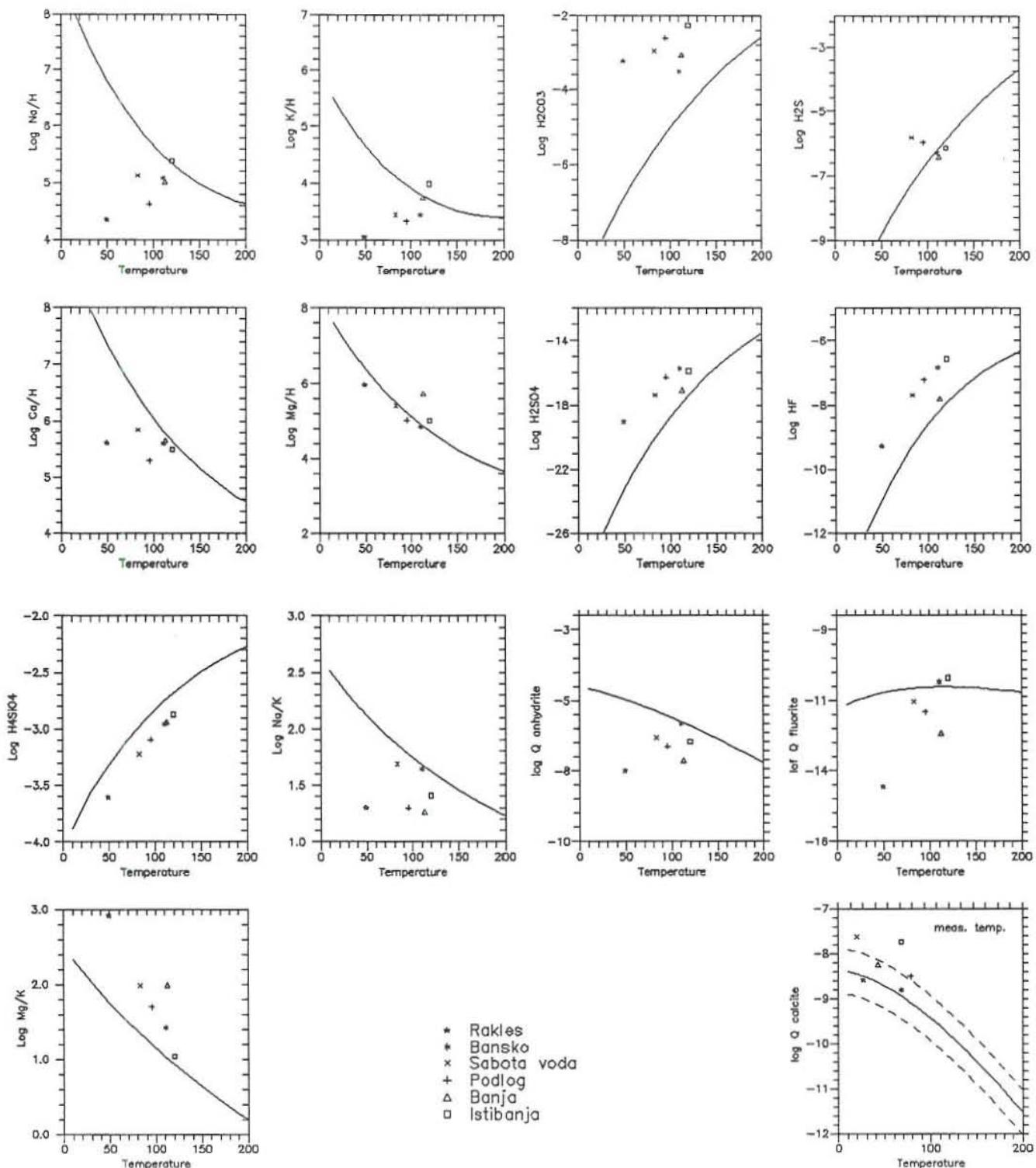


Figure 18. Equilibrium state for water samples from Tertiary sediments in Macedonia at quartz geothermometer temperature

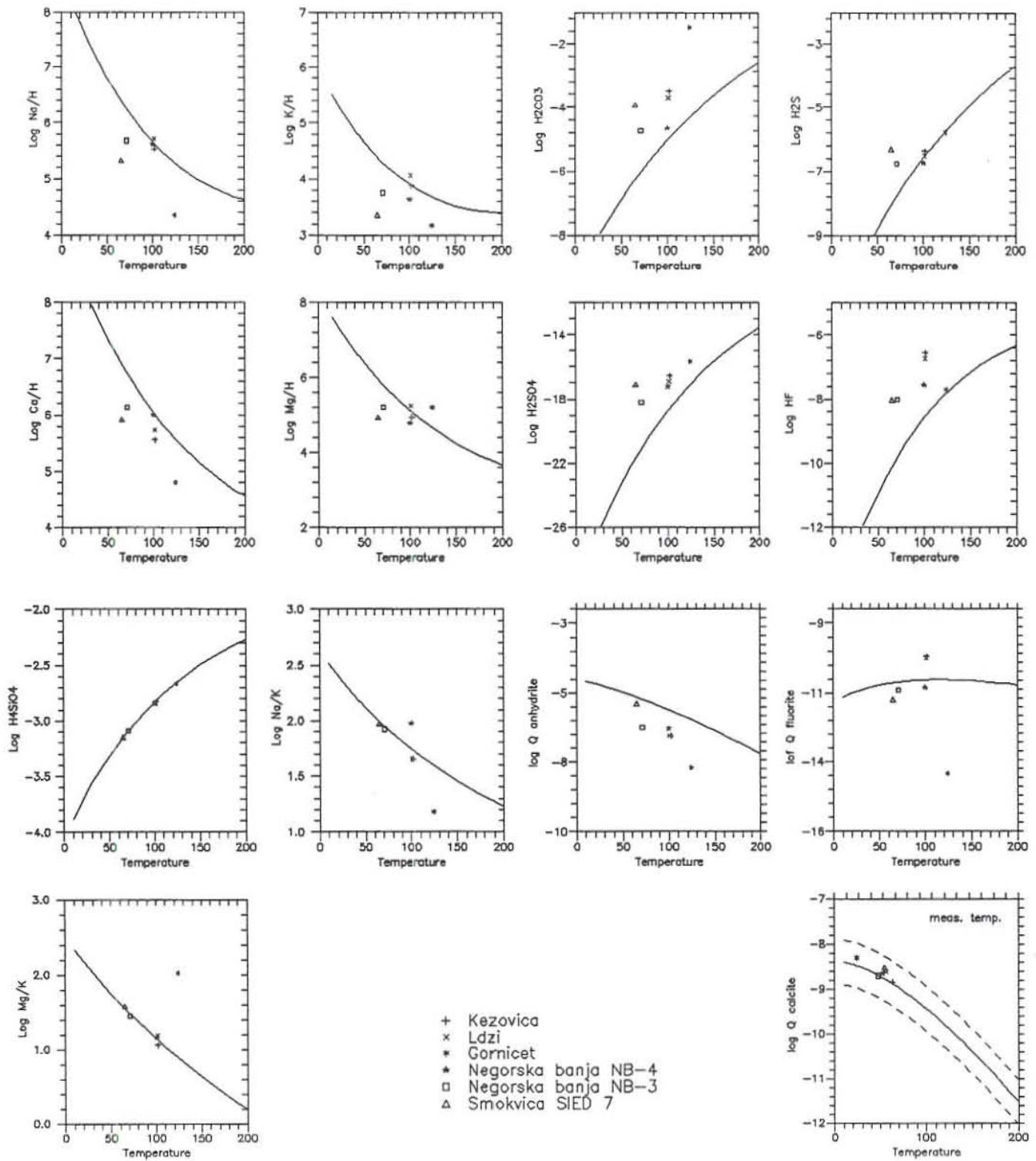


Figure 19. Equilibrium state for water samples from magmatic environment in Macedonia at chalcedony geothermometer temperature

Equilibrium temperature

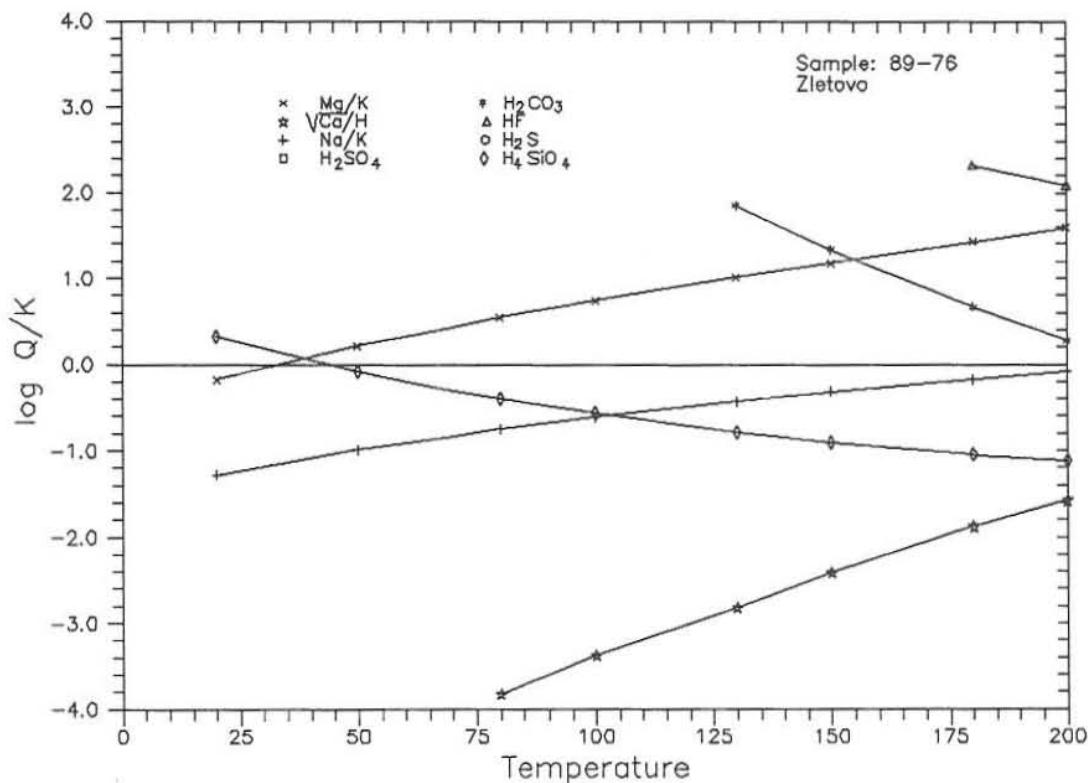


Figure 20. Equilibrium temperature graph for sample 89-76, Zletovo

Equilibrium temperature

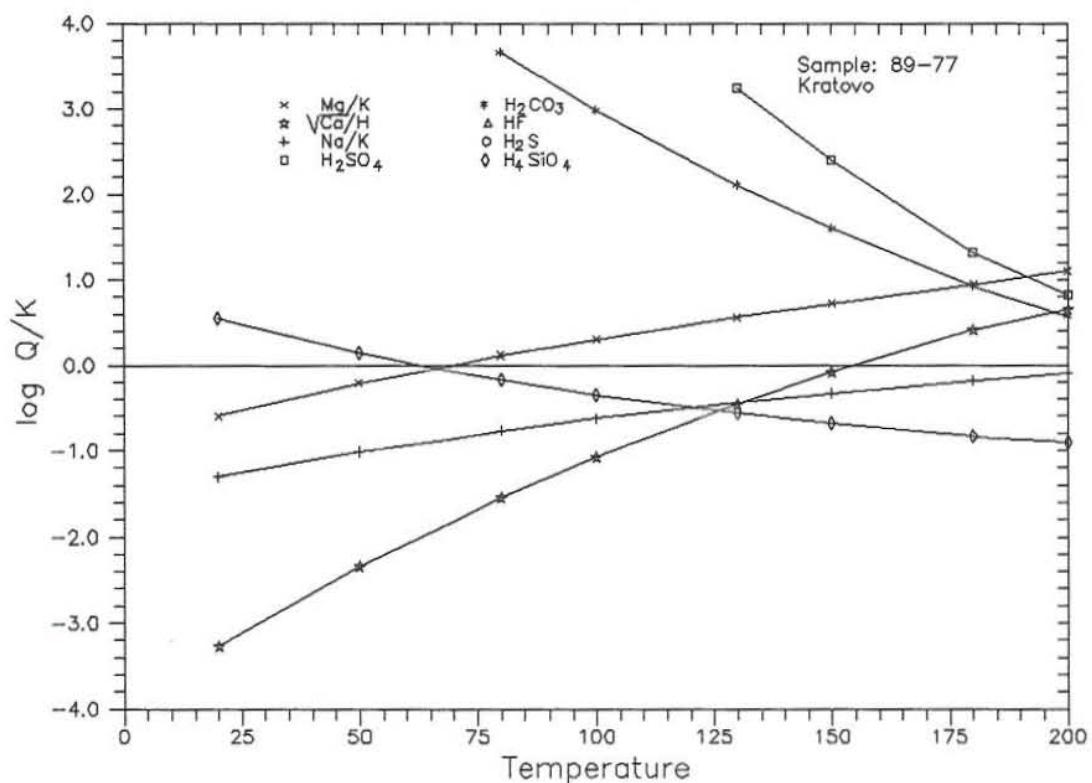


Figure 21. Equilibrium temperature graph for sample 89-77, Kratovo

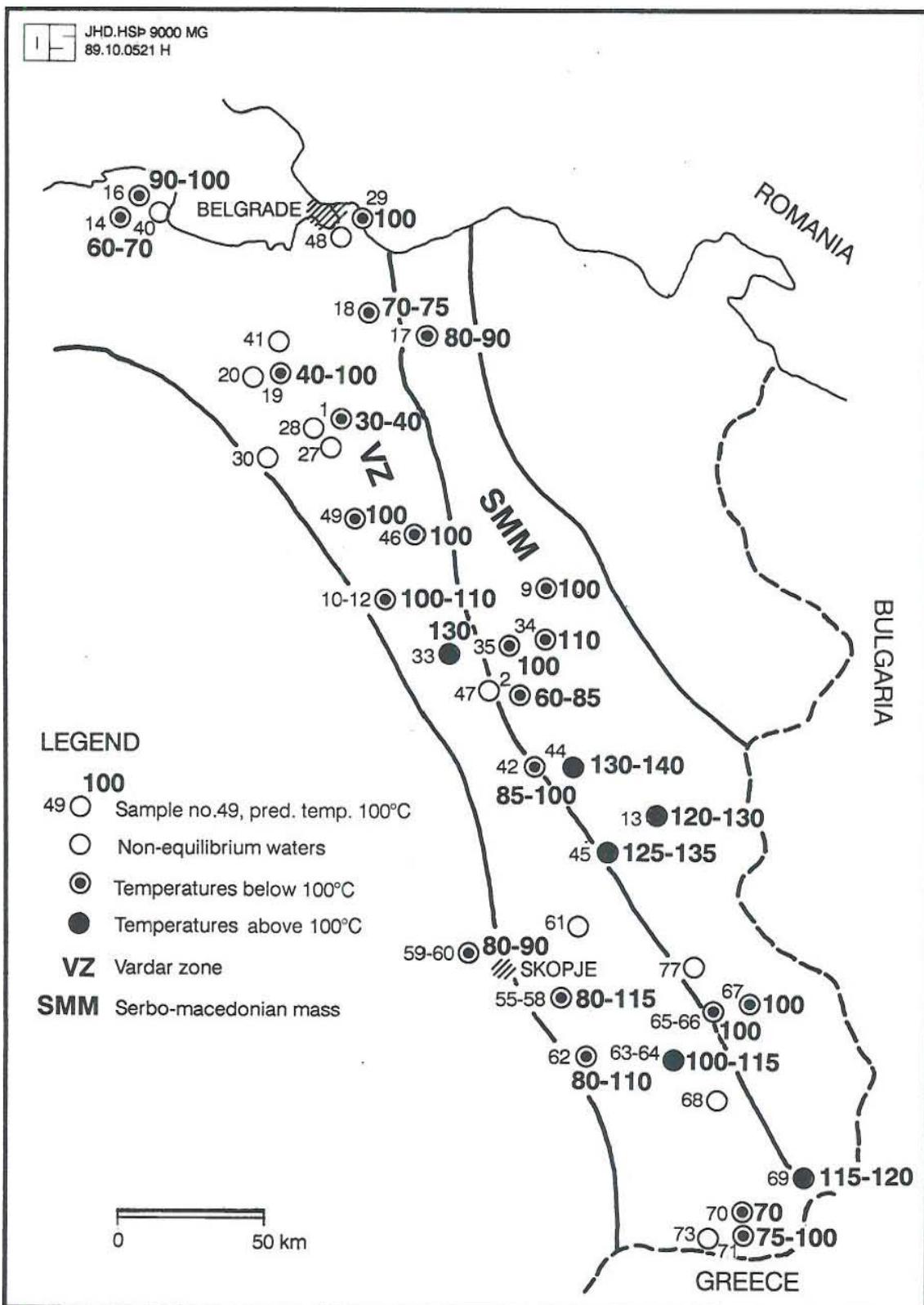


Figure 22. Predicting subsurface temperature in Vardar zone and Serbo-macedonian mass, Yugoslavia.