MONITORING OF CHEMICAL AND ISOTOPIC COMPOSITIONS OF GEOTHERMAL WATERS ALONG THE NORTH ANATOLIAN FAULT ZONE

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Approval of the Graduate School of the Natural and Applied Science

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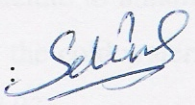
Signature : 

ABSTRACT

MONITORING OF CHEMICAL AND ISOTOPIC COMPOSITIONS
OF GEOTHERMAL WATERS ALONG
THE NORTH ANATOLIAN FAULT ZONE

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This study aims to determine the chemical (anion-cation) and isotopic compositions ($\delta^{18}O$-δD-^{3}H) of the geothermal waters along the North Anatolian Fault Zone (NAFZ) and highlight any possible seismicity-induced temporal variations during the course of two years (2002-2003) monitoring programme. The geothermal sites are alligned along a 800 km transect of the NAFZ and are, from west to east, Yalova, Efteni, Bolu, Mudurnu, Seben, Kurşunlu, Hamamözü, Gözlek and Reşadiye.

The thermal waters of NAFZ are dominantly Na-HCO_3, whereas the cold waters are dominantly Ca-HCO_3 in character. The highest temperature (72.3°C) is recorded in Seben. The hot waters are slightly acidic to alkaline in character with pH values ranging between 5.92-7.97, while the cold waters are comparatively more alkaline with pH values between 6.50-8.83.

Both hot and the cold waters are meteoric in origin. The hot waters have lower $\delta^{18}O$-δD and tritium values suggesting higher recharge altitudes for aquifers and longer residence times for waters, respectively, in the geothermal system (compared to the cold waters).

Temporal variations are detected in both ionic and isotopic compositions of the cold and the hot waters, and these reflect seasonal variations for cold and seismicity-induced variations for hot waters. Although no major earthquakes (M>5) occurred along the NAFZ during the monitoring period, temporal variations recorded in Cl and ^{3}H, and to a lesser extent in Ca and SO_4 contents seem to correlate with seismicity along the NAFZ. In this respect, Yalova field deserves the particular attention since seismicity induced variations were better recorded in this field.

Keywords: North Anatolian Fault Zone, Seismicity, Geothermal Waters, Isotopes, Chemical Composition

ÖZ

KUZEY ANADOLU FAY HATTINDAKİ JEOTERMAL SULARIN KİMYASAL VE İZOTOPİK BİLEŞİMLERİNİN İZLENMESİ

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Bu çalışma, Kuzey Anadolu Fay Hattı (KAFH) boyunca yer alan jeotermal suların, kimyasal (anyon-katyon) ve izotopik ($\delta^{18}O$-δD-^{3}H) bileşimlerinin belirlenmesini ve olası zamansal değişimlerinin, 2 yıllık izleme çalışması (2002-2003) süresince, sismik etkinlikler ile ilişkilendirilmesini amaçlamaktadır. Jeotermal sahalar Kuzey Anadolu Fayının 800 km'lik bir hattı boyunca yer almaktadır ve bunlar batıdan doğuya doğru Yalova, Efteni, Bolu, Mudurnu, Seben, Kurşunlu, Hamamözü, Gözlek ve Reşadiye sahalarıdır.

KAFH' nın termal suları egemen olarak Na-HCO_3, soğuk suları ise egemen olarak Ca-HCO_3 karakterindedir. En yüksek sıcaklık (72.3°C) Seben sahasında kaydedilmiştir. Sıcak sular, 5.92-7.97 arasında değişen pH değerleri ile hafif asidikten baziğe doğru eğilim gösterirken, soğuk sular 6.50-8.83 arasında değişen pH değerleri ile daha baziktir.

Hem sıcak hem de soğuk sular meteorik kökenlidir. Sıcak suların, soğuk sulara oranla daha düşük $\delta^{18}O$-δD ve tritium değerlerine sahip olması jeotermal sistemdeki akiferlerin daha yüksek seviyelerden beslendiğine ve suların yeraltı dolaşım sürelerinin uzun olduğuna işaret etmektedir (soğuk sularla karşılaştırıldığında).

Zamansal değişimler, soğuk ve sıcak suların, hem iyonik hem izotopik bileşimlerinde izlenmektedir ve bunlar, soğuk sular için mevsimsel değişimleri, sıcak sular için ise sismisite-bağımlı değişimleri yansıtmaktadır. İzleme süresi boyunca KAFH' nda önemli (M>5) depremler olmamasına rağmen, Cl, ^3H ve bir ölçüye kadar da Ca ve SO_4 bileşimlerinde kaydedilen zamansal değişimler, KAFH boyunca gerçekleşen sismik etkinlikler ile deneşmektedir. Bu bağlamda, Yalova sahası, sismisiteye bağlı değişimlerin daha iyi kaydedilmesinden dolayı özel önem arz etmektedir.

Anahtar Kelimeler: Kuzey Anadolu Fay Hattı, Sismisite, Jeotermal Sular, İzotoplar, Kimyasal Kompozisyon

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CHAPTER 1

INTRODUCTION

Geothermal energy is the energy recovered from the heat of the earth's interior. In nature, on the surface, geothermal systems show up in the form of volcanoes, hot springs, fumaroles and geysers, whereas in subsurface they are found as big geothermal reservoirs.

Geothermal fields throughout the world are mostly distributed along active plate boundaries, where volcanoes and earthquakes are concentrated. Turkey, one of the most important countries in terms of geothermal energy, is dominated by geothermal fields mainly located along the major fault systems and in the vicinity of Tertiary to Quaternary volcanics (Figure 1.1).

Geothermal waters are effectively used for many purposes such as bathing, heating systems, greenhouses and also in the generation of electricity together with other industrial sectors.

Monitoring of the chemistry of geothermal fluids in seismically-active areas is a technique widely used for understanding both the mechanisms inducing earthquakes and the associated response in the affected region of the crust (Thomas, 1988; Toutain and Baubron, 1999). The variations in chemical and isotopic composition of thermal waters reflect the physical and chemical processes occuring at depths, such as fluid mixing, micro-fracturing and permeability modification.

The present study involves the monitoring of chemical and isotopic compositions of geothermal fluids located along the North Anatolian Fault

Zone (NAFZ) (Figure 1.2), in an attempt to determine the possible relation of the compositional variations to the seismic activities.

1.1. Purpose and Scope

The purpose of this study is the monitoring of the chemical and isotopic compositions of geothermal fluids and the correlation of the possible variations with seismicity associated with the movement along the North Anatolian Fault Zone. The thesis study was realized as part of a 3-year monitoring programme which is supported by TÜBİTAK and NSF.

The geothermal sites included in the study are located along an 800 km long transect extending from Yalova at the west to Reşadiye (Tokat) at the east, covering together with Yalova and Reşadiye fields, Efteni-Gölyaka, Mudurnu-Babas, Seben-Kesenözü, Bolu, Kurşunlu-Çankırı, Hamamözü-Amasya and Gözlek-Amasya (Figure 1.2).

The geothermal sites were sampled 3 times a year including March-July-October 2002 and April-July-October 2003 periods. During sampling both hot and cold waters were collected. Natural springs and production wells were utilized during the sample collection.

The samples were analyzed for their i) major anion-cation contents, ii) tritium concentrations, and iii) $^{18}O/^{16}O$ and D/H ratios.

1.2. Materials and Method

This study is realized through 3 major steps: i) periodic sampling 3 times per year, ii) chemical and isotopic analyses, and iii) data interpretation.

Samples were collected either from hot/cold springs or production wells into 1 litre polyethylene bottles separately for chemical (anion-cation) and isotopic (Oxygen-18, deuterium and tritium) analyses. Except for the first two sampling periods, where the chemical analyses were performed in the laboratories of the Geological Engineering Department of the Middle East

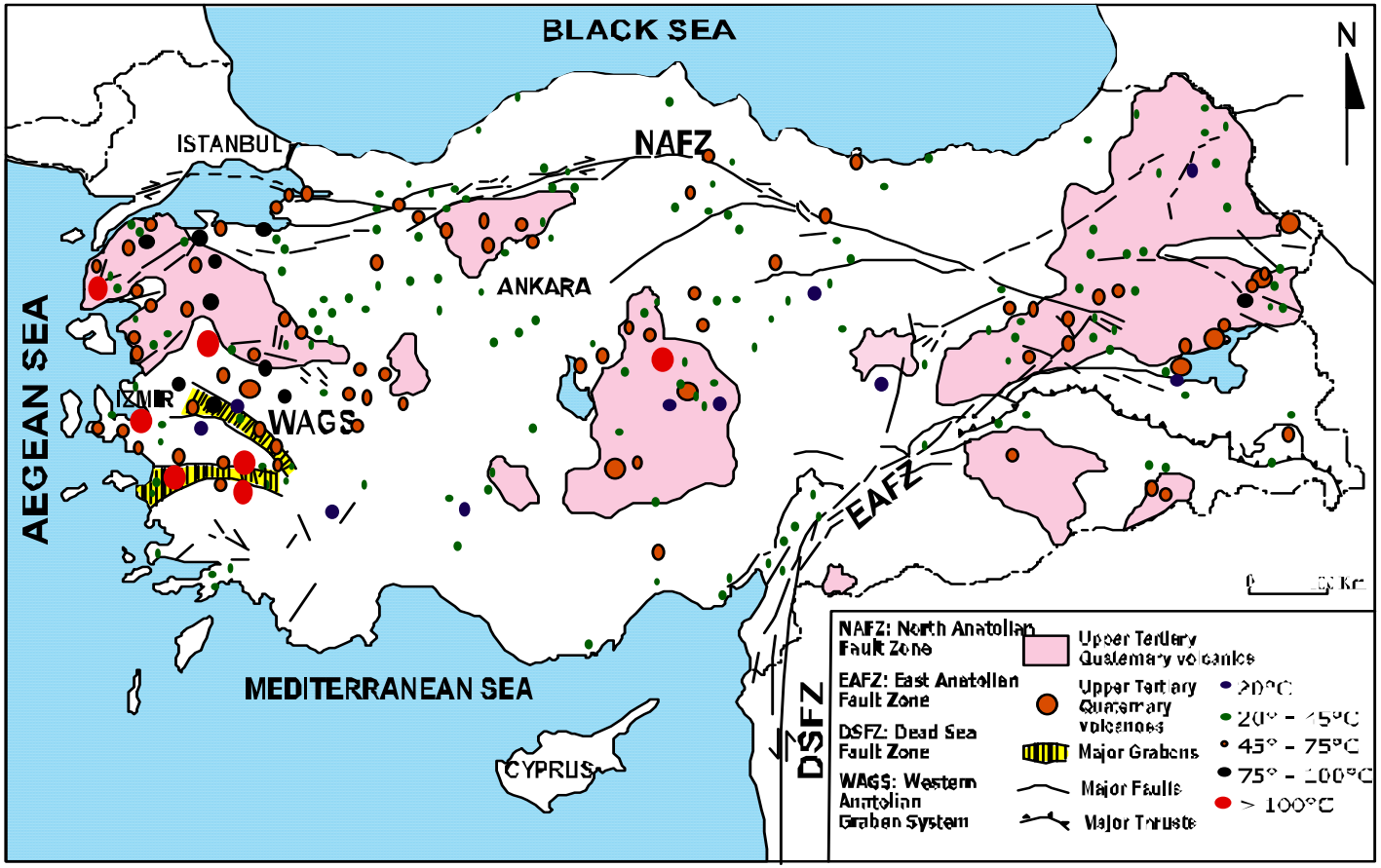


Figure 1.1. Distribution of hot springs in Turkey together with major tectonic and volcanic features (Şimşek and Güleç, 1994).

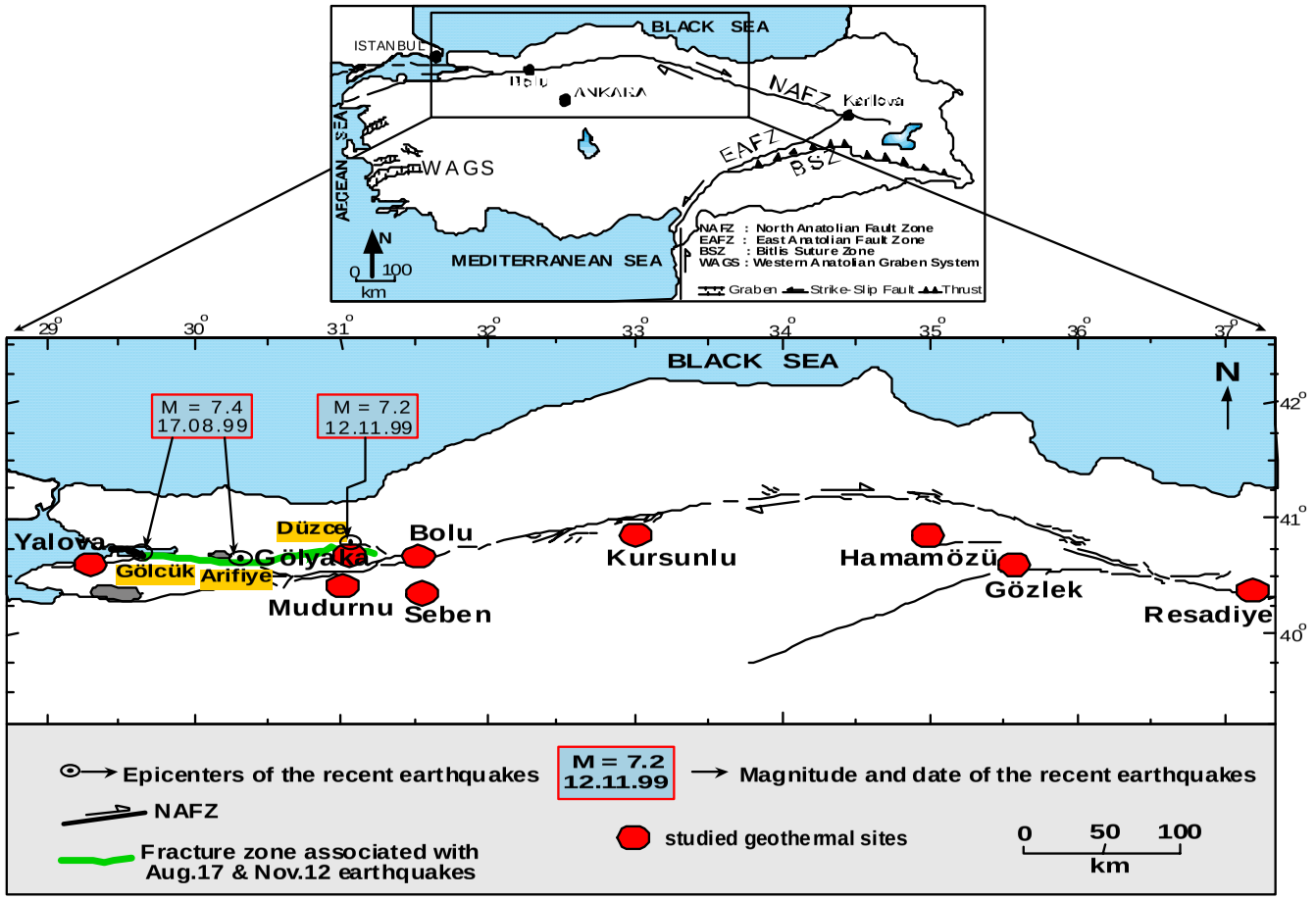


Figure 1.2. Location map of the sampled geothermal fields along the NAFZ (after Çemen et al., 2000).

Technical University, the chemical and isotopic compositions of the sampled waters were analysed in the laboratories of the State Hydraulic Works of Turkey in Ankara. Data interpretation involved the evaluation of the origin of waters, the physico-chemical subsurface processes, and the possible relations to seismicity associated with the NAFZ.

1.3. Layout of Thesis

This thesis has 9 chapters. Following this introduction chapter (Chapter1):

Chapter 2 gives an overview of chemical and isotopic techniques in geothermal investigation, including a general background about the chemical components in geothermal fluids, environmental isotopes, and the use of chemical and isotopic components in tracing seismic activities.

Chapter 3 is about the tectonic setting of, and the recent seismic activities associated with the North Anatolian Fault Zone (NAFZ).

Chapter 4 is concerned with the regional geology, as well as the geologic and hydrogeologic outline of the studied geothermal fields.

Chapter 5 gives information about sampling procedure and analytical techniques used in the study.

Chapter 6 presents the results of chemical analyses, together with a discussion of the results with regard to the hydrogeochemical facies and possible subsurface processes.

Chapter 7 is about the isotope compositions, covering $^{18}O/^{16}O$ and D/H ratios together with tritium (^{3}H) contents. The presentation of the results of analyses is followed by a discussion as to the origin of waters and the possible subsurface processes.

Chapter 8 discusses the temporal variations in chemical and isotopic composition of waters in relation to the recent seismic activities along the NAFZ.

Chapter 9 gives the conclusions derived from the thesis study, as well as the recommendations for future studies.

CHAPTER 2

CHEMICAL AND ISOTOPIC TECHNIQUES IN GEOTHERMAL INVESTIGATION: AN OVERVIEW

2.1. Chemical Components of Geothermal Fluids

Geothermal fluids are mainly characterized by high **T**otal **D**issolved **S**olid (TDS) contents and their compositions are controlled by temperature dependent reactions between minerals and fluids defining water-rock interaction. The major constituents of geothermal waters are SiO_2, Na, K, Ca, Mg, Cl, SO_4, HCO_3 and CO_3, the relative concentrations of the latter two being pH dependent (CO_3 dominating at pH> 10.33) (Drever, 1982; Arnorsson, 2000). Geothermal fluids also contain, in minor quantities, Fe, Al, Li, Rb, NH_3, NH_4, CH_4, N_2, Rn, B, As and Hg.

The chemical and isotopic components in geothermal waters can be divided into two major groups as reactive constituents (*geoindicators*) and conservative constituents (*tracers*) (Giggenbach and Goguel, 1989).

The geoindicators are the constituents such as Na, K, Mg and SiO_2, which tend to equilibrate with other reactive constituents and/or minerals of the rock in the geothermal system. They are used to obtain information on the physical state of geothermal reservoirs (e.g. reservoir temperature, steam/water ratio in reservoir). One of the most common utilization of geoindicators is geothermometry applications (i.e. determination of reservoir temperatures). The main assumption in these applications is that water preserves its chemical composition during its ascend from the reservoir to the surface and the water-

rock equilibrium prevails in the source aquifer. The chemical geothermometers used in geothermal applications are divided into two as silica and alkali (cation) geothermometers. Silica geothermometers are based on experimentally determined temperature dependent variation in solubility of silica in water, whereas alkali geothermometers are based on the partition of alkalis between solid and liquid phases (Fournier, 1977; Fournier, 1979; Arnorrson, 2000).

The tracers, on the other hand, are chemically inert and, therefore, conserved in water-rock systems and provide information about the origin of both geothermal fluid and the tracer itself. Cl, B, Li, Rb and noble gases such as He, Ne, Ar, Kr, and Xe are definitive tracers for heat and fluid sources (Arnorsson, 2000)**.** Isotopes such as tritium (^{3}H) and deuterium (D = ^{2}H) are also conservative and they are used in geothermal studies. Oxygen-18 (^{18}O), on the other hand, can be used as a tracer like deuterium in waters having temperatures less than 100˚C, since, in waters having greater temperatures, it shows significant oxygen isotope shift and loses its tracer capacity (Arnorson, 2000). The tracers are effectively used in geothermal investigations since they highlight many processes, such as mixing and boiling, due to their ability to remain in the fluid phase without being changed once they are introduced into the system. Almost all geothermal waters reaching the surface are mixed, that is, they contain both hot and cold reservoir characteristics. The geothermal water ascending from the hot reservoir, on its way to the surface, mixes with cold shallow groundwater at different levels and loses its initial composition and temperature. Boiling is particularly realized in high enthalpy systems, is often associated with pressure release (adiabatic cooling), and results in steam loss from the geothermal fluid which changes the fluid's original composition. Mixing and boiling in geothermal systems can be revealed by considerable variations in i) Cl concentrations, ii) tritium contents, iii) oxygen and hydrogen isotope compositions, and iv) conservative elements ratios, such as Cl/B (Rybach and Muffler, 1981).

2.2. Environmental Isotopes in Geothermal Investigation

Isotopes are the atoms of an element with the same atomic number (i.e. number of protons) but different atomic masses (i.e. proton number + neutron number). Isotopes are classified into two groups as radioactive and stable isotopes. Radioactive isotopes are those which break down into isotopes of other elements. The variation in the natural abundances of radioactive isotopes is governed by radioactive decay. Stable isotopes, on the other hand, do not show any radioactive decay, and their abundances are controlled by isotope fractionation process which is simply the fractionation of the isotopes into different phases during natural processes, such as evaporation, condensation, magmatic differentiation and mineral-water interaction.

Environmental isotopes are those which are naturally found in the hydrologic cycle. Since the isotope ratios are sensitive to changes in temperature, water-rock interaction and other physicochemical processes, such as mixing and steam separation, environmental isotopes provide solution for many hydrologic and hydrogeologic problems (Öztürk, 2001), including,

- determination of groundwater origin,
- determination of the relationship between groundwater and surface waters,
- precipitation-flow relations and determination of groundwater flow direction,
- determination of the recharge altitude of groundwaters,
- study of leakages from dams and lakes,
- dating groundwaters,
- determination of quality of water from radioactive point of view,
- identification of different aquifer systems and their relations.

2.2.1. Oxygen and Hydrogen Isotopes

Oxygen has three stable isotopes which are ^{16}O, ^{17}O and ^{18}O. The most abundant oxygen isotope is ^{16}O accounting for about 99.76% of all oxygen, while ^{18}O and ^{17}O comprise only 0.20% and 0.048%, respectively, of the total oxygen in nature. Hydrogen, on the other hand, has two stable isotopes which are ^{1}H and ^{2}H (Deuterium, D) comprising, respectively, 99.985% and 0.015% of hydrogen abundance, and one radioactive isotope, ^{3}H (Tritium), found as a trace component (Faure, 1986). Because of the existence of three stable isotopes of oxygen and two stable isotopes of hydrogen, the ordinary water molecules have a number of different isotopic configurations (e.g. $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, $HD^{18}O$, $D_2{}^{16}O$, $D_2{}^{17}O$, $D_2{}^{18}O$). Since ^{17}O is not very abundant in nature, it is not used in geologic and/or hydrogeologic studies.

The isotopic composition of a water sample is expressed as deviations – in delta notations in per mil (‰) - of sample's $^{18}O / ^{16}O$ and D/H ratios from those of a standard called SMOW (**S**tandard **M**ean **O**cean **W**ater).

$$\delta\,^{18}O\,(‰) = [\,(^{18}O / ^{16}O)_{sample} - (^{18}O / ^{16}O)_{standard}\,] / [\,(^{18}O / ^{16}O)_{standard}\,] * 1000$$

$$\delta D\,(‰) = [\,(D / ^{1}H)_{sample} - (D / ^{1}H)_{standard}\,] / [\,(D / ^{1}H)_{standard}\,] * 1000$$

Positive values of $\delta^{18}O$ and δD indicate enrichment of a sample in heavy isotopes (^{18}O and D) compared to SMOW, and negative values indicate depletion in heavy isotopes. SMOW has, by definition, $\delta^{18}O=0$ and $\delta D=0$.

Most of the world's precipitation originates from the evaporation of ocean and seawater. The $\delta^{18}O$ and δD compositions of precipitation throughout the world are linearly correlated and distributed along a line known as the *Global Meteoric Water Line*, given by the equation below and shown in Figure 2.1.

$$\delta D = 8\,\delta^{18}O + 10 \quad \text{..... (Craig, 1961)}$$

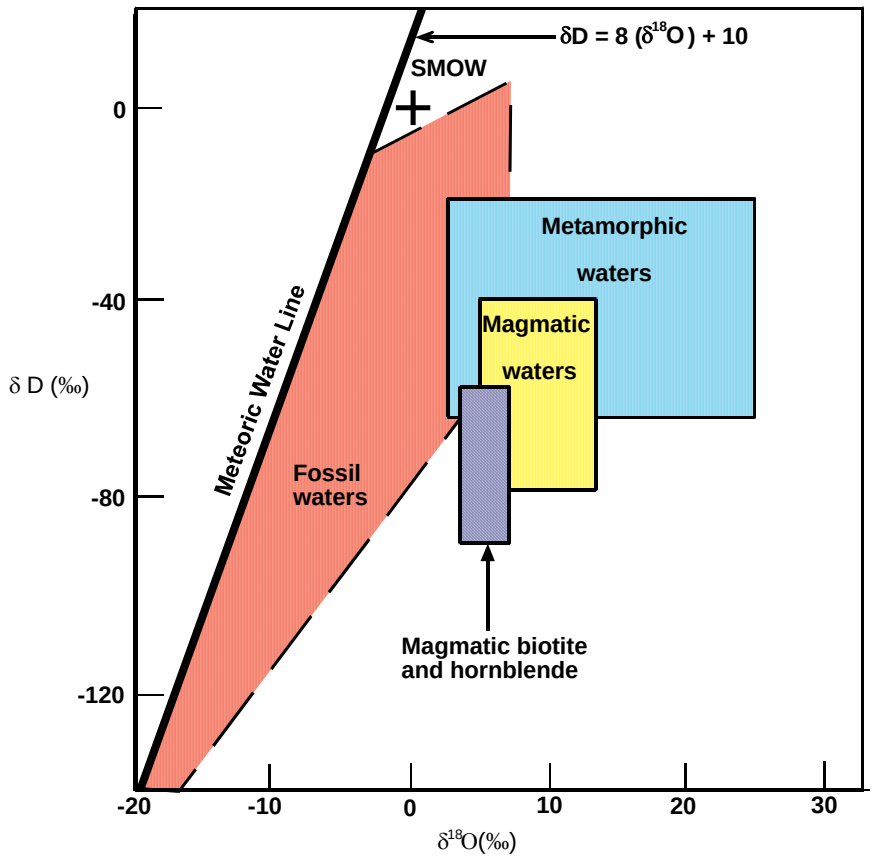


Figure 2.1. δD-δ^{18}O diagram showing isotopic compositions of different water types and the effects of physico-chemical processes on the water compositions (meteoric water line-Craig, 1961; magmatic waters-Taylor, 1974; Sheppard, 1977; metamorphic waters-Taylor, 1974; Sheppard, 1981; fossil waters-Taylor, 1974; magmatic biotite and hornblende-Taylor,1974).

The position, along this meteoric water line, of isotope composition of local precipitations depends on temperature, amount of precipitation, distance from the sea (continental effect), altitude and latitude. In temperature effect, the composition of precipitation changes with temperature at which oceanic water is evaporated, any increase in temperature being associated with an increase in δ D and δ^{18}O values. The amount of precipitation is also important: heavy rain events result in more negative δ D and δ^{18}O values and, since the amount of rain varies with seasons, a seasonal variation is also observed. In case of continental effect, the isotopic composition of precipitation tends to have more negative

values further away from the ocean coast where condensation of heavy isotopes take place and the residual air mass gets enriched in light isotopes as it travels inland. Regarding the altitude effect, as clouds rise up the mountains, the heavy isotopes become depleted and the residual precipitation gets isotopically lighter. The altitude effect is used as a tool to estimate the recharge altitude from δD and $\delta^{18}O$ data of springs and wells (Mazor, 1997). The latitude effect works in such a way that as it increases, the isotope composition of waters becomes lighter.

Deviation from the meteoric water line can be due to several processes such as i) evaporation and condensation, ii) water-rock interaction, and iii) mixing with non-meteoric waters such as formation (fossil) waters, metamorphic waters, magmatic waters (Albu et al., 1997).

During evaporation isotopic fractionation takes place in such a way that the light isotopes partition into the steam (gas) phase, and the heavy isotopes partition into the residual liquid phase. That is, evaporation changes the water's composition towards more positive δD and δO^{18} values (Figure 2.1). In case of condensation, just the reverse is observed, the water's composition shifts towards low (less positive / more negative) δD and δO^{18} values (Mazor, 1997).

The water-rock interaction is particularly realized at high temperatures (i.e. in geothermal systems). Since hydrogen is not one of the major constituents of rocks, there is almost no change in D/H ratios of water during water-rock interaction. However, since oxygen is one of the major constituents of rocks, and since the rocks are in general enriched in heavy oxygen-isotope, the water-rock interaction shifts the water's composition towards more positive $\delta^{18}O$ values (Figure 2.1).

Regarding the mixing process, there are 5 major components of natural waters: i) meteoric water (precipitation, lakes, rivers), ii) ocean water, iii) formation (fossil) water, iv) metamorphic water, and v) magmatic water. Each of these components have unique isotope compositions (Figure 2.1). As has

been outlined above, O- and H-isotope ratios of meteoric waters are linearly related to each other. Ocean water is enriched in heavy isotopes compared to meteoric water. Fossil waters are those kept in deep sedimentary bodies at the time of their formation, and they are originally sea or meteoric waters. The isotopic composition of magmatic waters is estimated from the isotopic composition of igneous rocks, whereas that of metamorphic waters is controlled by equilibration with oxygen and hydrogen bearing minerals during metamorphism. The isotope compositions of these natural water components provide a basis for the determination of the origin of geothermal waters. It has long been debated that the geothermal waters represent mixtures of meteoric waters with the other (metamorphic, magmatic, fossil) water components. In this respect, the geothermal waters of mixed origin are supposed to plot on the δD vs. $\delta^{18}O$ diagram along lines converging from meteoric water line towards the areas representing isotopic compositions of magmatic, metamorphic and fossil waters. Studies, however, have shown that the geothermal waters have almost the same δD values as the meteoric waters in the respective geothermal sites, while their $\delta^{18}O$ values are less negative than those of local meteoric waters (Figure 2.2). This has then led to the idea that geothermal waters are essentially meteoric in origin but their O-isotope compositions have been modified by water-rock interaction.

As a summary, δD and $\delta^{18}O$ isotopes can be utilized in tracing the origin of water (meteoric, magmatic or metamorphic) and studying the physico-chemical processes (e.g. boiling, mixing) in the hydrologic cycle.

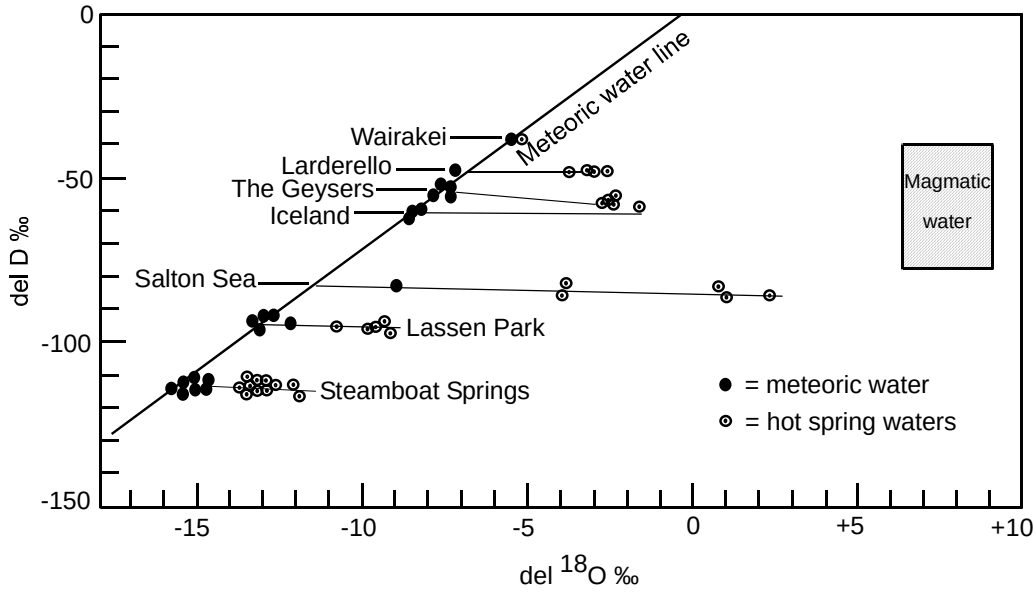


Figure 2.2. $\delta^{18}O$ and δD values for meteoric and thermal waters in several geothermal fields (Ellis and Mahon, 1977).

2.2.2. Tritium

Tritium, ^{3}H, is a short-lived radioactive isotope of hydrogen produced in the upper atmosphere by the interaction of cosmic ray produced neutrons with nitrogen atoms as shown below:

$$_{7}^{14}N + n \longrightarrow {}^{3}_{1}H + {}_{6}^{12}C$$

Half life of tritium is 12.26 years (Faure, 1986) and it decays by beta emission and produces tritiogenic helium ($_{2}^{3}He$) according to the following equation.

$$^{3}H \longrightarrow {}_{2}^{3}He + \beta$$

Tritium has both natural and anthropogenic sources which are both introduced into the hydrologic cycle via precipitation. In Figure 2.3, the origin and distribution of tritium in the hydrologic cycle is shown. About 3 to 5% of

all neutrons in the upper atmosphere react with nitrogen to form small but measurable amounts of tritium in the stratosphere. The natural rate of production of tritium is 0.25 atom cm^{-2} s^{-1} and it often combines with oxygen in the form of HTO, where H is ^{1}H or ^{2}H, T is tritium and O is oxygen. The tritium content of natural waters is expressed in units of TU (**T**ritium **U**nits) where 1 TU corresponds to one atom of ^{3}H per 10^{18} atoms of hydrogen. Tritium occurs naturally in rainfall at levels less than 20 TU (Albu et al., 1997).

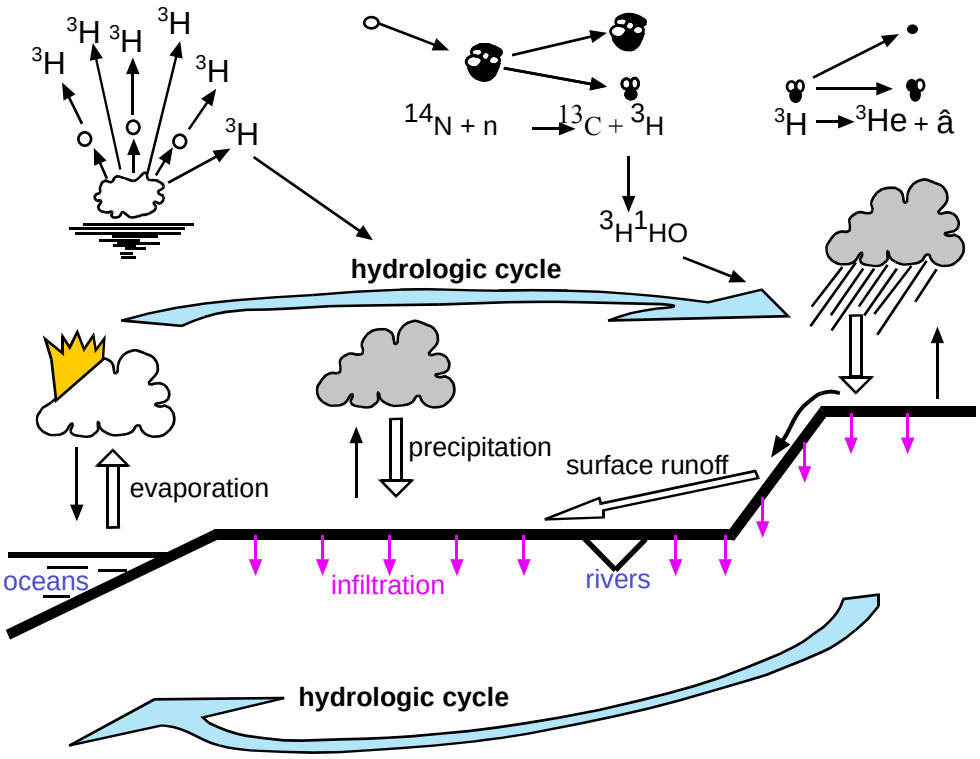


Figure 2.3. Origin and distribution of tritium in the hydrologic cycle.

Large quantities of tritium have been introduced into the atmosphere since the beginning of atmospheric nuclear testing and resulted in an increase in tritium in precipitation up to values as high as 2900 TU in the northern hemisphere by 1963 (Altay and Çifter, 1996; Attendorn and Bowen, 1997). The injection of tritium resulted in a long term effect on the concentration of tritium

in precipitation. The concentration of tritium fell steadily until 1968 as a result of the moratorium on atmospheric bomb testing (Attendorn and Bowen, 1997). In Figure 2.4, the distribution of tritium throughout the years is shown according to the precipitation in Ottowa Canada.

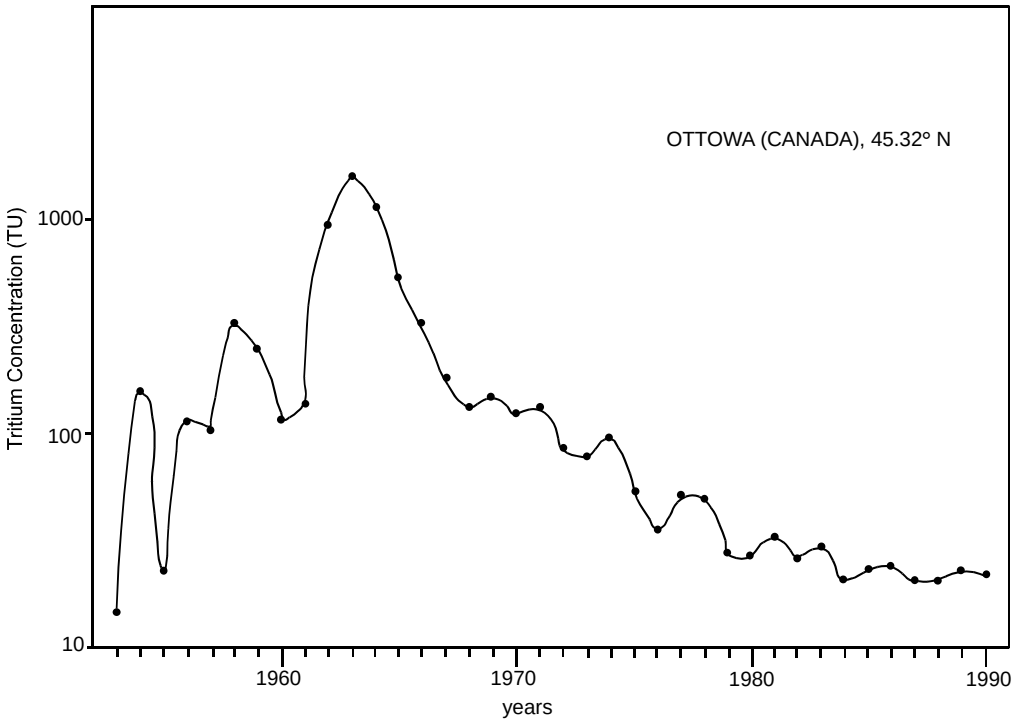


Figure 2.4. Annual change in tritium in Ottowa precipitations (Altay and Çifter, 1996).

The concentration of tritium in precipitation is affected by three processes which are seasonal effects, continental versus oceanic effects, and hemispherical and latitudinal effects.

Seasonal effects: Concentration of tritium in precipitation shows seasonal variations. The maximum concentrations occur in spring and summer termed as spring injection, while minimum concentrations occur in fall or

winter. These variations are related to air exchange between the stratosphere and troposphere.

Continental versus oceanic effects: Landmasses affect the content of tritium in precipitation. At constant latitude, the tritium concentration of precipitation over a large landmass is greater than the concentration of precipitation over the ocean. The increase in concentration over large landmasses is due to the lack of molecular exchange between the ocean and tropospheric tritium.

Hemispherical and latitudinal effects: During nuclear testing, most tritium was released into the northern hemisphere. Since 1963, the concentration of tritium in northern hemisphere has decreased dramatically while the tritium concentration in the southern hemisphere has increased due to stratospheric transfer of the bomb produced tritium. Tritium concentration also shows a trend with latitude, concentration increases almost exponentially with increasing latitude

Tritium is a useful tool in measuring the isolation time of water from the surface. The tritium age is defined as the time elapsed since the body of water has been isolated from atmospheric conditions following its recharge. The equation relevant to this tritium age is as follows:

$$^{3}H_{gw} = {}^{3}H_{atm}\, e^{-\lambda t}$$

where,

$^{3}H_{gw}$ is the tritium concentration in groundwater,

$^{3}H_{atm}$ is the tritium concentration in the atmosphere,

t is the time elapsed since the isolation of the water body from the atmosphere,

λ is the decay constant for $^{3}H = 0.056$ year^{-1} (Faure, 1986)

Since the tritium concentration in the atmosphere has not been constant due to the introduction of bomb-produced tritium after 1953 (i.e. the tritium

concentration in the atmosphere shows a time dependent change), the above equation can not provide an absolute age for groundwaters. For this reason, instead of an absolute age, tritium concentrations are used to determine the relative ages of waters. For example, spring and shallow well waters recharged by recent precipitations have tritium contents higher than deep circulating waters which have a longer residence time at subsurface.

2.3. Geothermal Fluid Compositions as Seismic Precursors

Earthquake prediction has long drawn attention from the geoscientists. The geophysical methods, traditionally utilized for this purpose, have started to be accompanied by geochemical studies after the documentation of the increases in radon gas release prior to large earthquakes in Japan in early 1950's and in Russia in the early 1970's (Hatuda, 1953; Okabe, 1956; Sadovsky et al, 1972).

The most widely used geochemical parameters as seismic precursors are gases like radon, helium, carbon dioxide, hydrogen, nitrogen and methane, and some of the constituents of thermal waters like chlorine, tritium, sulphate and trace metals. Of these, the oldest parameter used in earthquake prediction studies is radon, a radioactive noble gas with a half life of 3.82 days. In many earthquake prediction studies, anomalous radon increase is observed in either groundwaters or soil gases which starts as a pre-seismic signal and usually lasts for a couple of days. Radon is presently used in several countries such as Russia, China, Japan and the US (Teng, 1980; King, 1980; Wakita et al, 1980; Craig et al, 1980; Hauksson, 1981; Teng and Sun, 1986). For example, in the San Andreas fault system, along a segment from the Tejon area to California-Cajon region, starting from 1974, continuous radon measurement stations were constructed (Teng and Sun, 1986). The reported radon anomalies appeared days or even weeks before large earthquakes and more than 50 % of these anomalies lasted only for a couple of days. However, due to the complex hydrologic system dynamics, the relation between seismicity and radon anomalies is not fully understood and studies are being continued.

Another geochemical parameter used in monitoring of seismicity is the hydrogen gas, and in 1980‘s along the San Andreas fault in California, continuous monitoring studies were made (Sato et al, 1986). The sudden hydrogen gas releases recorded in two stations along the San Andreas fault between the years July 1982 and November 1983 were correlated with the earthquakes (M>5) which occurred in the vicinity of Coalinga in the same period (Sato et al, 1980). Therefore, hydrogen gas together with radon gas, can be used as a tracer in identifying deep originated plate movements.

He, Ar, N_2 and CH_4 are the other gases used effectively in monitoring seismic activities. About 1-3 months before the 14 September 1984 earthquake in Japan (epicenter: Western Nagano, M: 6.8), anomalies were identified in He/Ar, N_2/Ar and CH_4/Ar ratios of gas bubbles within the mineral water discharges of about 50-70 km from the epicenter (Sugisaki and Sugiura, 1986). These anomalies were related to the change in pore pressures resulting from the crustal extension due to seismicity. Following these increases in gas ratios, increases in hydrogen gas release were observed and these increases were related to the reaction between groundwater and the newly formed fracture systems. In other words, He and CH_4 type gases concentrate in the crust and reach surface via crustal extension, while H_2 appears with water-rock interaction (Sugisaki and Sugiura, 1986).

In monitoring seismicity, not only the emission amounts but also the isotopic compositions of gases are used. In this respect, $^3He/^4He$ ratios are used as potential tracers in identification of source areas of gases, since they are sensitive parameters. Mantle derived gases have 8-30 times higher $^3He/^4He$ ratios with respect to atmospheric gases. In crustal derived gases, this ratio is 10-100 times smaller than the atmospheric gases. Helium isotope compositions are used effectively in recent years in monitoring seismicity due to their variations in mantle-crust interaction. For example, Hilton (1996) reported large variations in $^3He/^4He$ isotope ratios correlated with the regional seismicity in the Long Valley Caldera (USA) in between the years 1978 and 1985.

Among the constituents of thermal waters, tritium is one of the most important potential tracer used in the identification of seismicity induced variations. Sano et al. (1998) reported significant variations in tritium contents of groundwaters during the 1995 Kobe (Japan) earthquake. Variations in tritium contents were attributed to mixing of low tritium water in the clay layers with high tritium water in the aquifers embedded within the clay layers. Moreover, the variations were related to flow path mixing in the region of the sample screen by the earthquake.

In some cases, variations in major anion contents (Nishizawa et al., 1998; Balderer et al., 2002), particularly Cl contents (Toutain et al., 1997) are also correlated with seismicity.

According to the study done by Toutain et al. (1997), anomalies in Cl concentrations in the Alet spring mineral waters were identified 5 days prior to the 5.2 magnitude Pyrenean earthquake in France, and lasted for about 10-13 days. About 36 % of increase in the Cl content relative to the mean value in the mineral water was observed, accompanied by a slight increase in sulphate content (reaching to about 14 % above the mean value), prior to the earthquake. The increase in Cl content dropped down to its background levels 5-8 days after the main shock. The Cl anomaly was attributed to mixing of Cl-rich waters rising between the epicentre of the earthquake and the Alet area, induced by changes in pre-seismic strain. This study revealed the importance of mineral springs as suitable sites for investigation of seismic precursors.

In the study done by Nishizawa et al. (1998), Cl and SO_4 anomalies were detected in the Yugano hot spring waters, 12 days after the onset of the 1995 seismic swarm activity in Izu Peninsula, central Japan. Two fold increase in both Cl and SO_4 concentrations were observed during the swarm activity in two respective sampling days between 22nd and 23rd of September, just 5 days before the activity became most active. A linear correlation between Cl and SO_4 concentrations was identified, suggesting that variations were related to a

simple 2-component mixing process, that is, mixing with high Cl and SO_4 waters, triggered by the associated seismic swarm activities resulting in crustal stress changes.

Balderer et al. (2002) reported changes in both chemical and isotopic compositions of the thermal and mineral waters along the North Anatolian Fault Zone, including Kuzuluk, Bursa, and Yalova/Gemlik. Sampling was done before and after the earthquake and variations related to the seismic activity were identified. The variations in the chemical constituents including calcium, potassium, sodium, nitrate, sulphate and chloride were interpreted as both the results of mobilisation of deep seated brines in response to the tectonic activity and variations related to mixing of waters of superficial origin, which may contain some anthropogenic pollutants such as nitrates. Variations in δD and $\delta^{18}O$ contents of the waters, on the other hand, were attributed to mixing processes with groundwater of shallow or deep origin of different infiltration conditions.

In the study done by Favara et al. (2001), temporal variations were detected in temperature and some chemical species in waters of the thermal springs of Western Sicily during the seismically active period especially between 1966 and 1969 coinciding with the 1968 Belice Valley earthquake. The temperature, Na, Cl, SO_4 and TDS of the thermal springs showed minimum values before the earthquake, and maximum values after the event. The changes in these parameters were attributed to permanent change in aquifers caused by tectonic activities. Moreover, continuous increase in temperature values starting from 1965 till 1991 was detected (from 31 to 41ºC) and was attributed to increased fluid released from a deep system. In Terme Selinuntine spring, increase in CO_2 values in the spring was also observed during the seismic swarm activity with values returning back to their previous levels after the earthquakes. The temporal variations in this water was related to temporary contribution of deep fluids rich in CO_2, as a consequence of the strain release during the 1968 earthquake.

In the geochemical monitoring study done by Federico et al. (2004), between 1998 and 2001, temporal variations in two distinct groups of water bodies were studied in the Vesuvius volcano area in Italy. The first group, rising through the southern flanks of the Vesuvius volcano, was characterized by high temperature, high TDS and high carbon dioxide contents, representing deep circulating waters. The second group, discharging from the northern flanks of the volcano, was represented by lower temperatures and low TDS contents, which probably resulted from i) weak interaction of these groundwaters with deep rising volcanic volatiles, and ii) the shallow circulation depth. In waters from Group 1, no seasonal variation was observed and the fairly constant trend in T, pH, chemistry and oxygen isotope composition of the waters were attributed to the considerable isolation of these groundwaters from the surface (supported by the low TU contents, 0-7 TU), pointing to the existence of a deep reservoir having a long hydrologic circuit and hardly affected by any seasonal variation. In groundwaters from group 2, on the other hand, temporal variations were recorded in the water chemistry and they were attributed either to seasonal variations, anthropogenic effects or mixing of different types of waters. The waters from Group 2 responded seasonal effects due to their shallow circulation and contact with the surface, which is further supported by high TU contents (> 7 TU). The variations in water chemistry, especially in the Olivella cold spring, characterized by a short hydrologic circuit, revealed synchronous variations in temperature, pH and major ion contents, which were attributed to variable meteoric input over the hydrological year. Variations were also related to mixing of different water bodies in Vesuvius volcano where small aquifers overlap. A systematic shift from Ca bicarbonate to alkali chloride-sulphate composition was observed in several sites highlighting the effects of mixing of different water bodies controlled by either time fluctuations in hydrological mass budget or local variations in permeability due to rock fracturing prior to or during seismic energy release. During the monitoring study, in response to the October 1999 earthquake, seismicity related variations covering a great decrease in pH, a corresponding

fall in redox potential (related to the presence of H_2S in the gas phase), an increase in dissolved CO_2 and a rise in $^3He/^4He$ ratio were detected in the Olivella cold spring from Group 2, with values later turning back to their original levels. These variations in the corresponding spring were attributed to enhanced magmatic influx of CO_2 and He to the aquifer feeding the spring, through rock fracturing and increased permeability, associated with the seismic phase. The rock fracturing process is thought to be reason behind the ascending of deep rising volatiles through the fault cutting the volcano close to the emergence of the Olivella spring. Moreover, the variations in He ratios, a couple of months before the earthquake, revealed increasing crustal contribution which was attributed to increase in pressure build up before the earthquake.

In Turkey, following the 1999 earthquakes in Düzce and Izmit, geochemical monitoring studies have been started by several researchers and institutions. Included in these are the soil radon gas measurements carried out by TUBITAK-MAM laboratories the in Marmara region (İnan et al., 2003 a,b), the anion-cation and stable isotope ratio measurements performed by Hacettepe University in Efteni (Şimşek and Karakuş, in press), and the $^3He/^4He$, $^{13}C/^{12}C$, $^{18}O/^{16}O$, D/H, ^3H and anion-cation measurements carried out by Middle East Technical University (in colloboration with Scripps Institution of Oceanography, Osmangazi University and State Hydraulic Works of Turkey) along the NAFZ from Yalova to Tokat (Gulec et al., 2002; Gulec et al., in press).

CHAPTER 3

THE NORTH ANATOLIAN FAULT ZONE: TECTONIC SETTING AND RECENT SEISMIC ACTIVITIES

3.1. Tectonic Setting

The North Anatolian Fault Zone (NAFZ) (Figure 3.1) is one of the most important features representing the neotectonic period of Turkey which has been governed since the late Miocene by the collision and further convergence of the Arabian Block in the south, and the Eurasian block in the north (Mc Kenzie, 1972; Dewey and Şengör, 1979). The NAFZ is a broad arc-shaped dextral strike-slip fault system, a few hundreds to 40 km wide, consisting of several parallel to subparallel fault segments extending about 1500 km from mainland Greece in the west to Karlıova triple junction in the east of Turkey (Bozkurt, 2001 and the references therein). In addition to the NAFZ, the other neotectonic features that originated from the post-collisional convergence are the East Anatolian Fault Zone (EAFZ), Bitlis Suture Zone (BSZ) and the Western Anatolian Graben System (WAGS) (Inset map of Figure 3.1). The EAFZ is a 550 km long sinistral left lateral strike-slip fault zone extending from Karlıova, where it forms a triple junction with the NAFZ, to Kahramanmaraş triple junction in the southwest where it intersects the Dead Sea Fault (references in Bozkurt, 2001). The Bitlis Suture Zone extends from the southeastern Turkey to the Zagros mountains in Iran (Şengör and Yılmaz, 1981). During the early to middle Miocene, collision of Arabia and Eurasia started along the Bitlis Suture Zone (Şengör and Yılmaz, 1981). The Western Anatolian Graben System is an area of intense seismic activity which is related

to the east-west trending graben complexes in the Aegean region. It consists of several grabens and horsts bounded by oblique E-W trending normal faults.

The NAFZ has a definitive trace about 900 km between Karlıova in the east and Dokurcun town in the west, and it bifurcates into two strands, the northern and southern strands known as the Adapazarı and Geyve fault zones, respectively (Koçyiğit, 1988). The age of the NAFZ is highly debated, covering the range of Middle Miocene-Early Pliocene (see Bozkurt, 2001 for a review). The total offset along the NAFZ is estimated as ranging between 85 ± 5 km and 20-25 km by various studies (Şengör, 1979, Şaroğlu, 1988, Toprak, 1988, Koçyiğit, 1989, Rojay, 1993, Dirik, 1993, Barka, 1992; Tüysüz et al., 1998).

3.2. Recent Seismic Activities

The North Anatolian Fault Zone is one of the most active systems and one of the best known strike slip faults in the world creating several small to large scale earthquakes along its length. The most destructive earthquakes that occurred throughout the history of the NAFZ with magnitudes greater than 6.7, and resulting in more than 1000 km surface rupture along the fault, are the 1939 Erzincan (M: 7.9.), 1942 Erbaa-Niksar (M: 6.9), 1943 Tosya (M: 7.7), 1944 Bolu-Gerede (M: 7.5), 1957 Abant (M: 6.8), 1967 Mudurnu valley (M: 7.0), 1992 Erzincan (M: 6.5), the recently occured 1999 İzmit and Düzce earthquakes (Bozkurt, 2001). The 1999 İzmit (17 August 1999, M: 7.4, depth 17 km) and Düzce (12 November 1999, M: 7.2, depth 10 km) earthquakes, that occurred successively within less than 3 months, resulted in more than 25,000 fatalities in the region. The İzmit earthquake occurred with two successive shocks at the epicenters Gölcük and Arifiye, and produced a 137-km long surface rupture (Koçyiğit et al., 1999a) between Gölcük in the west and Gölyaka in the east. The Düzce earthquake created a surface rupture along a 40-km segment of NAFZ from Gölyaka eastwards (Koçyiğit et al., 1999b; Çemen et al., 2000) (Figure 3.1).

The earthquakes that occurred during the course of this monitoring study all have magnitutes below 5.0. The seismic activities, that occurred between early 2002 and late 2003 periods with epicenters close to the sampled geothermal fields along the NAFZ, are given in Table 3.1 and shown in Figure 3.1. As can be seen from Figure 3.1, the density of the earthquakes are higher in the western and central segments, compared to those in the eastern segment of the NAFZ. Of these, the ones that gained the attention most (in terms of possible connections to water chemistry – chapter 8) are 23.3.2002 Marmara Sea (M: 4.7), 3 & 13.7.2002 Armutlu-Yalova (M: 3.1), 14.7.2002 Yığılca-Bolu (M: 3.1), 15.7.2002 Yığılca-Düzce (M: 2.8), 21.10.2002 Bolu (M: 2.6), 1.11.2002 Mudurnu-Bolu (M: 3.4), 11.5.2003 Gölyaka-Düzce (M: 2.8), 26.6.2003 Gümüşhacıköy-Amasya (M: 3.4), 22.7.2003 Çınarcık-Yalova (M: 3.5), 24.7.2003 Armutlu-Yalova (M: 3.3), 25.7.2003 Yığılca-Düzce (M: 3.1-4.0), and 1.8.2003 Gölyaka-Düzce (M:2.3) earthquakes.

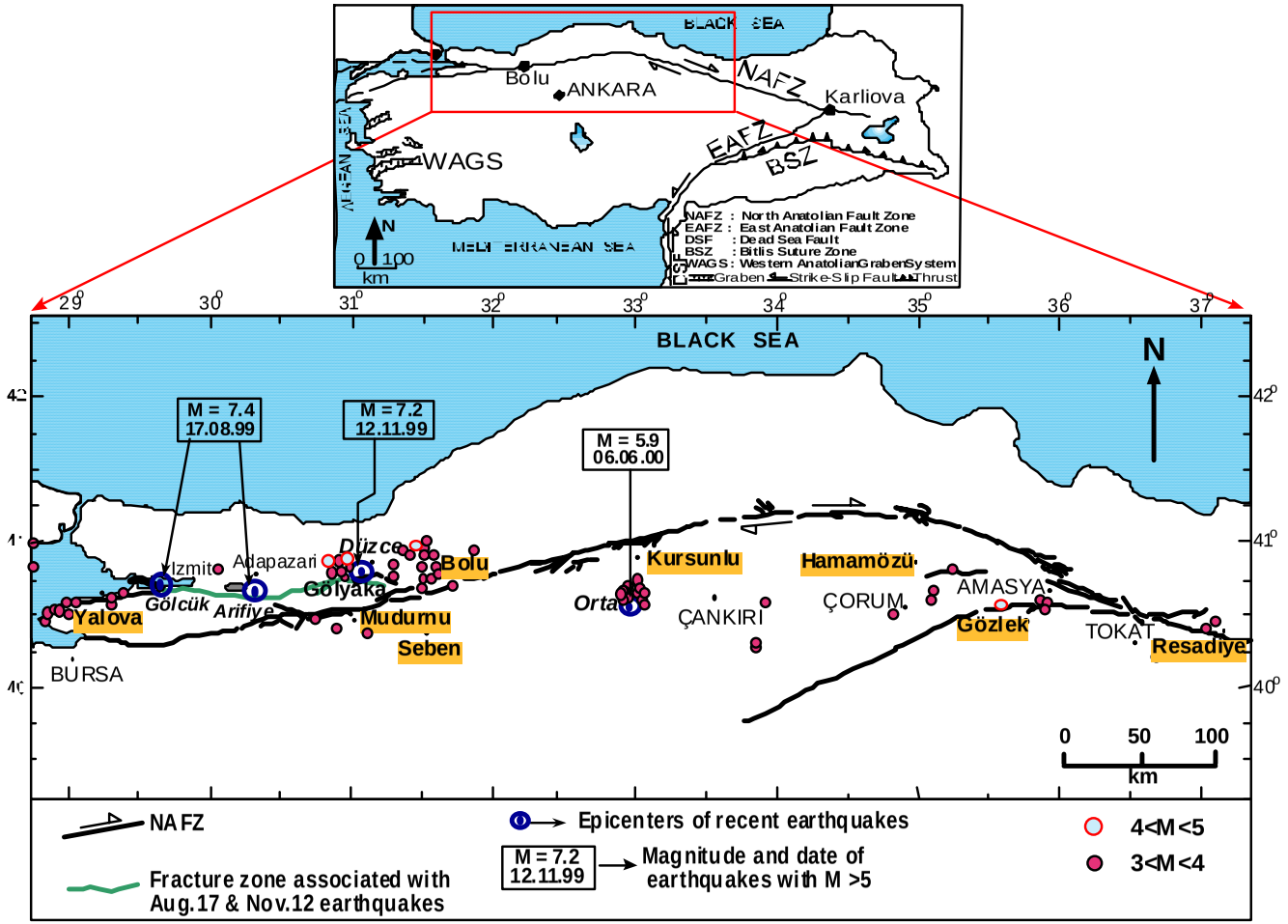


Figure 3.1. Recent seismic activities (2002-2003) along the NAFZ, close to the sampled geothermal fields.

Table 3.1. List of earthquakes that occured between 04.01.2002 - 1.11.2003 (from the web site of the Turkish General Directorate of Disaster Affairs, Earthquake Research Department: http://deprem.gov.tr)

DATE	LATITUDE (N)	LONGITUDE (E)	DEPTH (Km)	MAGNITUDE (Md)	SITE
04.01.2002	40.21	34.28	02,2	3,1	Sungurlu-ÇORUM
04.01.2002	40.95	30.93	04,6	3,4	Cumayeri-BOLU
10.01.2002	40.79	30.97	05,8	3,2	Gölyaka-DÜZCE
11.01.2002	40.78	31.50	04,0	3,2	BOLU
11.01.2002	40.71	31.50	05,9	2,3	BOLU
15.01.2002	40.58	33.00	05,3	2,6	Orta-ÇANKIRI
20.01.2002	40.62	32.98	07,4	3,5	Çerkeş-ÇANKIRI
26.01.2002	41.17	34.23	20,6	2,8	Kargı-ÇORUM
29.01.2002	40.92	31.39	11,0	3,1	Yığılca-DÜZCE
30.01.2002	40.88	31.57	03,0	3,1	Yığılca-DÜZCE
31.01.2002	40.48	30.76	07,5	3,1	Göynük-BOLU
01.02.2002	41.06	34.25	04,8	3,3	Kargı-ÇORUM
03.02.2002	40.10	35.66	12,2	4,2	TOKAT
01.03.2002	40.64	32.86	17,0	2,8	Çerkeş-ÇANKIRI
01.03.2002	40.81	34.85	08,0	2,7	Laçin-ÇORUM
23.03.2002	39.49	28.81	01,0	4,7	Marmara Denizi
25.03.2002	40.97	28.74	11,1	3,1	Marmara Denizi
02.04.2002	40.59	29.23	02,0	2,8	Marmara Denizi
05.04.2002	40.68	32.96	05,1	3,9	Orta-ÇANKIRI
30.04.2002	40.27	33.86	01.0	3.6	Kızılırmak CANKIRI
30.04.2002	40.27	33.86	01.0	3.6	Kızılırmak-ÇANKIRI
02.05.2002	40.68	32.70	02.0	2.7	Çerkeş-ÇANKIRI
04.05.2002	40.04	34.61	12.2	3.3	Sungurlu-ÇORUM
04.05.2002	40.72	31.67	08.3	3.4	BOLU
08.05.2002	41.01	31.20	01.0	2.7	Akcakoca-BOLU
12.05.2002	40.56	28.78	10.5	3.0	Armutlu - YALOVA
14.05.2002	40.60	32.96	12.4	2.8	Orta - ÇANKIRI
14.05.2002	40.43	28.72	12.5	3.2	Armutlu - YALOVA
17.05.2002	40.70	31.64	03.6	2.3	BOLU
29.05.2002	40.88	34.55	10.6	3.2	Oguzlar - CORUM
09.06.2002	40.60	32.99	05.8	4.0	Orta - ÇANKIRI
19.06.2002	40.04	35.94	09.3	3.3	Sulusaray-TOKAT
02.07.2002	40.74	33.04	04.0	2.4	Atkaracalar ÇANKIRI
03.07.2002	40.57	28.94	05.0	3.1	Armutlu - YALOVA
12.07.2002	41.13	34.43	04.0	2.9	Kargı - ÇORUM
12.07.2002	41.12	34.43	03.5	2.6	Kargı - ÇORUM
13.07.2002	40.57	28.94	05.0	3.1	Armutlu - YALOVA
14.07.2002	40.89	31.34	09.6	3.1	Yığılca - BOLU
14.07.2002	41.17	31.46	14.2	2.6	Akçakoca - BOLU

Table 3.1. (continued).

DATE	LATITUDE (N)	LONGITUDE (E)	DEPTH (Km)	MAGNITUDE (Md)	SITE
15.07.2002	41.35	31.55	01.0	2.8	Yığılca - DÜZCE
15.07.2002	40.82	33.09	01.0	2.8	Atkaracalar - ÇANKIRI
23.07.2002	40.72	35.21	01.0	2.5	Gümüşhacıköy - AMASYA
27.07.2002	40.52	32.92	01.0	2.5	Orta-ÇANKIRI
04.08.2002	40.18	31.11	12.8	3.3	Sungurlu-ÇORUM
06.08.2002	40.64	32.99	01.6	2.4	Orta-ÇANKIRI
11.08.2002	40.59	33.01	03.8	3.6	Orta-ÇANKARA
14.08.2002	40.04	34.72	08.0	3.6	Boğazkale-ÇORUM
21.08.2002	40.67	32.95	01.0	2.8	Orta-ÇANKIRI
22.08.2002	40.57	33.00	04.6	2.4	Orta-ÇANKIRI
26.08.2002	40.84	31.05	10.4	3.6	DÜZCE
29.08.2002	40.66	32.97	01.6	3.1	Orta-ÇANKIRI
31.08.2002	40.73	31.49	06.0	3.3	BOLU
08.09.2002	40.45	32.98	12.4	2.1	Orta-ÇANKIRI
02.09.2002	40.95	29.01	06.3	2.3	Kadıköy-İstanbul
10.09.2002	40.55	32.95	02.0	2.7	Orta-ÇANKIRI
10.09.2002	40.81	33.05	05.7	2.7	Atkaracalar-ÇANKIRI
12.09.2002	41.09	33.76	08.3	2.9	Ilgaz-ÇANKIRI
12.09.2002	40.99	33.41	04.2	2.6	Ilgaz-ÇANKIRI
16.09.2002	41.12	34.22	07.3	3.4	Kargı-ÇORUM
21.09.2002	40.58	32.99	13.6	2.6	Orta-ÇANKIRI
28.09.2002	40.53	33.00	05.6	2.2	Orta-ÇANKIRI
11.10.2002	40.88	31.42	10.0	3.1	Yığılca-DÜZCE
16.10.2002	40.64	32.98	01.0	2.4	Orta-ÇANKIRI
16.10.2002	40.66	32.99	01.0	3.0	Orta-ÇANKIRI
17.10.2002	40.68	33.01	01.2	2.5	Orta-ÇANKIRI
18.10.2002	40.60	33.00	05.0	2.8	Orta-ÇANKIRI
19.10.2002	41.02	33.46	08.7	3.2	Ilgaz-ÇANKIRI
20.10.2002	40.10	34.32	02.5	3.3	Sungurlu-ÇORUM
21.10.2002	40.89	31.76	01.2	2.6	Merkez-BOLU
22.10.2002	40.64	32.97	03.0	2.9	Orta-ÇANKIRI
22.10.2002	40.69	32.94	01.2	3.4	Çerkeş-ÇANKIRI
27.10.2002	40.80	30.59	05.4	2.6	Hendek-SAKARYA
27.10.2002	40.86	30.60	07.8	2.7	Hendek-SAKARYA
27.10.2002	40.86	30.60	05.1	2.9	Hendek-SAKARYA
27.10.2002	40.86	30.60	07.4	2.5	Hendek-SAKARYA
27.10.2002	40.80	30.62	07.2	2.5	Hendek-SAKARYA
31.10.2002	40.52	32.94	06.0	3.0	Orta-ÇANKIRI
01.11.2002	40.36	31.19	04.8	3.4	Mudurnu-BOLU
04.11.2002	40.62	32.95	05.0	2.6	Orta-ÇANKIRI
07.11.2002	40.69	31.61	01.0	2.9	Merkez-BOLU
10.11.2002	40.79	31.53	03.3	3.4	Merkez-BOLU

Table 3.1. (continued).

DATE	LATITUDE (N)	LONGITUDE (E)	DEPTH (Km)	MAGNITUDE (Md)	SITE
18.11.2002	40.76	29.92	09.0	3.1	İzmit-KOCAELİ
18.11.2002	40.68	32.89	03.2	2.5	Orta-ÇANKIRI
19.11.2002	40.91	31.60	10.6	3.7	Yığılca-BOLU
20.11.2002	40.57	30.42	06.1	2.6	Karapürçek-SAKARYA
22.11.2002	41.18	34.58	04.6	2.6	Kargı-ÇORUM
23.11.2002	40.86	31.55	04.8	3.2	Merkez-BOLU
29.11.2002	40.57	29.03	07.2	3.0	Çınarcık-YALOVA
03.12.2002	40.73	31.24	05.5	2.9	DÜZCE
05.12.2002	40.48	32.94	06.6	2.6	Orta-ÇANKIRI
13.12.2002	40.24	36.76	06.0	3.4	Almus-TOKAT
13.12.2002	40.60	33.07	06.0	3.2	Orta-ÇANKIRI
19.12.2002	40.88	31.48	04.4	3.3	Yığılca-DÜZCE
20.12.2002	40.76	35.29	13.7	3.1	Gümüşhacıköy-AMASYA
20.12.2002	40.74	35.24	05.0	3.0	Gümüşhacıköy-AMASYA
22.12.2002	40.69	29.44	09.8	3.2	Altınova-YALOVA
24.12.2002	40.65	30.69	05.3	3.2	Akyazı-SAKARYA
04.01.2003	40.84	31.64	02.0	3.2	BOLU
04.01.2003	40.62	33.02	18.4	2.7	Orta-ÇANKIRI
04.01.2003	40.62	33.13	03.7	2.6	Orta-ÇANKIRI
10.01.2003	40.62	33.02	05.8	3.0	Orta-ÇANKIRI
11.01.2003	40.60	33.00	12.4	2.2	Orta-ÇANKIRI
13.01.2003	40.64	32.98	05.3	2.8	Orta-ÇANKIRI
13.01.2003	41.01	33.32	08.2	2.5	Bayramören-ÇANKIRI
14.01.2003	40.58	29.33	10.3	2.8	Termal-YALOVA
14.01.2003	40.46	33.00	05.1	2.5	Orta-ÇANKIRI
17.01.2003	40.40	34.94	08.6	2.7	ÇORUM
18.01.2003	40.74	32.99	06.1	2.6	Atkaracalar-ÇANKIRI
20.01.2003	40.59	29.27	15.0	2.8	YALOVA
21.01.2003	40.65	29.27	05.1	3.0	YALOVA
21.01.2003	40.64	29.26	09.0	2.8	YALOVA
23.01.2003	40.55	32.96	03.0	2.6	Orta-ÇANKIRI
23.01.2003	40.55	32.92	01.0	2.3	Orta-ÇANKIRI
23.01.2003	40.63	33.04	03.0	2.3	Orta-ÇANKIRI
27.01.2003	40.59	33.79	03.4	3.0	Yapraklı-ÇANKIRI
28.01.2003	40.70	32.97	05.8	3.3	Atkaracalar-ÇANKIRI
30.01.2003	40.69	30.50	05.1	3.2	Karapürçek-SAKARYA
31.01.2003	40.80	30.88	06.9	3.4	Gümüşova-DUZCE
31.01.2003	40.64	32.95	03.7	3.7	Orta-ÇANKIRI
03.02.2003	40.63	33.07	09.3	3.1	Orta-ÇANKIRI
13.02.2003	40.46	33.04	06.5	3.6	Orta-ÇANKIRI
13.02.2003	40.73	31.55	08.3	2.7	Merkez-BOLU
14.02.2003	40.57	33.02	04.5	3.6	Orta-ÇANKIRI

Table 3.1. (continued).

.

DATE	LATITUDE (N)	LONGITUDE (E)	DEPTH (Km)	MAGNITUDE (Md)	SITE
17.02.2003	40.48	34.31	16.0	3.3	Uğurludağ-ÇORUM
21.02.2003	40.80	30.89	10.6	2.8	Gölyaka-BOLU
28.02.2003	40.63	29.14	02.9	3.1	Çınarcık-YALOVA
09.03.2003	40.50	33.05	06.6	2.6	Orta-ÇANKIRI
10.03.2003	40.71	30.65	01.0	3.6	Akyazi-SAKARYA
10.03.2003	40.73	30.62	01.0	2.6	Akyazi-SAKARYA
10.03.2003	40.73	30.59	10.2	2.9	Akyazı-SAKARYA
10.03.2003	40.70	30.64	16.2	3.5	Akyazı-SAKARYA
11.03.2003	40.88	31.62	03.7	2.9	Yığılca-DÜZCE
11.03.2003	40.85	30.64	09.9	3.1	Hendek-SAKARYA
11.03.2003	40.21	34.60	06.3	3.0	Boğazkale-ÇORUM
12.03.2003	40.70	33.98	01.2	3.1	Yapraklı-ÇANKIRI
12.03.2003	40.54	33.05	09.2	3.7	Orta-ÇANKIRI
18.03.2003	40.60	32.99	13.0	2.5	Orta-ÇANKIRI
25.03.2003	40.66	30.59	01.0	2.8	Akyazi-SAKARYA
25.03.2003	40.44	33.29	04.6	2.7	Şabanözü-ÇANKIRI
26.03.2003	40.75	30.62	10.1	2.9	Akyazı-SAKARYA
02.04.2003	40.78	28.63	10.6	3.4	MarmaraDenizi
02.04.2003	41.00	30.84	05.4	3.2	Kocaali-SAKARYA
10.04.2003	40.45	30.90	38.7	3.0	Göynük-BOLU
10.04.2003	40.62	33.07	05.9	2.2	Orta-ÇANKIRI
10.04.2003	40.58	33.04	11.2	2.2	Orta-ÇANKIRI
10.04.2003	40.60	33.00	06.7	3.5	Orta-ÇANKIRI
10.04.2003	40.61	33.01	03.8	3.7	Orta-ÇANKIRI
10.04.2003	40.68	33.11	04.1	2.9	Orta-ÇANKIRI
11.04.2003	40.60	33.01	02.3	2.5	Orta-ÇANKIRI
11.04.2003	40.63	33.01	07.3	2.3	Orta-ÇANKIRI
11.04.2003	40.62	33.02	01.9	3.0	Orta-ÇANKIRI
12.04.2003	40.60	33.00	01.0	2.5	Orta-ÇANKIRI
22.04.2003	40.69	32.96	01.0	2.7	Orta-ÇANKIRI
26.04.2003	40.93	34.35	05.8	2.8	İskilip-ÇORUM
11.05.2003	40.82	30.86	06.8	2.8	Gölyaka-DÜZCE
11.05.2003	40.84	30.81	04.7	2.6	Gümüşova-BOLU
15.05.2003	40.64	35.91	10.1	3.4	Merkez-AMASYA
15.05.2003	40.64	35.92	10.6	3.5	Merkez-AMASYA
16.05.2003	40.44	33.01	18.0	2.5	Orta-ÇANKIRI
19.05.2003	40.57	33.06	01.2	2.9	Orta-ÇANKIRI
21.05.2003	40.84	30.95	16.2	4.0	Gümüşova-BOLU
22.05.2003	40.60	33.02	02.5	3.4	Orta-ÇANKIRI
23.05.2003	40.59	33.01	08.0	3.5	Orta-ÇANKIRI
26.05.2003	40.68	33.95	02.0	3.2	Orta-ÇANKIRI
27.05.2003	40.82	31.01	05.0	3.9	Gölyaka-DÜZCE
27.05.2003	40.52	33.50	04.0	2.9	Eldivan-ÇANKIRI
27.05.2003	40.82	31.00	05.3	3.7	Gölyaka-DÜZCE
16.06.2003	40.58	33.00	02.8	2.9	Orta-ÇANKIRI
25.06.2003	40.68	33.48	01.0	2.7	Korgun-ÇANKIRI
26.06.2003	40.79	35.25	06.1	3.4	Gümüşhacıköy-AMASYA
01.07.2003	40.82	31.31	10.7	3.2	Kaynasli-DUZCE
04.07.2003	40.68	33.01	05.6	3.2	Orta-ÇANKIRI

Table 3.1. (continued).

DATE	LATITUDE (N)	LONGITUDE (E)	DEPTH (Km)	MAGNITUDE (Md)	SITE
16.07.2003	40.74	32.99	04.6	3.4	Çerkeş-ÇANKIRI
22.07.2003	40.62	29.00	08.7	3.5	Çınarcık-YALOVA
24.07.2003	40.47	28.82	02.6	3.3	Armutlu-YALOVA
25.07.2003	40.95	31.48	06.9	4.0	Yığılca-DÜZCE
25.07.2003	40.86	31.62	06.1	3.1	Yığılca-DÜZCE
01.08.2003	40.69	31.02	04.6	2.3	Gölyaka-DÜZCE
07.08.2003	40.87	31.79	03.8	3.5	BOLU
12.08.2003	40.61	33.12	15.0	2.9	Orta-ÇANKIRI
15.08.2003	40.50	34.87	09.2	3.0	ÇORUM
16.08.2003	41.07	32.17	08.4	2.9	Mengen-BOLU
17.08.2003	40.34	37.19	05.2	3.0	Reşadiye-TOKAT
17.08.2003	40.44	37.42	10.5	3.6	Reşadiye-TOKAT
20.08.2003	40.61	33.00	01.0	2.8	Orta-ÇANKIRI
21.08.2003	41.13	34.66	10.2	2.6	Kargı-ÇORUM
21.08.2003	41.15	34.66	12.9	3.4	Kargı-ÇORUM
24.08.2003	40.03	35.99	09.3	3.1	Artova-TOKAT
26.08.2003	40.62	32.97	02.4	3.0	Orta-ÇANKIRI
26.08.2003	40.60	32.99	02.2	2.9	Orta-ÇANKIRI
26.08.2003	40.67	32.93	04.2	2.7	Çerkeş-ÇANKIRI
07.09.2003	40.66	33.00	04.5	3.2	Orta-ÇANKIRI
17.09.2003	40.48	32.91	01.0	3.0	Orta-ÇANKIRI
17.09.2003	40.42	33.04	02.4	3.0	Orta-ÇANKIRI
27.09.2003	40.61	35.61	10.6	4.2	Merkez-AMASYA
27.09.2003	40.56	32.99	03.6	3.1	Orta-ÇANKIRI
05.10.2003	40.97	30.97	01.0	3.2	Çilimli-DÜZCE
10.10.2003	40.46	33.08	01.2	3.0	Orta-ÇANKIRI
15.10.2003	40.83	28.75	08.8	2.7	MarmaraDenizi
21.10.2003	40.67	34.45	11.9	2.6	İskilip-ÇORUM
22.10.2003	40.87	31.51	01.0	2.9	Yigilca-DUZCE
23.10.2003	40.58	34.65	13.9	3.1	İskilip-ÇORUM
23.10.2003	40.61	34.61	11.4	3.6	Iskilip-CORUM
31.10.2003	40.21	34.23	06.1	3.0	Sungurlu-ÇORUM
01.11.2003	40.68	34.52	05.3	3.0	İskilip-ÇORUM

CHAPTER 4

GEOTHERMAL FIELDS ALONG THE NAFZ

4.1. Geologic Setting and Regional Geology

Turkey forms an important segment of the Alpine-Mediterranian Belt. The present geologic framework of Turkey was established during the Alpine orogeny as a result of the collision between the African and the Arabian plates. During this orogeny, various suture zones were developed due to the separation, rotation, collision and deformation of small continental fragments (Şengör and Yılmaz, 1981; Okay, 1986; Bozkurt and Mittwede, 2001).

One of the earliest tectonic subdivisions of Turkey was by Ketin (1966) who differentiated 4 major belts, namely, Pontides, Anatolides, Taurides and Border Folds. Later, several subdivisions were proposed by several authors (e.g. Şengör and Yılmaz, 1981; Şengör, 1984; Okay, 1986; Okay and Tüysüz, 1999). The tectonic units differentiated in these subdivision schemes are the microcontinental fragments the boundaries of which are formed by the Neo-Tethyan suture zones.

Figure 4.1 shows the main tectonic units of Turkey based on the division scheme of Şengör (1984). According to this scheme, the major paleotectonic units of Turkey are the Rhodope-Pontide fragment, Sakarya continent, Kırşehir block and the Menderes-Taurus Platform. These units are separated from each other by various Neo-Tethyan suture zones.

In terms of their geologic setting, the geothermal fields studied in this thesis are located in the Rhodope-Pontide fragment and the Sakarya continent.

The Rhodope-Pontide fragment has a complex structure formed by progressive accreation of continental terrains, amalgamating various rock units as Paleozoic metamorphics, ophiolitic melanges representing the remnants of Paleo-Tethys and Neo-Tethys, and Mesozoic to Tertiary sedimentary and magmatic rocks.

The Sakarya continent is bounded to the north by the Intra Pontide, and to the south by the Izmir-Ankara suture zones. The basement consist of unmetamorphosed to variably metamorphosed rocks ranging in age from Late Paleozoic to Late Triassic. The cover rocks are Jurassic to Tertiary clastics and carbonates.

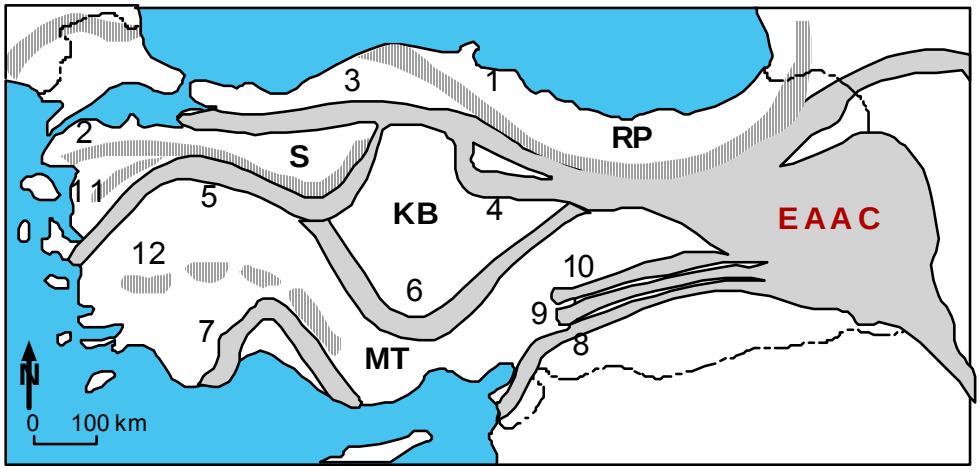


Figure 4.1. Palaeotectonic units and suture zones of Turkey (RP: Rhodope-Pontide Fragment, KB: Kırşehir Block, S: Sakarya Continent, MT: Menderes-Taurus Platform, EAAC: East Anatolian Accretionary Complex, 1: Main Palaeo-Tethys Suture, 2: Karakaya Suture, 3: Intra Pontide Suture, 4: Erzincan Suture, 5: İzmir-Ankara Suture, 6: Inner Tauride Suture, 7: Antalya Suture, 8: Asurid Suture, 9: Çüngüş Suture, 10: Maden Suture, 11: Hercinian Suture, 12: Pan-African Suture) (Şengör, 1984).

4.2. Geologic and Hydrogeologic Outline of Geothermal Fields

4.2.1. Efteni-Gölyaka

Efteni-Gölyaka geothermal field is at about 45 km WNW of Bolu town centre. To the west of Efteni (within 4-5 km distance), Derdin baths are located and both fields are collectively termed in the literature as Efteni-Derdin geothermal field. The field is located in the southern part of the Düzce basin where average yearly precipitation is 852.4 mm, and the average altitude is 100-150 m (Akman, 1966).

Forming part of the Bolu region, the basement in Efteni-Gölyaka field is comprised by the metagranitoids of the Yedigöller Formation (Aydın et al., 1997) which is overlain by the sandstones and limestones of the Paleozoic Kurtköy, Ereğli and Yılanlı formations (Aydın et al., 1997). Mesozoic is represented by Almacık ophiolitic melange (gabbro, serpentinite, peridotite) and Cretaceous flysch consisting of conglomerate, sandstone, marl, limestone, sandy and clayey limestone alternation (Aydın et al., 1997; MTA, 1996). Eocene lava flows, volcanosedimentary rocks and sedimentary flysch (composed of conglomerate, sandstone, clayey-sandy limestone and marl intercalation) overlie this unit unconformably and give wide exposures in the area (Figure 4.1). On top of all these units lies the Pliocene fluvial deposits composed of clay, sandstone and siltstone. (Canik, 1972; MTA, 1996) (Figure 4.2).

The Düzce basin, where Efteni field is located, shows a graben character and numerous faults appear in the north and the south of the basin. Faults are mostly observed in Cretaceous and Eocene formations (Akman, 1966). In the Efteni field, major faults are E-W, NE-SW and NW-SE trending (MTA, 1996) (Figure 4.2). The hot waters discharge from these faults which make up the Düzce segment of the NAFZ.

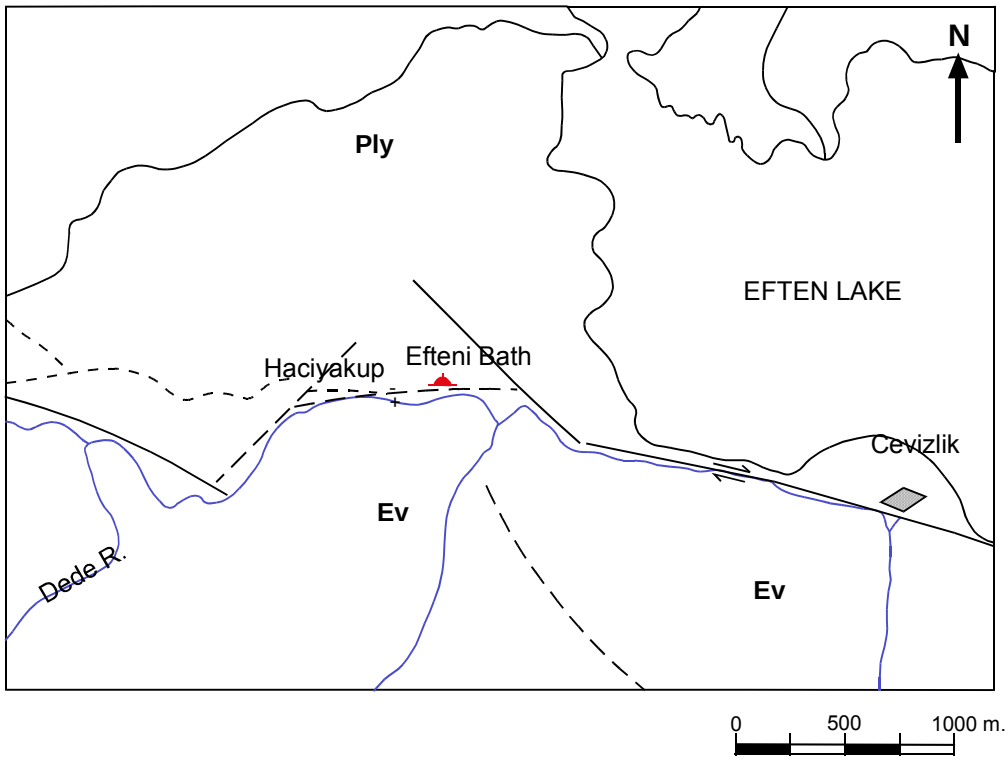
Akman (1966) reports the presence of both confined and unconfined aquifers in Düzce basin. The sand and conglomerate layers of the alluvium are the most important cold water aquifers; the Cretaceous and Eocene flysch, having conglomerate levels, with thicknesses of 8-10 m, are also reported to be suitable groundwater aquifers (Akman, 1966). According to Canik (1972), limestone and sandstone levels in Cretaceous flysch comprise the reservoir rocks, whereas impervious clayey levels form cap rocks of the geothermal system. According to Karakuş (2004), on the other hand, the granodioritic rocks of the Yedigöller Formation (Aydın et al., 1997) and the andesite and basalt layers of Eocene volcanics are the probable reservoir rocks for the Efteni geothermal field.

The temperature of the Efteni and Derdin waters are 42ºC and 31ºC, respectively. The flow rate for Efteni bath is 2-3 l/sec while for Derdin bath flow rate is 4 l/sec. Until now no drilling activity was performed in the area. The hot waters are used for bathing (MTA, 1996). The geothermometry studies done by Yapmış (2002) and Yapmış et al. (in press) indicate reservoir temperatures in a range of 143 to 150 ºC, whereas the studies performed by. Karakuş (2004) estimate temperatures ranging from 90 to 136ºC.

4.2.2. Yalova-Termal

The Yalova thermal baths are located about 15 km southwest of the Yalova town center. Marine climate is observed in the area. Annual precipitation is about 350 mm. Mainly the plant cover is fruit trees.

Paleozoic metamorphic schists comprise the basement in the field. The basement is overlain unconformably by white to yellow coloured Permo–Carboniferous crystalline limestone. Above this layer is the unconformably lying Eocene flysch facies where conglomerate, sandstone, clay and limestone intercalation is observed. Eocene andesites, tuffs and agglomerates overlie the Eocene flysch. Neogene layers cover all these units and start with red conglomerate, marly and clayey layers and end with lacustrine limestone.



EXPLANATIONS

CENOZOIC

- Ply — Claystone-sandstone-siltstone
- Ev — Lava and volcaniclastic sediment
- Strike slip fault
- Fault (uncertain)
- Thermal bath

Figure 4.2. Geologic map of Efteni geothermal field (MTA, 1996).

Quaternary alluvium is the youngest unit (Kartal, 1974a; MTA, 1996) (Figure 4.3).

Major faults in the field are NE-SW and NW-SE trending (Figure 4.3).

In Yalova geothermal field, Eocene andesites and Paleozoic crystalline limestone comprise the reservoir rocks and the Neogene unit acts as the cap rock since they contain marly and clayey layers (Kartal, 1974a; MTA, 1996).

The temperature of hot springs is 66 ºC and the flow rates change between 15-20 l/sec (MTA, 1996). No drilling studies have been performed in the area. The hot waters are mostly used in balneology (rehabilitation), drinking water sectors, greenhouse and space heating**.**

4.2.3. Bolu-Town Center

The thermal baths of Bolu are located about 5 km south of Bolu town center. The effects of both marine and continental climate is observed in the area.

Mesozoic (Upper Cretaceous) olistostromal sedimentary series in flysch facies is the bottommost unit in the area (Upper Cretaceous). Intercalation of Upper Cretaceous limestone-sandstone-marl-claystone is observed at the upper levels of this series. Neogene volcanics (agglomerate and tuff) and lacustrine sediments (intercalations of conglomerate, sandstone and siltstone) overlie these units. Quaternary debris and alluvium are the youngest units in the area (Canik, 1971; MTA, 1996) (Figure 4.4).

Bolu bath is located in an active tectonic province. The general trend of faults passing through the field is ENE-WNW (MTA, 1996). The limestones and volcanics in the area are intensely fractured (Canik, 1971) (Figure 4.4).

Canik (1971) reports the presence of unconfined and artesian type aquifers in the Bolu basin. Upper Cretaceous limestone and sandstone are the

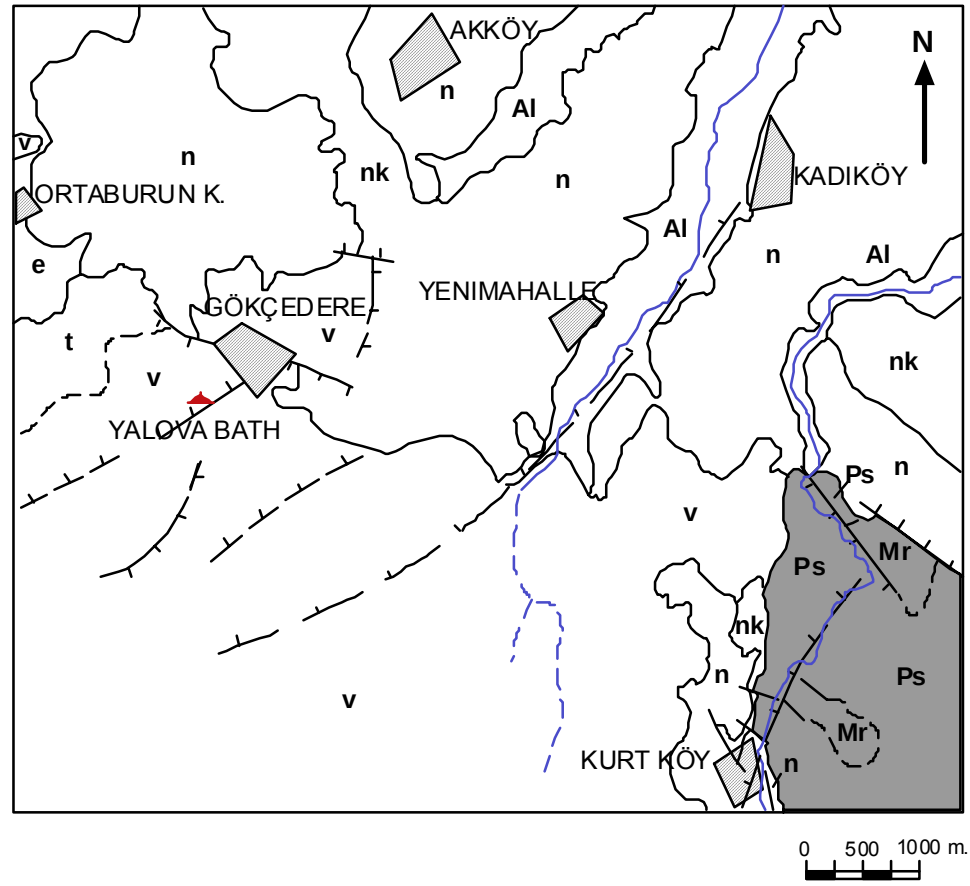
reservoir rocks for the hot waters, and impervious clayey levels act as the cap rock (MTA, 1996).

In the Bolu field, to supply water to the baths, two artesian wells were drilled in 1971 having depths of 83 m (Büyük Bath well) and 97 m (Küçük Bath well). Their temperatures are 45 ^{o}C and 43 ^{o}C and their flow rates are 4.63 and 4.25 l/sec, respectively. Another artesian well was drilled in 1993 by MTA which penetrates to a depth of 758.5 m and has a temperature of 40 ^{o}C and a flow rate of 1.1 l/sec (MTA, 1996). In 1980s, one hot water drilling was made by a private firm called Petrokent but it was later stopped since the water from the artesian wells was affected negatively in terms of flow rate (Yücel et al., 1994; MTA, 1996). In June 2000, another well was drilled 4 m away form the Büyük Bath well, with a depth of 150 m and a flow rate of 30 l/sec. During the production of this well, other wells do not supply water. The geothermometry studies done by Yapmış (2002) and Yapmış et al. (in press) estimate reservoir temperatures ranging from 85 to 88 ºC for Bolu field.

4.2.4. Mudurnu – Babas (Bolu)

Mudurnu-Babas geothermal field is located about 40 km southwest of Bolu and 4 km southwest of Mudurnu town centre. Continental climate is dominant in the region. The area is totally covered with dense forest. Average precipitation in the area is about 520 mm/year.

The stratigraphic succession in the field starts at the bottom with Middle Jurassic–Lower Cretaceous limestone, continues with Upper Cretaceous flysch facies composed of intercalations of limestone, conglomerate, marl, sandstone, claystone and siltstone, and ends up with the Plio-Quaternary alluvium and travertine (MTA, 1996) (Figure 4.5).



EXPLANATIONS

CENOZOIC

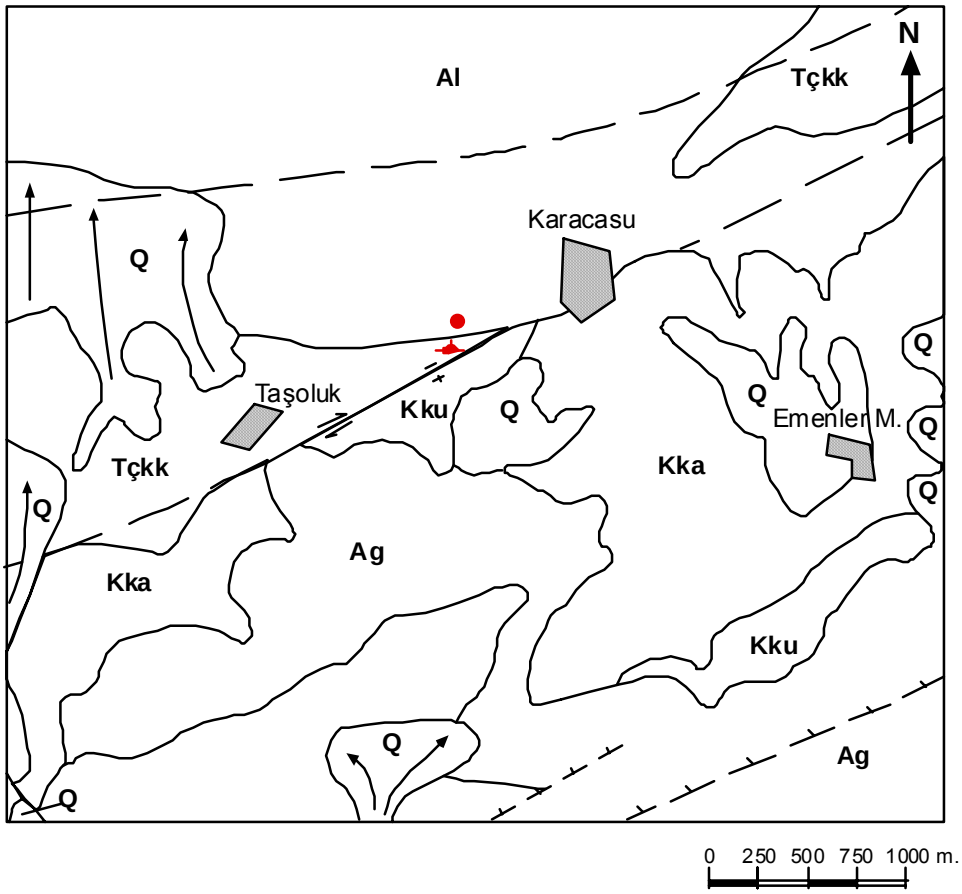
- Quaternary
  - Al — Alluvium
- Neogene
  - nk — Lacustrine limestone
  - n — Conglomerate, lignite bearing marl
- Eocene
  - e — Conglomerate, sandstone, marl, clay
  - v — Andesite
  - t — Tuff, Agglomerate

PALEOZOIC

- Mr — Crystallized limestone
- Ps — Metamorphic schist: graywacke, calc-schist,

- Fault
- Fault (uncertain)
- 33 — Strike and dip
- Thermal bath

Figure 4.3. Geologic map of Yalova geothermal field (MTA, 1996).



EXPLANATIONS

CENOZOIC

- Al — Alluvium
- Q — Alluvial fan
- Q — Talus
- Tçkk — Intercalation of conglomerate, sandstone, claystone
- Ag — Agglomerate-tuff

MESOZOIC

- Kku — Intercalation of limestone, sandstone, claystone, marl
- Kka — Olistrostrom

- Normal fault (uncertain)
- Strike-slip fault
- Thermal bath
- Thermal water drilling

Figure 4.4. Geologic map of Bolu geothermal field (MTA, 1996).

The normal faults in the area are mainly NE-SW trending while reverse faults are E-W trending (MTA, 1996) (Figure 4.5).

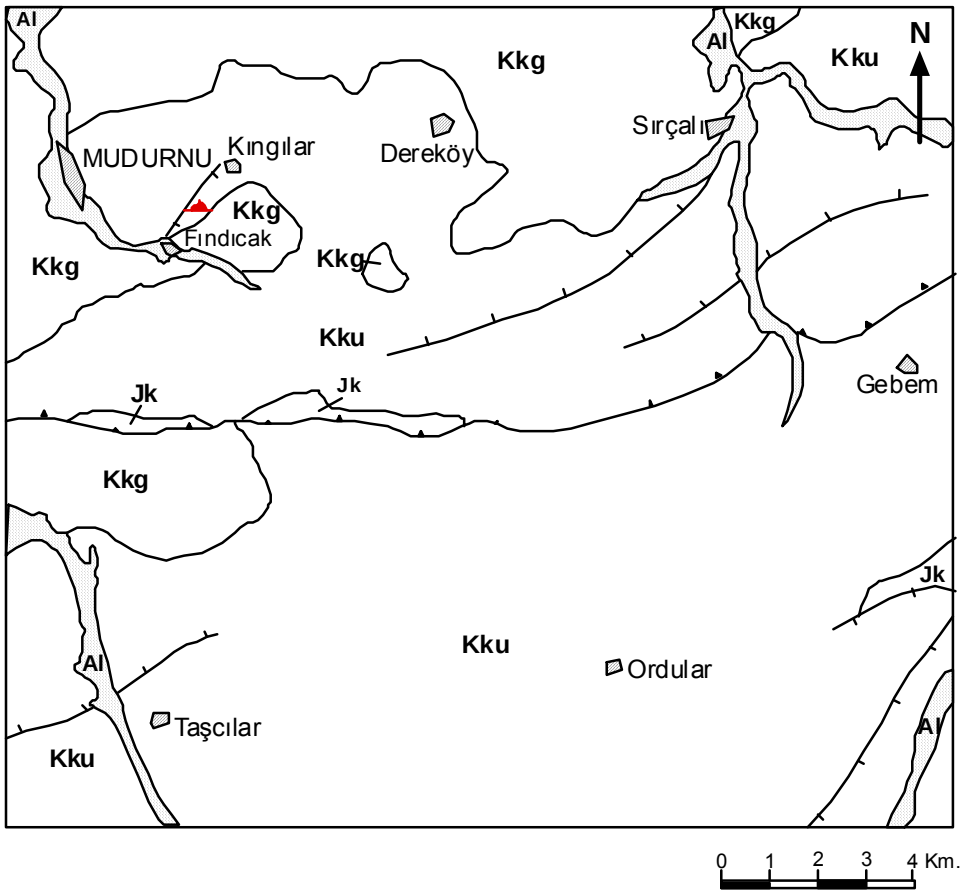
Cold springs issue from various levels of the flysch formation. In the limestone levels of the Cretaceous flysch, groundwater exists but due to very steep topography the water can not be kept in the reservoir and flows directly into the streams (Şahinci, 1970). Quaternary alluvium composed of clay, sand, gravel and silt seems to be the most suitable unit to hold groundwater but still due to its small thickness and the steep topography of the region, the groundwater is drained through the streams (Savaşkan, 1972). The reservoir rock of hot waters is composed of faulted, fractured and karstic Middle Jurassic–Lower Cretaceous limestone. The thick and impermeable layers of flysch facies act as a cap rock for the hot waters. The hot waters passing through the thick layers of the flysch probably mixes with the cold groundwater on their way to the surface (Şahinci, 1970).

The temperature of the Mudurnu thermal waters is between 30 ºC-37 ºC and have a flow rate of 0.5-5.6 l/sec (MTA, 1996). There are two artesian type - 30 m in proximity - drilling wells in Babas. Their depths are 80 m and 125 m and they have temperatures about 38 ºC and 40 ºC, respectively. Thermal water is used for bathing purposes. The geothermometry studies performed by Yapmış (2002) and Yapmış et al. (in press) indicate reservoir temperatures in a range of 77 to 101 ºC for Mudurnu field.

4.2.5. Seben-Kesenözü (Bolu)

Seben–Kesenözü-Pavlu geothermal field is located about 40 km south of Bolu town centre and 10 km southwest of Seben. The area is under the effects of continental climate and is bordered by the Karageriş mountain range in the south and by the Çamlıtepe mountain in the north.

At the basement of the field, Uzun member belonging to Upper Cretaceous Kesenözü formation and composing of sandstone, limestone, marl



EXPLANATIONS

CENOZOIC
- Al — Alluvium

MESOZOIC
- Kkg — Marl
- Kku — Intercalation of limestone, sandstone, marl, claystone
- Jk — Limestone

- Normal fault
- Reverse fault
- Thermal bath

Figure 4.5. Geologic map of Mudurnu geothermal field (MTA, 1996).

and claystone, is observed. The formation continues with marl and sandstone levels of the Güneyce member. The Pliocene Topraklı formation, composed of conglomerate and sandstone, overlies the Kesenözü formation. Quaternary alluvium is the uppermost unit (Müftüoğlu and Akıncı, 1989; Özcan and Ünay, 1978; MTA, 1996) (Figure 4.6).

Major structural faults and folds are E–W trending (MTA, 1996) (Figure 4.6). Also N-S and WNW-ESE trending faults are observed.

The alluvium composed of clay, sand, gravel and silt is the only formation suitable to contain groundwater. However, due to the thin alluvial cover and steep topography of the area, the water is lost from the units and drained into the nearby streams. This reduces the groundwater capacity of the area (Savaşkan, 1972). The limestone and sandstone levels of the Kesenözü Formation form the reservoir rocks in the geothermal field. Impermeable clayey levels of the Kesenözü formation are the cap rocks (Özcan and Ünay, 1978; MTA, 1996).

The temperature of the springs is 74 ºC and flow rate is 4 l/sec**.** There are two pumping wells having 2.5-3 m and 3.5-4 m depths with temperatures being 51 ºC and 58 ºC, respectively. Thermal waters are used for bathing purposes. Reservoir temperatures between 110 to 149 ºC are indicated by Yapmış (2002) and Yapmış et al. (in press) for Seben field.

4.2.6. Hamamözü-Amasya

Hamamözü geothermal field is located near the Gümüşhacıköy-Çorum highway and is 40 km to Çorum. The maximum altitude in the area is 1400 m asl and the altitude of the Hamamözü hot springs is 675 m. In the south of the area there are pine and oak trees, whereas other areas are barren.

Paleozoic clayey schist and meta-sandstone form the basement in the area. Mesozoic aged flysch (claystone, marl, sandstone, siltstone, clayey

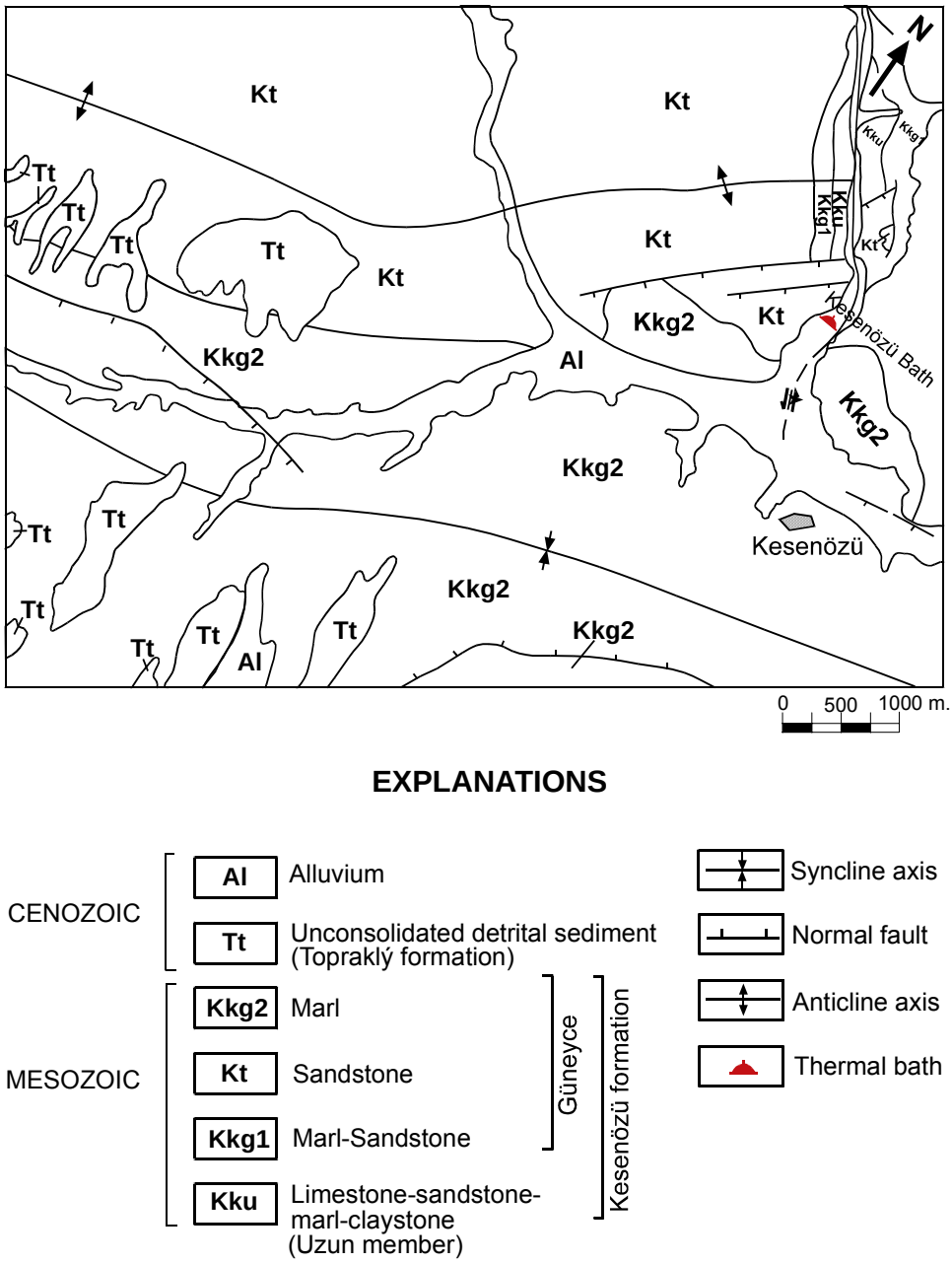


Figure 4.6. Geologic map of Seben geothermal field (MTA, 1996).

and limestone uncoformably overlies the basement rocks. At the upper levels, Cenozoic aged conglomerate, gypsum, sandstone, claystone and siltstone layers are observed. Quaternaty alluvium is the youngest unit in the area and is deposited along the Hamamözü stream. It has a thickness of 40 m and is composed of gravel, clay and silt. In the field, volcanic outcrops such as andesite and basalt type rocks are observed which outcrop from Cretaceous flysch (Koçak, 1976) (Figure 4.7).

Probable fault directions are NE-SW (MTA, 1996) (Figure 4.7). **S**tructural features are very rare in the area. Paleozoic schists show folded structures (Koçak, 1976).

The Mesozoic limestone and Quaternary alluvium show good aquifer characteristics. Hot waters in the area discharge from a probable fault in the alluvium (Koçak, 1976). Mesozoic limestone and secondary permeable zones of meta-schists have reservoir rock characteristics for the geothermal system (Koçak, 1976; MTA, 1996). The hot water rising from the reservoir reaches alluvium and mixes with the groundwater entrapped in pebble levels of alluvium and loses part of its heat.

The hot waters in the field discharge from two springs. The temperature of thermal waters is 40 ºC with 2.80 l/sec flow rate. An artesian well was drilled in 1989 penetrating to a depth of 500 m. It has a temperature of 42.5 ºC and a flow rate of 29 l/sec. The thermal waters in the area are used for balneological purposes (MTA, 1996).

4.2.7. Gözlek-Amasya

The field is located 20 km southwest of Amasya. The area is under the effects of continental climate.

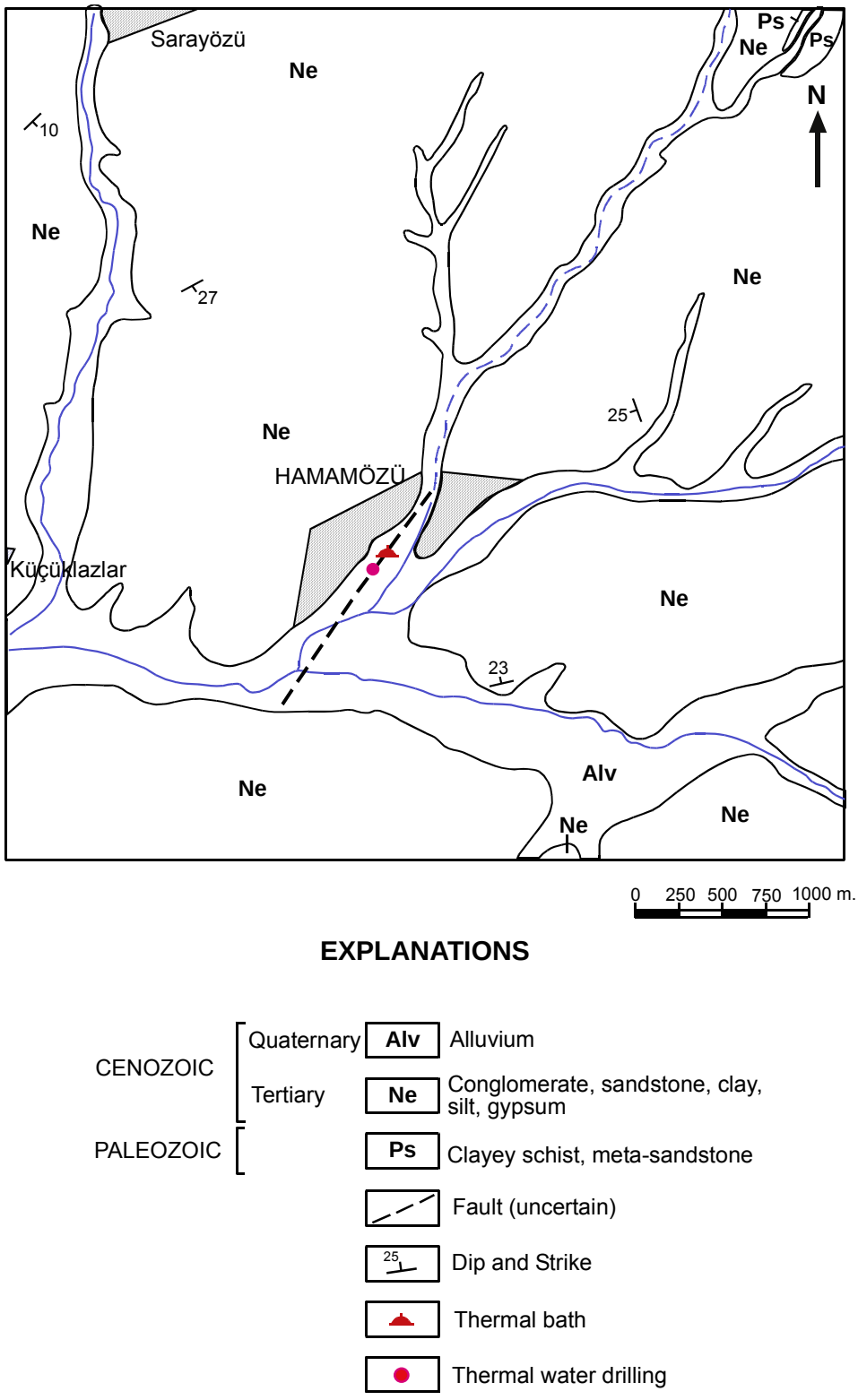


Figure 4.7. Geologic map of Hamamözü field (MTA, 1996).

The oldest unit in the field is the Paleozoic aged metamorphic schists. Upper Jurassic-Lower Cretaceous recrystallized massive limestone unconformably overlies the metamorphic schists. Eocene flysch facies composed of conglomerate, sandstone, marl and claystone intercalation lies unconformably above these units. Quaternary alluvium is the youngest unit in the field (MTA, 1996; Şentürk and Ünay, 1976) (Figure 4.8).

The Paleozoic schists in the area show folds and experienced intense metamorphism. E-W and NNW-SSE trending faults are observed in the area (Figure 4.8).

The conglomerate and sandstone levels of the Eocene flysch and alluvium contain groundwater. The hot springs issue through the fractures and the contacts of the Upper Jurassic-Lower Creatceous limestone (Kartal, 1974b). The main reservoir rock of the hot waters is the Upper Jurassic– Lower Cretaceous recrystallized limestone and the impervious layers of the Eocene flysch act as the cap rock (MTA, 1996). The water coming from the limestone reservoir rises through the NNW-SSE trending fault and produces the hot water spring (Kartal, 1974b; Şentürk and Ünay, 1976).

The thermal waters in the area are 39 ºC and have a flow rate of 2 l/sec. In Gözlek, three wells were drilled. In 1988 an artesian well penetrating to a depth of 398.5 m was drilled. The temperature and flow rate for this well is 40.5 ºC and 10.50 l/sec, respectively. In 1989 and 1991 two pumping wells were drilled with depths 393 m and 530.3 m, respectively. Their temperatures are 40.5 ºC and 35.5 ºC and flow rates are 0.1 l/sec and 0.8 l/sec, respectively. The hot waters are used for bathing (MTA, 1996). The geothermometry studies performed by Yapmış (2002) and Yapmış et al. (in press) indicate reservoir temperatures ranging from 67 to 72 ºC for Gözlek field.

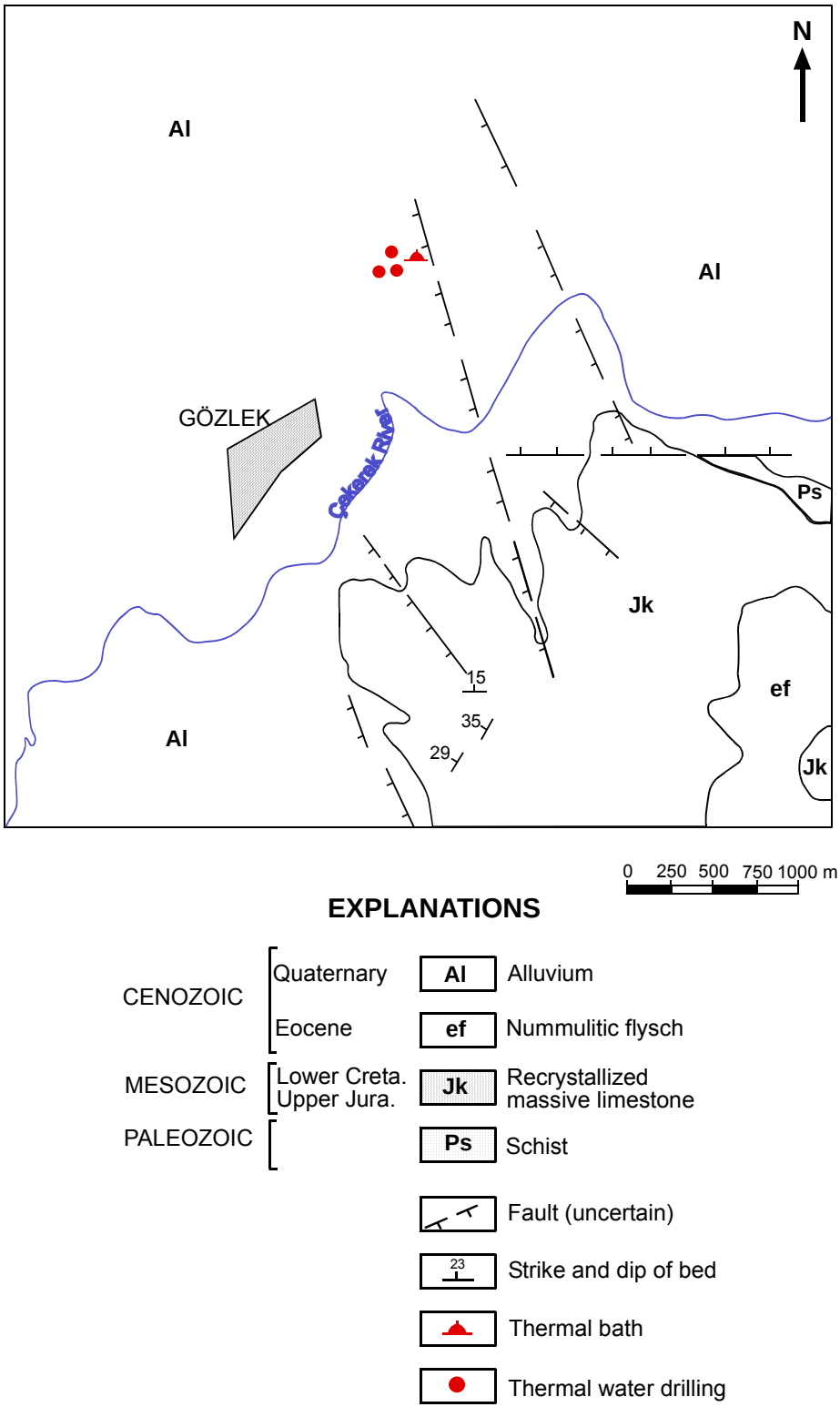


Figure 4.8. Geologic map of Gözlek geothermal field (MTA, 1996).

4.2.8. Reşadiye-Tokat

Reşadiye geothermal field is located about 65 km ENE of Tokat town center, near the Reşadiye–Aybastı highway. Reşadiye field is under the effects of continental climate and is bordered by the Canik mountains in the north and the Köse mountains in the south.

The bottommost unit in the area is the Jurassic–Cretaceous Zinav limestone. The Campanian Nebişeyh limestone having claystone and siltstone layers unconformably overlies the Zinav limestone. Upper Cretaceous flysch, composed of claystone, siltstone, clayey limestone and mudstone, overlies this unit. Paleocene aged Sırakayalar limestone unconformably overlies all the units. The volcanic rocks (andesite, tuff, agglomerate), observed in the field as intercalated with Upper Cretaceous flysch, represent the products of a magmatic activity which started in the Late Cretaceous and continued up to Quaternary. Quaternary alluvium and travertine are the youngest units in the area. Alluvium is composed of sand and gravel and has a thickness of about 60m (MTA, 1996; Erzenoğlu, 1991) (Figure 4.9).

The North Anatolian Fault Zone passes through the Reşadiye geothermal field. The fault is traced for a distance of about 11 km in the area and cuts the Quaternary units. An opening fissure (NW-SE trending) is observed in the bath travertines about 1 km near Reşadiye (Erzenoğlu, 1991) (Figure 4.9).

Quaternary alluvium and Zinav limestone are potential groundwater aquifers. In the NW of Reşadiye, along the Reşadiye-Bereketli highway, there are hot springs with gas emissions alligned along a fracture zone. These springs formed travertines in the area. The reservoir rock for the hot waters is the fractured and permeable Upper Jurassic – Lower Cretaceous Zinav limestone, whereas the clayey and silty levels of the Upper Cretaceous Nebişeyh formation act as a cap rock (Yücel and Özgür, 1992).

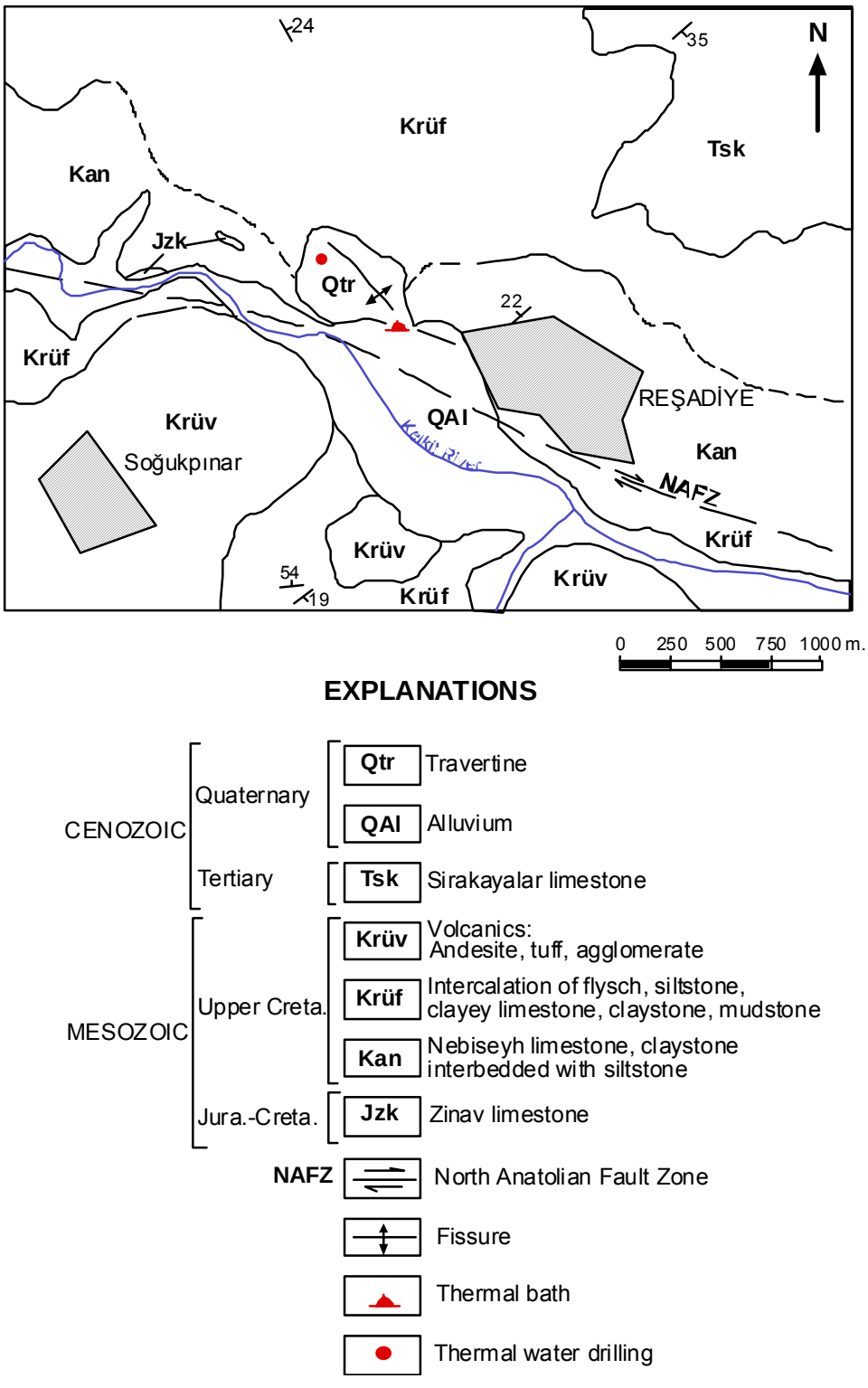


Figure 4.9. Geologic map of Reşadiye geothermal field (MTA, 1996).

In the Reşadiye geothermal field there are several hot water springs alligned along NW–SE trending fracture/fault zones. The flow rate of these waters are 4.3 l/sec and their temperature change between 29.5-48 ºC. Thermal waters are used in baths. An artesian well was opened in 1989 by General Directorate of the Turkish Mineral Research and Exploration (MTA) about 450m NW of the Reşadiye bath. The depth of the well is 238.9 m and has a temperature of 46.5 ºC with a flow rate of 30 l/sec. The water from this well is used to feed the baths in Reşadiye (Yücel and Özgür, 1992). The geothermometry calculations performed by Yapmış (2002) and Yapmış et al. (in press) estimate reservoir temperatures ranging from 97 to 99 ºC for the Reşadiye geothermal field.

4.2.9. Kurşunlu-Çavundur (Çankırı)

Çavundur bath is located about 13 km west of Kurşunlu town and is 45 km northwest of Çankırı. Continental climate is observed in the area. The average altitude is about 1200-1350 m.

The rocks cropping out in the field are all Cenozoic in age and are comprised by the Pliocene tuff, tuffite, agglomerate, basalt and unconsolidated sediments containing gravel, sand, silt, clay and marl. All these units are overlain by Quaternary alluvium and travertine. The travertine is formed over the Çavundur bath as a cone and it is intensely fractured. The fractures within the travertine provide pathways for hot waters to rise. The alluvial cover observed along the Saz and Ulu streams is composed of unconsolidated clay, silt, sand and gravel (MTA, 1996; Koçak, 1974) (Figure 4.10).

The major structural units in the field are E-W and NE-SW trending faults. Also a N-S trending extensional fissure is observed in the field. The volcanic rocks in the field shows a fractured structure (Koçak, 1974; MTA, 1996) (Figure 4.10).

The volcanic rocks in the field are suitable aquifers for groundwater since they have fracture permeability. The clayey and marly levels of the Pliocene act as aquicludes and let the water trapped in gravel levels. The alluvium, on the other hand, is not important in terms of groundwater due to its low thickness. In the field there are hot water springs which are distributed along a NE-SW trending fault. The reservoir rock for the hot waters in the Kurşunlu-Çavundur field is the jointed Pliocene volcanics whereas the clayey and marly levels of the Pliocene act as cap rock. Hot water rising to the surface mixes with the groundwater in the gravel levels of the Pliocene and loses part of its heat. The hot water in the area is probably being heated by a volcanic stock which has not completed its cooling at deeper parts (Koçak, 1974).

The temperature of hot waters is 38 ºC and flow rate is between 0.1-0.2 l/sec. A cold spring and a mineral water is observed near the bath having temperatures of 11 and 20 ºC, respectively. An artesian well was drilled in 1987 by the Turkish Mineral Research and Exploration (MTA) to a depth of 270 m. It has a temperature of 54 ºC and a flow rate of 47 l/sec. Hot waters are used in the baths (MTA, 1996). Reservoir temperatures ranging between 88 to 115 ºC are indicated in the studies performed by Yapmış (2002) and Yapmış et al. (in press) for the Kurşunlu geothermal field.

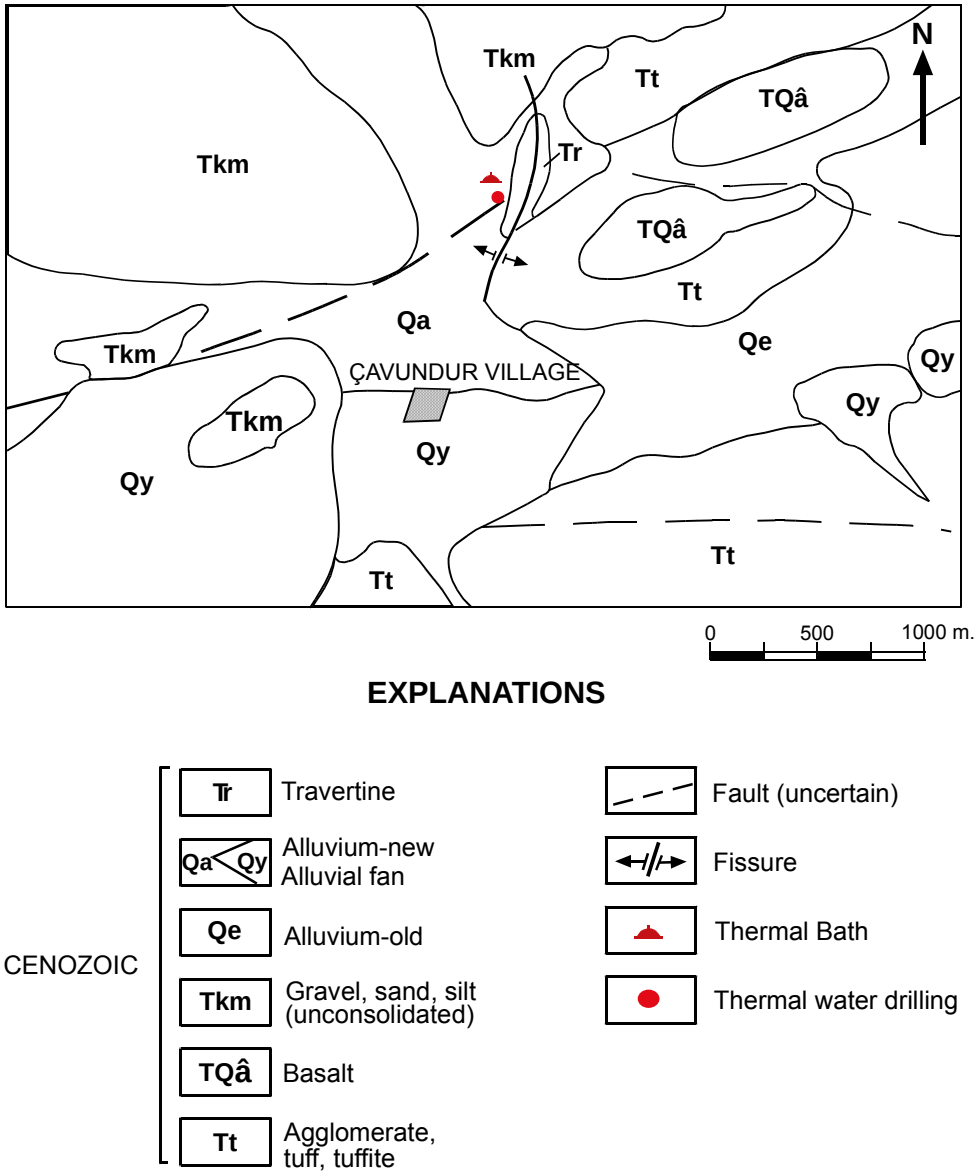


Figure 4.10. Geologic map of Kurşunlu geothermal field (MTA, 1996).

CHAPTER 5

METHODS OF STUDY

5.1. Sampling

The samples from each geothermal field (Figures 5.1 to 5.7) were collected three times per year comprising March-July-October 2002 and April-July-October 2003 periods. Two sets of hot and cold water samples were collected from natural springs and production wells for chemical and isotopic analyses. For Hamamözü and Gözlek fields, cold waters were collected starting from October 2002 sampling period, whereas for Efteni-Gölyaka, Yalova-Termal and Bolu-Karacasu fields, cold waters were collected in 2003 sampling periods. Reşadiye samples were only collected in 2002 sampling periods since the hot spring dried up in October 2002 as a result of over consumption of water in thermal baths. Also for Kurşunlu field, the mineral water sample could not be collected for the last two sampling periods again due to the dried-up spring. Samples other than these were collected for most of the sampling periods.

During the field studies, two sets of 1 litre polyethylene bottles were used (for each sample) separately for chemical and isotopic analyses. The bottles were filled completely until no space was left for a possible air exchange of the water, and sealed with two lids to avoid leaking. Filtering was only performed in Efteni-Gölyaka geothermal field where the water was turbulent and muddy in almost all of the periods. The temperature and pH of the waters were measured directly in the field for each sampling period. The UTM coordinates, on the other hand, were noted for each sampling site using

GPS (Global Positioning System). The samples were then sent to the laboratories of the State Hydraulic Works of Turkey in Ankara within a week to be analysed. The data comprising sample locations, sample numbers, UTM coordinates, temperature, pH and sample types are presented in Table 5.1.

Figure 5.1. A view from the (covered) hot-spring source (sample no. 1a) feeding the bath in the Efteni-Gölyaka geothermal field.

a)

b)

Figure 5.2. Sampling hot water in Yalova: **a)**sample no.2a, **b)** sample no. 2b.

Figure 5.3. Drilling well in Bolu where sample no. 3a is collected.

a)

b)

Figure 5.4. a) Drilling well in Mudurnu where sample no. 4a is collected, **b)** cold water springs (sample nos. 4c and 4d) in Mudurnu.

a)

b)

c)

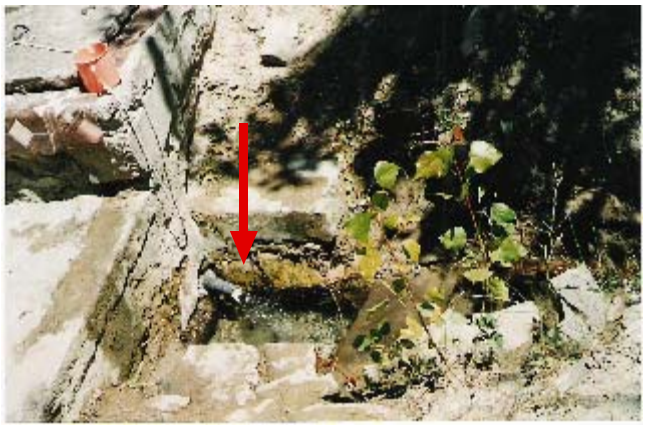


Figure 5.5. a) sampling hot water (sample no. 5a) in Seben, **b)** pumping well in Seben where sample no. 5c is collected**, c)** cold water sample 5d.

a)

b)

Figure 5.6. a) Sampling hot water (sample no. 6a) in Hamamözü, **b)** the fountain constructed over the cold water spring (sample no. 6b) in Hamamözü.

Figure 5.7. Drilling well in Kurşunlu where sample no. 9a is collected.

Table 5.1. Data comprising sample locations, sample numbers, UTM coordinates, temperature, pH and sample types.

Locality	Samp. No.	UTM		March 2002		July 2002		October 2002		April 2003		July 2003		October 2003		Sample Type
		N	E	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	
Efteni-Gölyaka	1a-hot	4514266	333558	42.3	6.47	41.4	7.36	43.4	6.31	43.0	6.22	43.1	6.28	43.3	6.44	Spring
	1b-cold	4514266	333558			-	-	-	-	11.2	8.83	20.0	8.75	12.6	8.60	+Spring
Yalova-Termal	2a-hot	4497215	683618	60.1	7.90	60.6	7.82	56.9	7.67	64.3	7.37	65.0	7.57	63.4	7.66	Spring
	2b-hot	4497156	683718	57.7	7.78	60.4	7.62	60.5	7.39	61.0	7.26	61.1	7.38	59.7	7.53	Spring
	2c-cold	4499094	687703	-	-	-	-	-	-	13.5	7.41	20.0	7.58	18.2	7.82	+Spring
Bolu-Karacasu	3a-hot	4504891	383479	41.6	6.96	41.6	6.24	43.0	6.12	42.5	6.06	43.1	5.92	41.8	6.29	Production Well(P)-83 m
	3b-cold	4504761	383217	-	-	-	-	-	-	6.7	7.47	13.7	7.70	11.6	7.71	©Spring
Babas-Mudurnu	4a-hot	4480254	350839	38.3	6.26	38.3	6.28	44.3	6.24	39.1	6.14	39.2	6.28	39.3	6.29	Production Well(A)-80 m
	4b-hot	4480362	350861	38.5	6.25	38.7	6.32	39.7	6.23	39.7	6.13	39.8	6.29	39.8	6.36	Production Well(A)-125 m
	4c-cold	4480348	350809	19.6	6.90	19.4	6.86	20.2	6.75	19.7	6.67	19.9	6.83	20.0	6.86	+Spring
	4d-cold	4480348	350809	11.3	7.25	15.4	7.13	16.9	6.91	12.2	6.97	15.7	7.07	17.4	7.07	+Spring
Seben-Pavlu	5a-hot	4464959	375960	70.1	6.73	69.9	6.87	72.3	6.46	70.7	6.36	71.8	6.58	72.3	6.77	Spring
	5b-hot	4464896	375887	55.8	6.84	57.3	6.76	59.3	6.48	55.7	6.61	60.0	6.79	58.2	6.86	Production Well(P)-4 m
	‡5c-hot	4464857	375870	35.0	7.25	-	-	47.8	7.14	-	-	53.0	6.69	-	-	Production Well(P)-2.5 m
	‡5d-cold	4464978	375873	13.1	7.32	-	-	15.1	7.30	14.5	7.23	14.5	7.47	15.7	7.40	+Spring

Table 5.1. (continued).

Locality	Samp.	UTM		March 2002		July 2002		October 2002		April 2003		July 2003		October 2003		Sample Type
	No.	N	E	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	¤T(ºC)	pH	
Hamamözü -Amasya	6a-hot	4516721	670722	41.3	7.83	41.1	7.71	42.6	7.24	42.1	7.02	42.7	7.29	42.5	7.30	Production Well(A)-500 m
	6b-cold	4516733	670744	-	-	-	-	15.8	7.57	10.6	7.30	19.3	7.39	17.4	7.77	+Spring
Gözlek-Amasya	7a-hot	4492622	726642	38.4	7.93	38.3	7.97	39.3	7.60	39.6	7.43	38.9	7.96	38.8	7.75	Production Well(A)-400 m
	7b-cold	4492622	726642	-	-	-	-	16.1	7.87	16.3	7.46	17.2	7.53	19.2	7.79	+Spring
‡‡Resadive-Tokat	8a-hot	-	-	41.3	6.44	41.1	6.41	-	-	-	-	-	-	-	-	Spring
	8b-cold	-	-	12.5	7.76	17.4	6.50	15.9	7.61	-	-	-	-	-	-	©Spring
Kurşunlu-Çavundur	9a-hot	4519543	514801	55.9	7.20	55.5	7.10	57.6	6.94	57.4	6.88	57.9	7.11	58.1	7.09	Production Well(A)-165 m
	§9b-hot	4520371	515043	12.6	6.46	14.7	6.43	15.3	6.45	10.6	6.45	-	-	-	-	Spring (mineral water)
	9c-cold	4520464	515048	9.0	8.17	14.9	7.76	13.3	8.06	11.9	7.69	12.5	7.92	13.4	7.95	+Spring

A: Artesian, P: Pumping, numbers for production wells are the depths of producing zones.

¤Temperatures for production wells are well head temperature.

+ taken from the fountain where the water is distributed by pipes from the spring.

©taken from the tap of the distributing pipes (connected to the spring).

‡since mud removal studies (following the heavy rain) were being performed in Seben, no sampling could be done in July 2002 period from localities 5c and 5d; likewise, since the pump was removed from the well, no sampling could be performed in Seben in April 2003 and October 2003 periods from locality 5c.

‡‡since the spring had dried up, no sampling could be performed from Reşadiye in periods following July 2002.

§since the spring had dried up, no sampling could be performed from locality 9b in periods following April 2003

5.2. Analytical Techniques

Chemical analyses (major anions-cations) for the first two sampling periods were carried out in the laboratories of the Department of Geological Engineering in METU and the rest were conducted by the laboratories of the State Hydraulic Works of Turkey in Ankara (DSI). The isotopic analyses of samples, on the other hand, comprising tritium, $^{18}O/^{16}O$ and D/H measurements were performed by the DSI laboratories for all sampling periods.

Anion-cation analyses were performed by conventional methods (titration for Ca, Mg, HCO_3, CO_3 and Cl, flame photometry for Na and K, and spectrophotometry for SO_4).

In measurement of tritium, liquid scintillation counting technique (Packard Tri-Carb 2260 XL) is used. This technique is widely used in measuring the radioactivity amount and in identifying the existence of radiation, and is applied for the identification of every particle and emission formed as a result of nucleus decay (alpha- beta particles, gamma rays).

The first stage in measuring tritium is primary distillation, which involves the purifying of water samples from the unwanted particles and the mineral salts which are found at soluble states. After the first distillation process, electrolysis is performed for the enrichment of the tritium contents of the water samples and then followed by a second distillation process. After this final distillation, 10 ml is taken from each sample and is placed into plastic bottles where they are mixed with 10 ml scintillators. By this way the samples are prepared for the counting stage which lasts for a couple of days (Altay and Çifter, 1996). The measured tritium contents are given together with the analytical errors for each sample. For more precise results, some of the samples were reanalysed.

In the measurement of the stable isotopes of oxygen and hydrogen, Micromass 602C Mass Spectrometer was used. In stable isotope measurements,

SMOW (Standard Mean Ocean Water) is used as a standard for the calculation of per mil deviations of the $^{18}O/^{16}O$ and D/H values. All values are expressed in delta notations, normalised to the standard SMOW. The typical standard uncertainities associated with the analyses are 0.1‰ for $\delta^{18}O$ and 1‰ for δD.

CHAPTER 6

HYDROGEOCHEMICAL CHARACTERISTICS

6.1. Results of Chemical Analyses

The results of the chemical analyses for all sampling periods are given in Table 6.1, which encompasses data from both the hot and the cold water samples.

As can be seen from Table 6.1, the temperatures range between 35-72.3 °C for the hot, and 6.7-20.2 °C for the cold waters. The hot waters are slightly acidic to slightly alkaline in character with pH values ranging between 5.92-7.97, while the cold waters are comparatively more alkaline with pH values between 6.50-8.83. The TDS values (**T**otal **D**issolved **S**olid content) are apparently much higher for the hot waters (ranging up to 12354.3 mg/l) compared to those for the cold waters (ranging up to 996 mg/l). Among all samples, Kurşunlu 9a hot water has the highest TDS value. On the other hand, Hamamözü-6a and Gözlek-7a hot water samples have the lowest TDS contents for different periods, ranging up to 431.4 mg/l and 434.4 mg/l, respectively.

Table 6.1. Results of chemical analyses for all sampling periods comprising all fields (concentrations are in mg/l).

Locality	Sample No.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Efteni	1a-hot	23.03.02	42.3	6.47	-	1835.4	0.0	197.0	1.0	450.0	18.0	164.0	134.9	n.d.	2800.2
		08.07.02	41.4	7.36	-	1792.7	0.0	209.0	1.0	520.0	18.0	104.0	148.2	n.d.	2792.9
		27.10.02	43.4	6.31	3090	1701.9	0.0	205.9	3.6	297.5	13.2	141.0	162.9	19.6	2545.6
		07.04.03	43.0	6.22	3020	1703.7	0.0	200.6	4.6	307.5	12.8	218.8	108.9	n.d.	2556.9
		09.07.03	43.1	6.28	3050	1764.7	0.0	196.3	5.4	347.0	12.0	63.0	193.9	21.0	2603.3
		15.10.03	43.3	6.44	-	1580.0	0.0	198.0	4.8	232.0	11.1	85.6	206.0	155.0	2472.5
	1b-cold	07.04.03	11.2	8.83	195	107.4	0.0	3.3	6.2	1.1	0.2	6.8	24.4	n.d.	149.4
		09.07.03	20.0	8.76	208	86.6	0.0	5.0	4.4	0.6	0.0	8.0	22.4	4.1	131.1
		15.10.03	12.6	8.60	-	72.0	0.0	4.3	8.7	7.6	0.3	10.0	23.7	4.6	131.2
Yalova	2a-hot	24.03.02	60.1	7.91	-	47.6	0.0	101.0	875.0	280.0	6.0	151.2	1.9	n.d.	1462.7
		09.07.02	60.6	7.82	-	28.0	0.0	68.6	950.0	330.0	6.0	154.0	0.5	n.d.	1537.1
		28.10.02	56.9	7.67	1922	30.5	0.0	95.8	816.0	240.5	4.8	162.0	15.8	19.9	1385.3
		08.04.03	64.3	7.37	1902	42.7	0.0	96.9	750.0	242.5	4.7	157.0	7.2	n.d.	1301.0
		10.07.03	65.0	7.57	1913	43.3	0.0	96.6	763.6	208.5	3.7	198.6	2.1	38.8	1355.2
		16.10.03	63.4	7.66	-	80.5	0.0	95.1	820.0	290.0	4.0	153.6	7.3	50.4	1500.9

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Yalova	2b-hot	24.03.02	57.7	7.78	-	45.1	0.0	96.9	925.0	300.0	6.0	150.0	0.5	n.d.	1523.5
		09.07.02	60.4	7.62	-	28.0	0.0	63.7	1025.0	320.0	6.0	154.0	6.1	n.d.	1602.8
		28.10.02	60.5	7.39	1924	45.7	0.0	92.3	778.8	235.0	4.7	163.0	13.4	19.8	1352.7
		08.04.03	61.0	7.26	1894	50.0	0.0	94.8	712.8	239.5	4.8	154.0	0.8	n.d.	1256.7
		10.07.03	61.1	7.38	1920	39.6	0.0	99.4	834.0	212.5	3.7	195.6	20.7	39.8	1445.3
		16.10.03	59.7	7.53	-	75.0	0.0	94.0	739.0	22.3	5.1	156.0	125.0	46.4	1262.8
	2c-cold	08.04.03	13.5	7.41	600	331.8	0.0	14.1	38.1	15.0	2.0	104.6	7.5	n.d.	513.1
		10.07.03	20.0	7.58	557	297.7	0.0	16.0	28.3	10.7	1.2	102.0	4.7	14.6	475.2
		15.10.03	18.2	7.82	-	320.2	0.0	14.6	29.5	37.0	1.6	74.6	10.3	13.4	501.2
Bolu	3a-hot	24.03.02	41.6	6.96	-	817.1	0.0	6.8	625.0	52.0	18.0	344.0	111.8	n.d.	1974.6
		09.07.02	41.6	6.24	-	512.2	0.0	4.9	675.0	55.0	17.0	304.0	53.5	n.d.	1621.5
		28.10.02	43.0	6.12	1980	786.9	0.0	10.6	373.0	46.6	17.6	328.0	26.7	19.6	1609.0
		08.04.03	42.5	6.06	1961	955.0	0.0	9.6	326.0	21.9	17.8	360.0	40.8	n.d.	1731.1
		10.07.03	43.1	5.92	1960	786.3	0.0	15.6	325.0	32.8	13.6	335.0	19.5	31.2	1559.0
		16.10.03	41.8	6.29	-	663.0	0.0	8.9	482.0	37.5	16.0	356.2	15.3	35.4	1614.3

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Bolu	3b-cold	08.04.03	6.7	7.47	78	25.0	0.0	2.9	14.7	3.6	2.2	10.6	0.8	n.d.	59.8
		10.07.03	13.7	7.70	86	40.9	0.0	4.5	7.5	2.5	1.6	12.2	2.3	31.4	102.9
		16.10.03	11.6	7.71	-	50.6	0.0	3.6	9.9	1.0	2.6	12.4	4.6	44.4	129.1
Mudurnu	4a-hot	25.03.02	38.3	6.26	-	767.1	0.0	1.4	30.0	30.0	9.0	168.0	24.3	n.d.	1029.8
		10.07.02	38.3	6.28	-	786.6	0.0	2.8	10.0	34.0	8.0	182.0	42.5	n.d.	1065.9
		29.10.02	44.3	6.24	1162	689.3	0.0	7.1	33.7	22.9	5.8	144.0	46.2	18.8	967.8
		09.04.03	39.1	6.14	1151	779.6	0.0	11.4	32.3	45.8	6.6	161.2	43.0	n.d.	1079.9
		11.07.03	39.2	6.28	1162	744.2	0.0	13.1	28.8	16.2	5.4	132.6	69.8	21.8	1031.9
		17.10.03	39.3	6.29	-	695.4	0.0	8.2	31.1	5.2	6.9	147.2	56.0	27.0	977.0
	4b-hot	25.03.02	38.5	6.25	-	759.8	0.0	2.2	25.0	29.0	9.0	168.0	24.3	n.d.	1017.2
		10.07.02	38.7	6.32	-	743.9	0.0	3.1	28.0	34.0	8.0	112.0	42.5	n.d.	971.5
		29.10.02	39.7	6.23	1162	686.2	0.0	7.1	32.9	22.1	6.3	144.0	45.0	18.8	962.4
		09.04.03	39.6	6.13	1148	778.4	0.0	7.4	31.8	3.6	6.4	165.6	61.3	n.d.	1054.5
		11.07.03	39.8	6.29	1159	741.8	0.0	13.1	32.6	17.5	5.4	103.8	86.5	20.8	1021.5
		17.10.03	39.8	6.36	-	686.0	0.0	7.8	31.7	15.8	6.4	74.0	92.0	27.2	940.9

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Mudurnu	4c-cold	25.03.02	19.6	6.89	-	535.4	0.0	5.0	50.0	23.0	6.0	128.0	21.9	n.d.	769.3
		10.07.02	19.4	6.86	-	497.6	0.0	4.5	55.0	27.0	5.0	140.0	25.5	n.d.	754.6
		29.10.02	20.2	6.75	933	564.2	0.0	8.9	38.5	17.9	4.2	95.0	55.3	15.2	799.2
		09.04.03	19.7	6.67	928	609.4	0.0	7.8	37.8	22.2	4.3	109.8	54.8	n.d.	846.1
		11.07.03	19.9	6.83	924	569.7	0.0	11.4	36.7	13.6	3.4	98.0	58.8	18.6	810.2
		17.10.03	20.0	6.86	-	594.1	0.0	8.2	28.6	38.6	4.4	91.0	52.3	17.8	835.0
	4d-cold	25.03.02	11.3	7.25	-	414.6	0.0	7.9	72.0	24.0	4.0	108.0	31.6	n.d.	662.1
		10.07.02	15.4	7.13	-	431.7	0.0	5.4	50.0	28.0	5.0	130.0	15.6	n.d.	665.6
		29.10.02	16.9	6.91	791	475.8	0.0	8.5	34.6	17.7	3.8	82.0	46.2	14.7	683.3
		09.04.03	12.2	6.97	743	464.2	0.0	8.5	35.5	16.5	3.6	96.6	36.8	n.d.	661.7
		11.07.03	15.7	7.07	808	495.3	0.0	12.2	37.2	13.0	2.3	69.4	63.0	18.0	710.4
		17.10.03	17.4	7.07	-	478.0	0.0	7.1	37.1	39.7	4.0	38.6	24.4	16.9	645.8

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Seben	5a-hot	25.03.02	70.1	6.73	-	1201.2	0.0	80.1	137.5	530.0	40.0	58.0	0.5	n.d.	2047.3
		10.07.02	69.9	6.87	-	1170.7	0.0	70.4	162.5	600.0	38.0	9.2	6.6	n.d.	2057.4
		29.10.02	72.3	6.46	2210	1171.2	0.0	60.3	98.4	427.0	30.8	40.0	18.8	19.9	1866.4
		09.04.03	70.7	6.36	2180	1109.0	0.0	65.3	138.4	441.0	32.2	50.8	5.6	n.d.	1842.3
		11.07.03	71.8	6.58	2200	1221.2	0.0	67.4	57.2	408.0	31.6	56.6	21.4	68.0	1931.4
		17.10.03	72.3	6.77	-	1201.7	0.0	62.1	55.4	434.0	27.8	45.6	21.3	69.5	1917.4
	5b-hot	25.03.02	55.8	6.84	-	1192.7	0.0	70.8	170.0	520.0	39.0	52.0	7.3	n.d.	2051.8
		10.07.02	57.3	6.76	-	1201.2	0.0	69.9	175.0	560.0	38.0	26.4	6.8	n.d.	2077.3
		29.10.02	59.3	6.48	2180	1140.7	0.0	60.3	93.6	407.0	31.0	47.0	18.8	20.0	1818.4
		09.04.03	55.7	6.61	2160	1210.2	0.0	64.2	48.7	424.0	32.8	53.0	8.9	n.d.	1841.8
		11.07.03	60.0	6.79	2170	1202.9	0.0	55.9	66.0	401.0	31.4	55.8	20.2	66.5	1899.7
		17.10.03	58.2	6.86	-	1186.4	0.0	60.3	30.7	384.0	31.2	30.0	35.7	72.0	1830.3

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Seben	#5c-hot	25.03.02	35.0	7.25	-	1204.9	0.0	79.8	172.5	500.0	38.0	56.0	14.6	n.d.	2065.8
		10.07.02	-	-	-	-	-	-	-	-	-	-	-	-	-
		29.10.02	47.8	7.14	-	1052.2	0.0	60.3	132.4	406.0	29.1	30.0	20.7	19.9	1750.6
		09.04.03	-	-	-	-	-	-	-	-	-	-	-	-	-
		11.07.03	53.0	6.69	2170	1205.4	0.0	60.0	58.1	402.0	29.3	49.4	23.3	65.5	1893.0
		17.10.03	-	-	-	-	-	-	-	-	-	-	-	-	-
	#5d-cold	25.03.02	13.1	7.32	-	331.7	0.0	12.2	400.0	100.0	6.0	106.0	40.1	n.d.	996.0
		10.07.02	-	-	-	-	-	-	-	-	-	-	-	-	-
		29.10.02	15.1	7.30	1076	329.4	0.0	10.6	291.0	61.6	5.7	112.0	40.1	10.5	860.9
		09.04.03	14.5	7.23	1070	352.6	0.0	13.5	248.5	12.5	5.8	114.2	59.2	n.d.	806.3
		11.07.03	14.5	7.47	1073	331.2	0.0	15.6	259.0	53.0	4.6	103.0	43.9	12.0	822.3
		17.10.03	15.7	7.40	-	625.0	0.0	13.1	36.5	65.5	5.8	98.4	41.8	11.7	897.8

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Hamamözü	6a-hot	26.03.02	41.3	7.83	-	234.1	0.0	36.4	15.0	49.0	8.0	35.2	16.0	n.d.	393.8
		11.07.02	41.1	7.71	-	220.7	0.0	39.0	28.0	62.0	8.0	37.2	13.1	n.d.	408.1
		30.10.02	42.6	7.24	516	234.8	0.0	32.7	25.3	44.3	5.5	39.0	17.0	17.7	416.3
		10.04.03	42.1	7.02	505	244.0	0.0	34.7	28.5	49.8	5.7	39.0	15.9	n.d.	417.6
		12.07.03	42.7	7.29	516	244.0	0.0	36.3	24.1	37.9	4.9	48.2	17.4	18.6	431.4
		18.10.03	42.5	7.30	-	244.0	0.0	33.4	25.4	41.4	5.6	30.2	24.2	24.0	428.2
	6b-cold	30.10.02	15.8	7.57	636	350.7	0.0	8.5	30.5	17.2	1.6	84.0	24.3	16.4	533.2
		10.04.03	10.6	7.30	505	340.4	0.0	20.7	38.0	12.5	1.7	98.2	16.7	n.d.	528.2
		12.07.03	19.3	7.39	609	330.0	0.0	12.1	45.8	10.5	1.1	44.8	46.9	19.5	510.7
		18.10.03	17.4	7.77	-	311.1	0.0	8.9	41.4	28.4	2.3	66.2	19.9	20.2	498.4

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Gözlek	7a-hot	27.03.02	38.4	7.93	-	251.2	0.0	13.5	5.0	78.0	6.0	17.2	4.9	n.d.	375.8
		11.07.02	38.3	7.97	-	247.6	0.0	13.4	40.0	89.0	6.0	17.6	6.1	n.d.	419.6
		31.10.02	39.3	7.60	497	237.9	0.0	14.2	36.9	66.8	4.2	22.0	10.9	16.0	408.9
		10.04.03	39.6	7.43	488	226.3	0.0	16.7	34.7	78.4	4.5	18.0	5.5	n.d.	384.1
		12.07.03	38.9	7.96	497	258.0	0.0	15.2	34.9	67.8	3.6	31.8	8.6	14.5	434.4
		18.10.03	38.8	7.75	-	245.2	0.0	13.5	33.8	73.4	4.4	17.0	12.3	18.9	418.5
	7b-cold	31.10.02	16.1	7.87	1063	362.9	0.0	42.6	228.0	46.8	3.7	80.0	69.9	18.4	852.3
		10.04.03	16.3	7.46	1157	439.8	0.0	54.3	199.6	49.5	4.3	109.6	63.6	n.d.	920.7
		12.07.03	17.2	7.53	1255	429.4	0.0	64.6	200.0	38.2	3.3	67.6	95.3	20.6	919.0
		18.10.03	19.2	7.79	-	433.1	0.0	65.7	51.0	31.5	4.1	94.0	95.4	29.0	803.8

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	[+]EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	[¤]TDS
Reşadiye	[¥]8a-hot	27.03.02	41.3	6.44	-	1804.9	0.0	786.0	40.0	760.0	49.0	280.0	85.1	n.d.	3804.9
		12.07.02	41.1	6.41	-	1829.3	0.0	821.0	195.0	840.0	54.0	328.0	92.3	n.d.	4159.6
	8b-cold	27.03.02	12.5	7.76	-	180.5	0.0	2.0	55.0	20.0	3.0	40.0	19.4	n.d.	319.9
		12.07.02	17.4	6.50	-	237.8	0.0	8.6	125.0	42.0	3.0	48.0	29.6	n.d.	494.1
		31.10.02	15.9	7.61	481	234.8	0.0	9.2	46.3	24.6	2.0	41.0	23.1	16.6	397.6
Kurşunlu	9a-hot	28.03.02	55.9	7.20	-	6975.6	0.0	776.0	7.0	3500.0	260.0	7.2	19.4	n.d.	11545.2
		13.07.02	55.5	7.10	-	6829.3	0.0	815.0	9.0	4300.0	280.0	104.0	17.0	n.d.	12354.3
		01.11.02	57.6	6.94	11300	6100.0	0.0	756.1	52.0	2650.0	44.2	73.0	28.0	0.0	9703.3
		11.04.03	57.4	6.88	11100	4906.2	0.0	773.2	45.5	2090.0	219.0	112.6	11.2	n.d.	8157.7
		12.07.03	57.9	7.11	11030	5612.0	0.0	796.6	57.6	2445.0	220.0	38.6	21.9	3.1	9194.8
		19.10.03	58.1	7.09	-	6002.4	0.0	761.8	103.0	2478.0	225.0	51.6	57.8	0.8	9680.4
	[§]9b-min. water	28.03.02	12.6	6.46	-	2658.5	0.0	207.0	7.0	1200.0	120.0	7.2	8.7	n.d.	4208.5
		13.07.02	14.7	6.43	-	1804.9	0.0	140.0	6.0	1200.0	100.0	98.0	4.9	n.d.	3353.7
		01.11.02	15.3	6.45	2660	1476.2	0.0	85.2	33.0	458.0	43.3	71.0	32.2	19.2	2218.1
		11.04.03	10.6	6.45	2440	1428.6	0.0	82.4	36.9	431.0	44.7	130.0	0.6	n.d.	2154.2

Table 6.1. (continued).

Locality	Sample no.	Sampling Date	*T (°C)	*pH	+EC mmho/cm	HCO_3	CO_3	Cl	SO_4	Na	K	Ca	Mg	SiO_2	¤TDS
Kurşunlu	9c-cold	28.03.02	9.0	8.17	-	241.5	0.0	21.6	7.0	8.0	1.0	66.0	8.0	n.d.	353.1
		13.07.02	14.9	7.76	-	240.2	0.0	2.0	5.0	13.0	1.0	72.0	3.9	n.d.	337.1
		01.11.02	13.3	8.06	416	247.0	0.0	7.1	10.3	6.9	0.5	64.0	9.7	19.8	365.3
		11.04.03	11.9	7.69	406	256.2	0.0	5.9	10.5	6.0	0.4	61.6	14.6	n.d.	355.2
		12.07.03	12.5	7.92	427	256.2	0.0	6.2	7.0	44.9	0.0	42.6	25.8	39.4	422.1
		19.10.03	13.4	7.95	-	250.1	0.0	3.9	11.5	31.0	0.5	56.6	2.7	46.0	402.3

*Field measurements, +Laboratory measurements

Since mud removal studies (following the heavy rain) were being performed in Seben, no sampling could be done in July 2002 period from localities 5c and 5d; likewise, since the pump was removed from the well, no sampling could be performed in Seben in April 2003 and October 2003 periods from locality 5c.

¥ since the spring had dried up, no sampling could be performed from Reşadiye in periods following July 2002.

§ since the spring had dried up, no sampling could be performed from locality 9b in periods following April 2003.

¤TDS: Total Dissolved Solid, contains silica where measured.

n.d.= not determined

6.2. Hydrogeochemical Facies

An evaluation of the results of chemical analyses are made here in terms of the determination of the hydrogeochemical facies of samples via the use of Piper diagrams. These diagrams are based on the use of major anion-cation concentrations in units of milli equivalents (meq), and are given separately for the hot and the cold waters in Figures 6.1 (a, b) and 6.2 (a, b), respectively. The hydrogeochemical facies of the samples are also displayed as pie diagrams in Figure 6.3 (a,b) using the average values (in meq units) of analyses obtained throughout the monitoring period. Additionally, a summary of the water types revealed in the Piper diagrams are also presented in Table 6.2.

According to the Piper diagrams, the hot waters are almost all Na-HCO_3 type waters (Efteni, Seben, Gözlek, Reşadiye and Kurşunlu samples), except for Ca-HCO_3 type Bolu and Mudurnu, and Na-SO_4 type Yalova samples. Hamamözü hot water sample, on the other hand, displays a mixed water character (for all periods), that is, none of the ions are greater than 50 % of the total composition. The cold waters are dominantly Ca-HCO_3 type. In Bolu, Seben, Gözlek, Hamamözü, Reşadiye and Kurşunlu fields, the hydrogeochemical facies for the hot waters are constant throughout all the sampling periods (from March 2002 to October 2003). Efteni, Yalova and Mudurnu hot waters, on the other hand, display slight changes in water type in time, which stands from an increase in Mg concentration for Efteni and Mudurnu, and an increase in Ca concentration for Yalova samples. These increases in Mg and Ca contents, with respect to the dominant cations of the concerned fields (Na for Yalova and Efteni, and Ca for Mudurnu), seem to have placed these waters into mixed water category in the 2003 sampling periods. For cold waters, slight chemical changes are observed in 2003 sampling periods, in association with a slight increase in Mg contents, inducing a mixed nature for those waters which are mostly Ca-HCO_3 type.

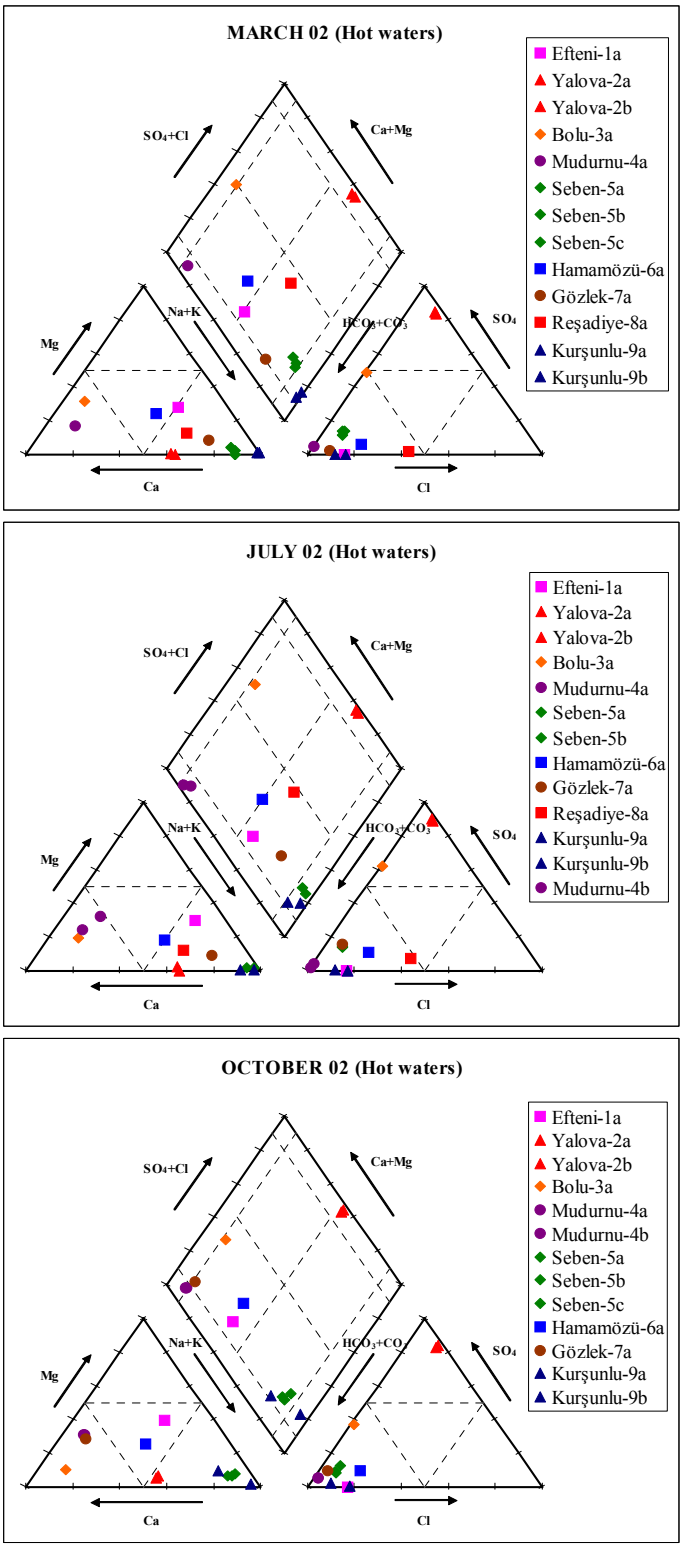


Figure 6.1.a. Piper diagrams of the hot waters for 2002 sampling periods.

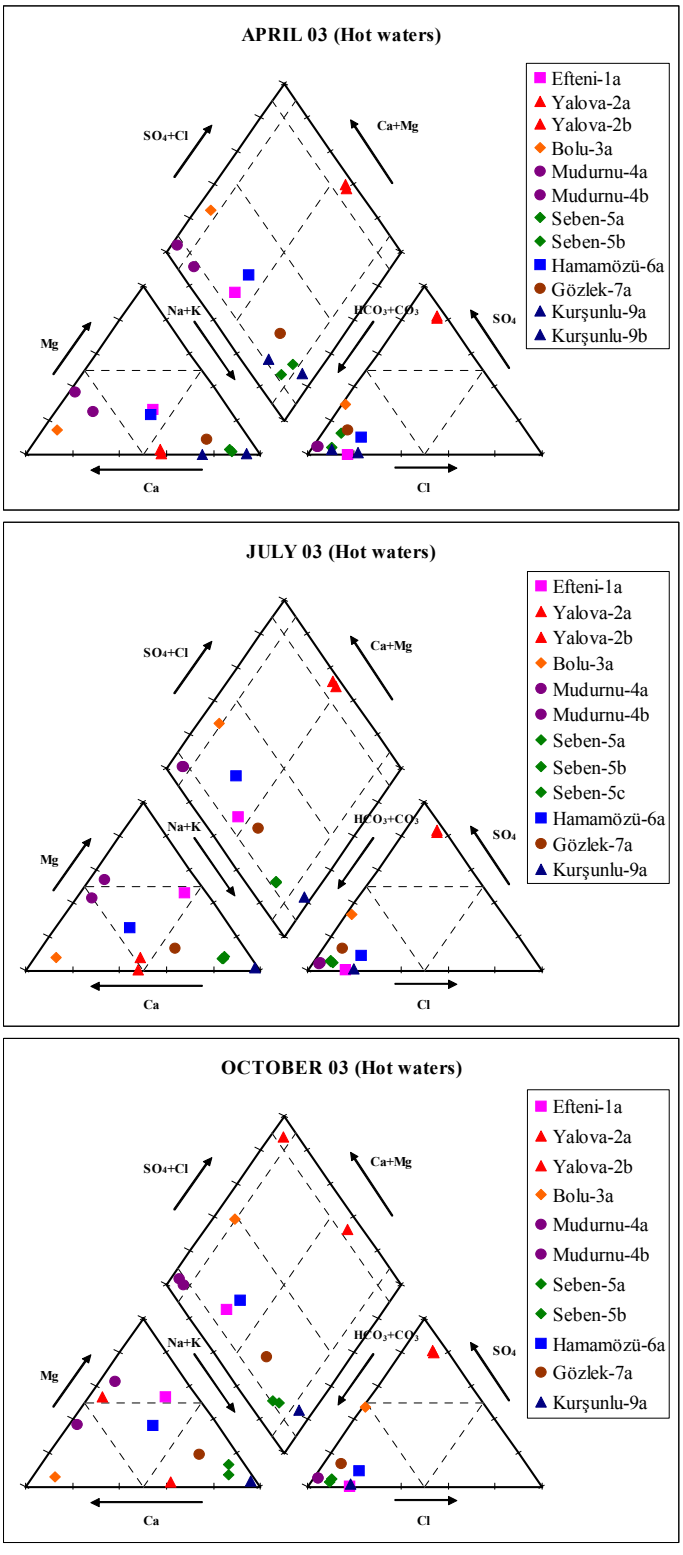


Figure 6.1.b. Piper diagrams of the hot waters for 2003 sampling periods.

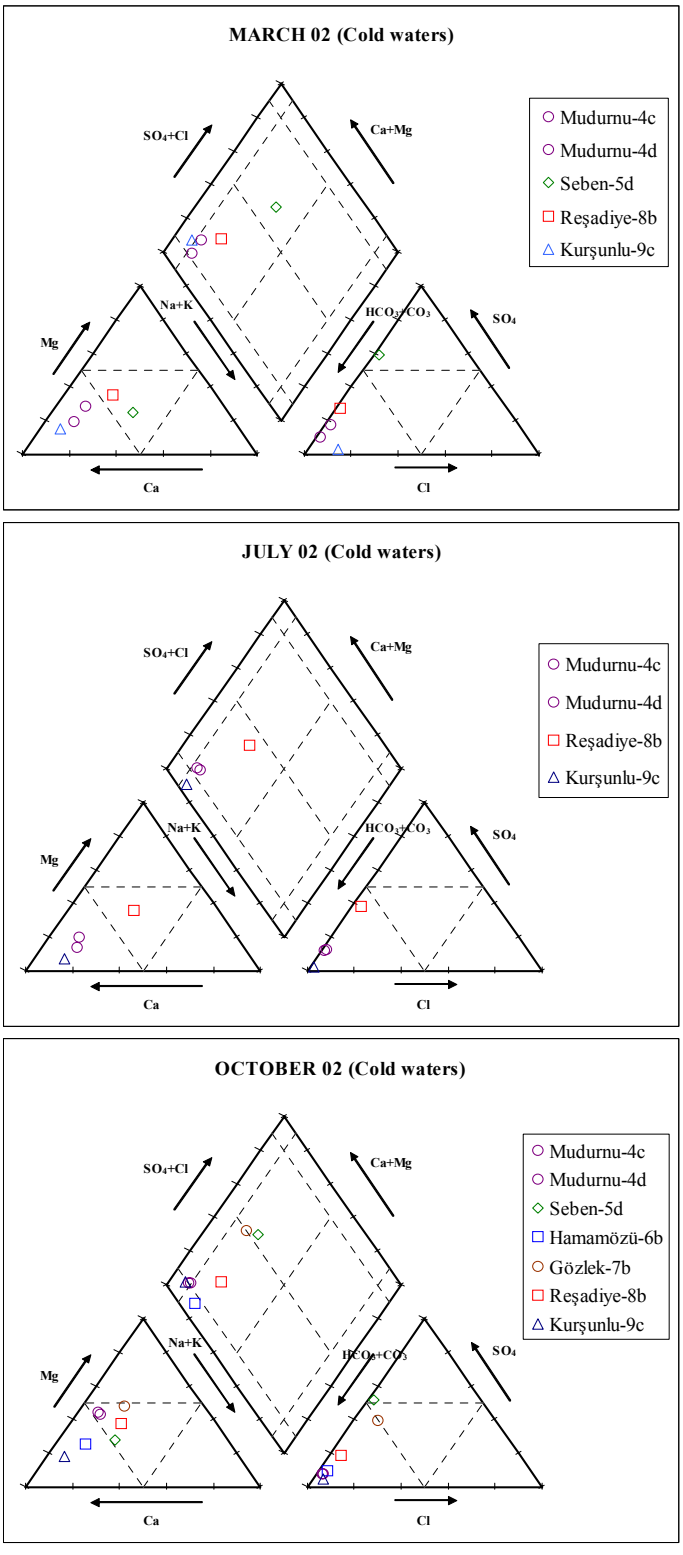


Figure 6.2.a. Piper diagrams of the cold waters for 2002 sampling periods.

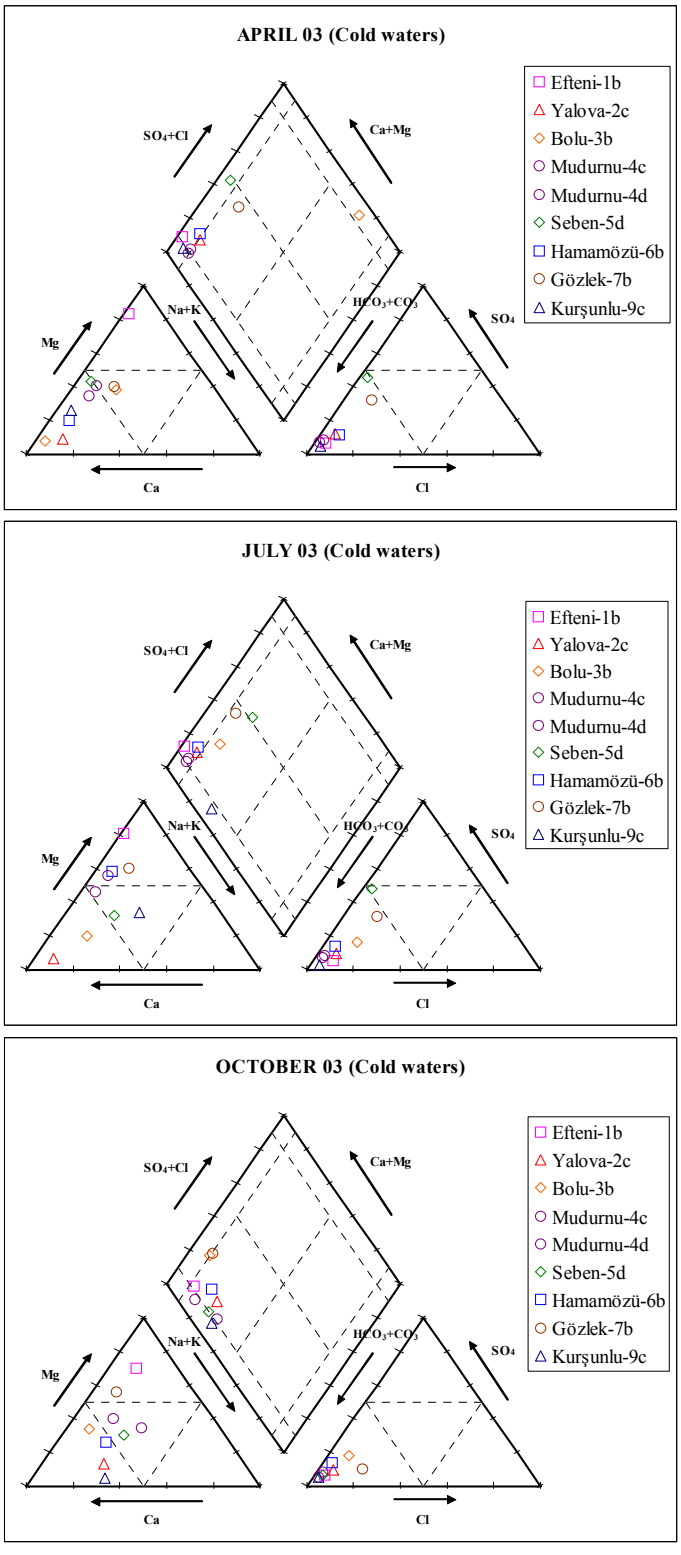


Figure 6.2.b. Piper diagrams of the cold waters for 2003 sampling periods.

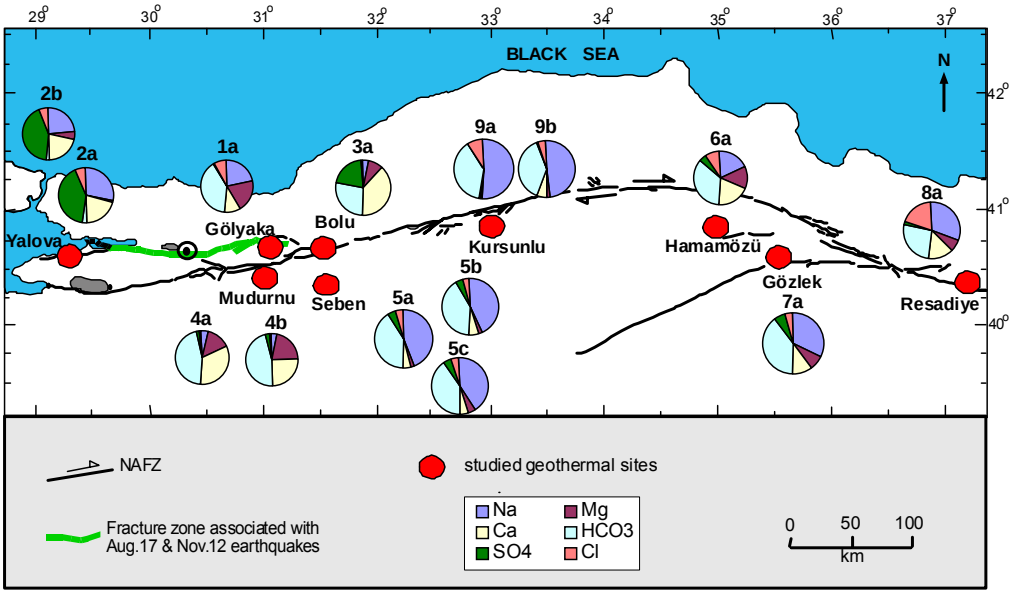


Figure 6.3.a. Pie diagrams of the thermal waters (relative percentages of ions are the averages of all sampling periods; TDS contents of samples are not to scale, i.e. not reflected in the diameter of the circles)

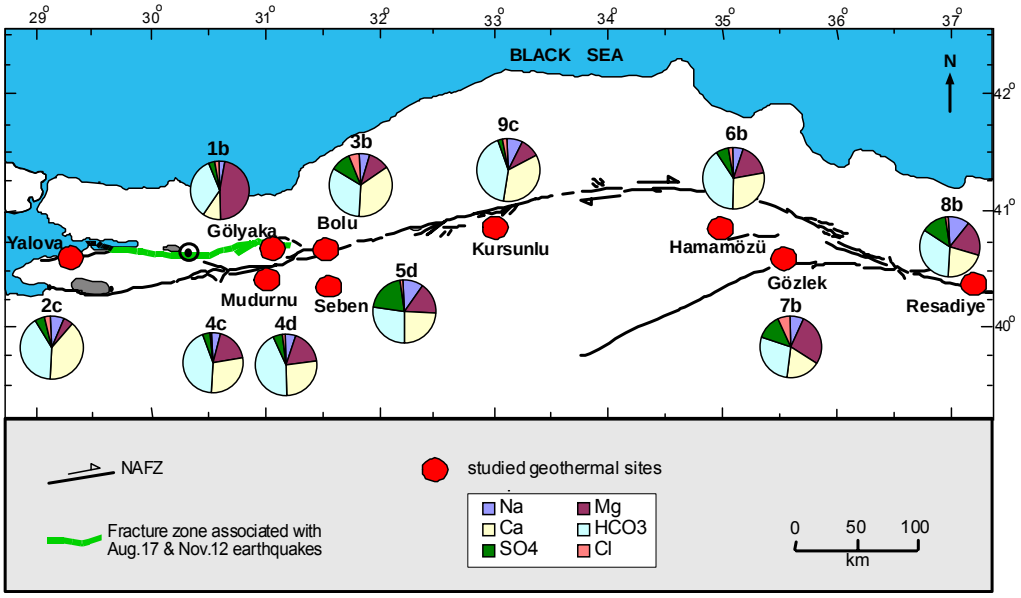


Figure 6.3.b. Pie diagrams of the cold waters. (relative percentages of ions are the averages of all sampling periods; TDS contents of samples are not to scale, i.e. not reflected in the diameter of the circles).

Table 6.2. Water types of samples belonging to each period.

Location	March 2002	July 2002	October 2002	April 2003	July 2003	October 2003
Efteni (hot)	Na-HCO_3	Na-HCO_3	(Na-Mg)-HCO_3	(Na-Ca)-HCO_3	(Mg-Na)-HCO_3	Mg-HCO_3
Efteni (cold)	-	-	-	Mg-HCO_3	Mg-HCO_3	Mg-HCO_3
Yalova (hot)	Na-SO_4	Na-SO_4	Na-SO_4	Na-SO_4	(Ca-Na)-SO_4	(Na-Mg)-SO_4
Yalova (cold)	-	-	-	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3
Bolu (hot)	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3
Bolu (cold)	-	-	-	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3
Mudurnu (hot)	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	(Ca-Mg)-HCO_3	(Ca-Mg)-HCO_3
Mudurnu (cold)	Ca-HCO_3	Ca-HCO_3	(Ca-Mg)-HCO_3	Ca-HCO_3	Mg-HCO_3	(Ca-Mg)-HCO_3
Seben (hot)	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3
Seben (cold)	(Ca-Na)-HCO_3	-	(Ca-Mg)-HCO_3	Ca-HCO_3	(Ca-Mg)-HCO_3	(Ca-Mg)-HCO_3
Hamamözü (hot)	(Na-Ca)-HCO_3	(Na-Ca)-HCO_3	(Na-Ca)-HCO_3	(Na-Ca)-HCO_3	(Ca-Na)-HCO_3	(Mg-Na)-HCO_3
Hamamözü (cold)	-	-	Ca-HCO_3	Ca-HCO_3	Mg-HCO_3	Ca-HCO_3
Gözlek (hot)	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3
Gözlek (cold)	--	-	(Mg-Ca)-HCO_3	(Ca-Mg)-HCO_3	Mg-HCO_3	Mg-HCO_3
Reşadiye (hot)	Na-HCO_3	Na-HCO_3	-	-	-	-
Reşadiye (cold)	(Ca-Mg)-HCO_3	(Mg-Ca)-HCO_3	(Ca-Mg)-HCO_3	-	-	-
Kurşunlu (hot)	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3	Na-HCO_3
Kurşunlu (cold)	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	Ca-HCO_3	(Ca-Mg)-HCO_3	Ca-HCO_3

The hydrogeochemical facies, determined for the water samples, point to the effects of subsurface processes such as the dissolution of reservoir lithologies and/or ion exchange between waters and the sedimentary units (overlying the reservoir rocks) along the circulation paths. While the dominant HCO_3 character in the hot and the cold waters (except Yalova hot waters) seems to be compatible with the dissolution of the reservoir rocks that are dominated by Mesozoic limestones, ion exchange with the overlying sediments, including impermeable clayey levels, is probably responsible for the dominancy of Na cation in the hot waters. It is important to note here that in Yalova geothermal field, where the only exceptional Na-SO_4 type water is encountered, the primary reservoir rocks are Neogene volcanics. The SO_4 in Yalova waters is believed to have some genetic connections with the young organic accumulations in the İzmit Bay, and probably reflects the release of sulphur (entrapped in these organic accumulations) induced by the seismic activities in the proximity.

The temporal changes observed in water compositions can probably be attributed to i) the seasonal effects (degree of meteoric precipitation, evaporation) for the cold waters, and ii) the water-rock interaction and/or differing degrees of mixing with waters from different aquifers which might have been triggered by seismic activities, for the hot waters.

CHAPTER 7

ISOTOPIC COMPOSITIONS

The results of isotopic analyses comprising all periods are given in Table 7.1 for $\delta^{18}O$ and δD, and in Table 7.2 for ^{3}H. The $\delta^{18}O$ values of the hot waters range between -13.44‰ and -8.37‰, while the cold waters have values ranging from -12.71‰ to -8.29‰. Regarding the deuterium contents, the hot waters have δD values ranging between -96.74‰ and -64.15‰, whereas the cold waters have δD values ranging between -86.70‰ and -54.67‰. When tritium concentrations are concerned, a wide range is seen in the hot waters from 0 TU to 12.55 TU. For the cold waters, on the other hand, the lowest and highest tritium concentrations are 3 TU and 15.7 TU, respectively.

7.1. Oxygen- and Hydrogen-Isotopes

The oxygen- and hydrogen-isotope composition of the samples are presented in Figure 7.1 as $\delta^{18}O$ vs. δD diagrams for 6 sampling periods, comprising March-July-October 2002 and April-July-October 2003. Also included in the diagrams are the Global Meteoric Water Line (as defined by Craig, 1961) and the Local Meteoric Water Lines for Bursa and Yozgat (as defined by Öztürk, 2001 and Şimşek, 1995, respectively). It is readily seen from Figure 7.1 that some of the samples lie along and/or close to, and the others plot off the defined (global/local) meteoric water lines. It is interesting to note that some of the samples plotting off the water lines are cold waters (e.g. from Seben, Mudurnu, Kurşunlu, Bolu, Hamamözü and Efteni fields) whose aquifers are supposed to be recharged with meteoric precipitations.

In this respect, the meteoric water lines for the concerned fields should have different configurations towards higher $\delta^{18}O$ values in case of Seben, Mudurnu and Kurşunlu, and lower $\delta^{18}O$ values in case of Bolu, Hamamözü and Efteni. Whether the cold waters define their own trends or they plot along the already defined water lines, their hot water companions also plot along the same trends suggesting a meteoric origin for both the hot and the cold waters. Only in Kurşunlu 9a hot water sample, the $\delta^{18}O$ value is relatively high. Although the effect of water-rock interaction can not be ruled out, the high $\delta^{18}O$ value of this sample is probably related to the (calcite) scaling problem encountered in the production well from which it is sampled. The boiling process (that caused the scaling problem) is thought to be responsible for the enrichment of heavy oxygen isotope in the liquid associated with the loss of volatiles during boiling. As a result, the $\delta^{18}O$ and δD compositions of the geothermal waters along the NAFZ reveal a meteoric origin for these waters since they are alligned along the same trend as their cold water companions.

The $\delta^{18}O$ and δD compositions of the samples are given separately in Figures 7.2 (a, b) and 7.3 (a, b), respectively, for 6 sampling periods. Nearly in all of the geothermal fields the hot waters have δD values lower than their cold water companions. Similarly, with the exception of Kurşunlu and Bolu fields, $\delta^{18}O$ values of the hot waters are lower than the values recorded for the cold waters. This is an unusual case in geothermal literature since thermal waters (along their way through subsurface to low pressure regimes such as fractures and faults) experience intense water-rock interaction and are mostly enriched in $\delta^{18}O$. In other words, the hot waters due to intense water-rock interaction, have more positive $\delta^{18}O$ values since the rocks through which they circulate have significant amounts of oxygen-18 in their mineral compositions available for exchange. Regarding the deuterium contents, on the other hand, since hydrogen is not a major constituent of rocks, the δD values of hot waters can not change significantly during water-rock interaction. In this respect, water-rock interaction does not seem to be the process controlling the isotope composition

of the NAFZ hot waters. Instead, the effect of altitude seems to be more significantly pronounced. Precipitations at high altitudes are characterized by low $\delta^{18}O$ and δD values since precipitation towards highlands becomes depleted in the heavy isotopes of oxygen and hydrogen which are the first to join precipitation. In the light of this fact, the hot waters having low $\delta^{18}O$ and δD values are probably recharged from higher altitudes and the cold waters are recharged from lower altitudes. It is important to note at this stage that the $\delta^{18}O$ and δD values of the Yalova hot waters recorded in this study (-11.09 to -11.73‰ and -72.19 to -79.86‰, respectively) are slightly more negative than the values reported by Eisenlohr (1997) (around -10.3 to -10.7‰ and -68 to -72‰). Apart from the effects of different laboratory conditions, this difference in the isotope compositions of Yalova hot waters may point to the changing recharge conditions in time.

A final evaluation of the $\delta^{18}O$ and δD values of the NAFZ waters is made in Figure 7.4 in terms of their comparison with the compositions from several geothermal fields in the world. As can be seen from this figure, the majority of the thermal waters, as well as the cold waters are mostly concentrated along the Global Meteoric Water Line and are characterized by more negative $\delta^{18}O$ values than the important geothermal fields throughout the world.

7.2. Tritium Contents

The tritium contents of the samples are given in Table 7.2. For the hot waters, the tritium values range between 0 TU and 12.55 TU, the majority being between 0-5 TU; the lowest values belong to Kurşunlu 9a sample having a tritium concentration of nearly 0 TU for almost all sampling periods. The tritium contents of the cold waters change between 3 TU-15.7 TU, although most of the samples have concentrations above 8 TU. Of all the cold water samples, Kurşunlu-9c gives the highest tritium content for almost every sampling period, while Mudurnu cold waters mostly show the lowest tritium

values except for April 2003 when a value as low as 3 TU was recorded from Efteni-Gölyaka 1b sample.

The tritium contents of the studied geothermal fields are given separately for each sampling period in Figure 7.5 (a, b) (March-July-October 2002, April-July-October 2003). For the cold waters, in March 2002 in Kurşunlu-9c sample the highest tritium value is recorded as 15.7 TU. For the hot waters, on the other hand, the highest tritium content is observed in July 2002 in Yalova 2a sample with a value of 12.55 TU. When compared to the tritium contents reported for Yalova hot waters by Eisenlohr (1997), which were all less than 1 TU, this high value seems to be rather interesting as it may point to either an analytical error (for July 2002 analyses) or to the effects of a change in the hydrogeological conditions.

An inspection of Figure 7.5 reveals that, for each field, the tritium contents of the hot waters are lower than those of the cold waters. This points to the fact that the cold water aquifers are recharged with young precipitation which enters the ground and flows through shallow rock environment without losing time and without letting tritium, having a half life of 12.26 years, to significantly decay. The hot waters are mostly deep circulating waters isolated from the shallow environment and are old when compared to the cold waters.

Table 7.1. The results of the isotopic analyses of water samples ($\delta^{18}O$ and δD values are given in ‰,; the errors for $\delta^{18}O$ and δD are 0.1‰ and 1 ‰, respectively).

Sample name	Sample no.	March 2002		July 2002		October 2002		April 2003		July 2003		October 2003	
		^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D
Efteni	1a-hot	-11.06	-83.12	-11.24	-83.45	-11.34	-80.00	-11.70	-81.80	-10.81	-81.87	-11.59	-79.52
	1b-cold	-	-	-	-	-	-	-11.12	-80.91	-12.05	-78.56	-11.72	-80.77
Yalova-Termal	2a-hot	-11.34	-74.95	-11.39	-75.42	-11.65	-72.19	-11.09	-75.04	-11.73	-77.33	-11.21	-73.84
	2b-hot	-11.41	-79.86	-11.37	-76.07	-11.62	-73.62	-11.54	-76.89	-10.84	-74.75	-11.14	-73.84
	2c-cold	-	-	-	-	-	-	-8.84	-60.43	-8.82	-54.67	-8.98	-57.28
Bolu	3a-hot	-11.90	-88.83	-12.24	-87.68	-8.56	-64.15	-11.43	-82.68	-12.08	-84.03	-11.47	-79.37
	3b-cold	-	-	-	-	-	-	-11.58	-79.14	-12.41	-79.15	-12.22	-75.12
Mudurnu-Babas	4a-hot	-11.77	-83.29	-12.23	-88.03	-12.24	-81.58	-11.71	-87.25	-12.07	-82.88	-11.98	-84.28
	4b-hot	-12.21	-82.62	-12.31	-87.76	-11.89	-83.87	-11.57	-83.72	-11.79	-83.53	-12.69	-79.12
	4c-cold	-10.98	-86.70	-11.37	-82.39	-11.98	-86.57	-9.32	-72.54	-12.01	-78.84	-11.49	-77.02
	4d-cold	-10.48	-80.70	-11.44	-82.70	-11.62	-82.04	-12.25	-82.61	-11.05	-76.71	-11.12	-74.45

Table 7.1. (continued).

Sample name	Sample no.	March 2002		July 2002		October 2002		April 2003		July 2003		October 2003	
		^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D	^{18}O	D
Seben	5a-hot	-12.37	-92.32	-12.30	-91.38	-11.68	-90.04	-11.81	-88.36	-12.53	-86.51	-12.74	-85.75
	5b-hot	-11.81	-92.36	-12.13	-91.68	-13.12	-92.26	-12.17	-88.68	-12.08	-86.93	-12.21	-84.13
	[#] 5c-hot	-11.56	-89.57	-	-	-12.28	-90.68	-	-	-11.82	-84.56	-	-
	[#] 5d-cold	-8.72	-69.34	-	-	-8.29	-68.68	-8.53	-66.81	-8.87	-67.20	-9.18	-67.78
Hamamözü	6a-hot	-12.43	-87.17	-12.25	-88.19	-11.89	-92.31	-11.72	-85.30	-12.46	-85.25	-11.93	-83.70
	6b-cold	-	-	-	-	-10.73	-78.28	-11.77	-73.75	-10.22	-70.75	-9.06	-66.27
Gözlek	7a-hot	-13.25	-95.49	-12.99	-95.34	-12.51	-96.74	-13.43	-92.78	-12.30	-91.33	-13.44	-90.09
	7b-cold	-	-	-	-	-10.74	-80.14	-10.10	-74.16	-9.93	-75.15	-9.87	-74.85
[¥] **Reşadiye**	8a-hot	-12.89	-93.30	-12.55	-92.51	-	-	-	-	-	-	-	-
	8b-cold	-12.71	-86.09	-11.64	-84.45	-11.85	-82.23	-	-	-	-	-	-
Kurşunlu	9a-hot	-8.52	-88.47	-8.45	-88.54	-8.37	-87.23	-8.74	-87.49	-8.52	-89.26	-8.61	-90.64
	[§] 9b-hot	-11.26	-86.25	-9.68	-83.46	-10.20	-77.73	-10.68	-77.94	-	-	-	-
	9c-cold	-10.37	-76.93	-9.98	-81.54	-10.00	-77.78	-9.76	-74.94	-9.34	-74.97	-10.26	-78.56

[#] Since mud removal studies (following the heavy rain) were being performed in Seben, no sampling could be done in July 2002 period from localities 5c and 5d; likewise, since the pump was removed from the well, no sampling could be performed in Seben in April 2003 and October 2003 periods from locality 5c.

[¥] since the spring had dried up, no sampling could be performed from Reşadiye in periods following July 2002.

[§] since the spring had dried up, no sampling could be performed from locality 9b in periods following April 2003.

Table 7.2. Results of tritium concentrations given as TU together with the associated analytical errors.

Sample name	Samp. no.	March 02 TU	July 02 TU	October 02 TU	April 03 TU	July 03 TU	October 03 TU
Efteni	1a	0.00±1.65	0.05±1.55	2.20±1.70	0.0±1.60	4.85±1.95	4.55±1.90
	1b	-	-	-	3.0±1.60	4.90±2.00	5.65±1.90
Yalova Termal	2a	8.90±1.90	12.55±2.00	3.30±1.75	3.70±1.70	0.05±1.80	0.0±0.60
	2b	9.90±2.00	9.70±1.80	2.90±1.70	5.50±1.75	7.20±2.05	0.0±0.55
	2c	-	-	-	7.10±1.80	8.95±2.10	8.10±0.90
Bolu	3a	9.75±1.90	4.65±1.80	3.35±1.75	3.30±1.65	1.0±1.85	1.85±0.70
	3b	-	-	-	15.20±2.00	11.95±2.15	8.40±0.90
Mudurnu	4a	6.00±1.80	3.90±1.85	0±1.60	0.65±1.65	0.0±1.75	0.25±0.60
	4b	3.0±2.20	3.70±1.80	1.50±1.65	4.95±1.80	2.35±1.85	0.50±0.60
	4c	11.41±2.10	10.10±2.05	5.40±1.70	5.16±1.95	4.90±1.80	3.95±0.75
	4d	12.46±2.05	9.30±1.95	6.35±1.70	4.95±1.85	8.15±2.05	5.20±0.80
Seben	5a	0.0±1.60	0.85±1.50	0.0±1.60	0.80±1.55	0.0±1.75	0.40±0.60
	5b	1.80±1.70	3.25±1.55	1.05±1.55	1.55±1.60	0.0±1.70	0.75±0.60
	[#]5c	0.90±1.65	-	1.55±1.65	-	1.45±1.60	-
	[#]5d	8.40±1.80	-	10.2±1.90	10.20±1.90	11.20±1.80	9.70±1.00
Hamamözü	6a	2.10±1.65	1.75±1.55	1.15±1.65	0.55±1.50	1.40±1.75	0.05±0.60
	6b	-	-	9.65±1.80	10.55±1.90	12.50±1.90	10.0±0.95
Gözlek	7a	2.10±1.65	2.45±1.65	0.55±1.60	1.40±1.55	2.12±1.65	0.25±0.60
	7b	-	-	11.20±1.80	9.0±1.80	9.96±1.85	9.50±0.95
[¥]Reşadiye	8a	3.05±1.70	2.10±1.65	-	-	-	-
	8b	9.20±1.80	9.25±1.70	7.55±1.80	-	-	-
Kurşunlu	9a	0.35±1.70	0.0±1.55	0.0±1.65	1.35±1.60	0.0±1.60	0.40±0.60
	[§] 9b	7.25±1.80	9.85±1.70	9.65±1.80	11.85±1.90	-	-
	9c	15.7±2.00	13.75±1.90	13.25±1.85	14.75±2.00	13.85±2.05	14.25±1.1

[#] Since mud removal studies (following the heavy rain) were being performed in Seben, no sampling could be done in July 2002 period from localities 5c and 5d; likewise, since the pump was removed from the well, no sampling could be performed in Seben in April 2003 and October 2003 periods from locality 5c.

[¥] since the spring had dried up, no sampling could be performed from Reşadiye in periods following July 2002.

[§] since the spring had dried up, no sampling could be performed from locality 9b in periods following April 2003.

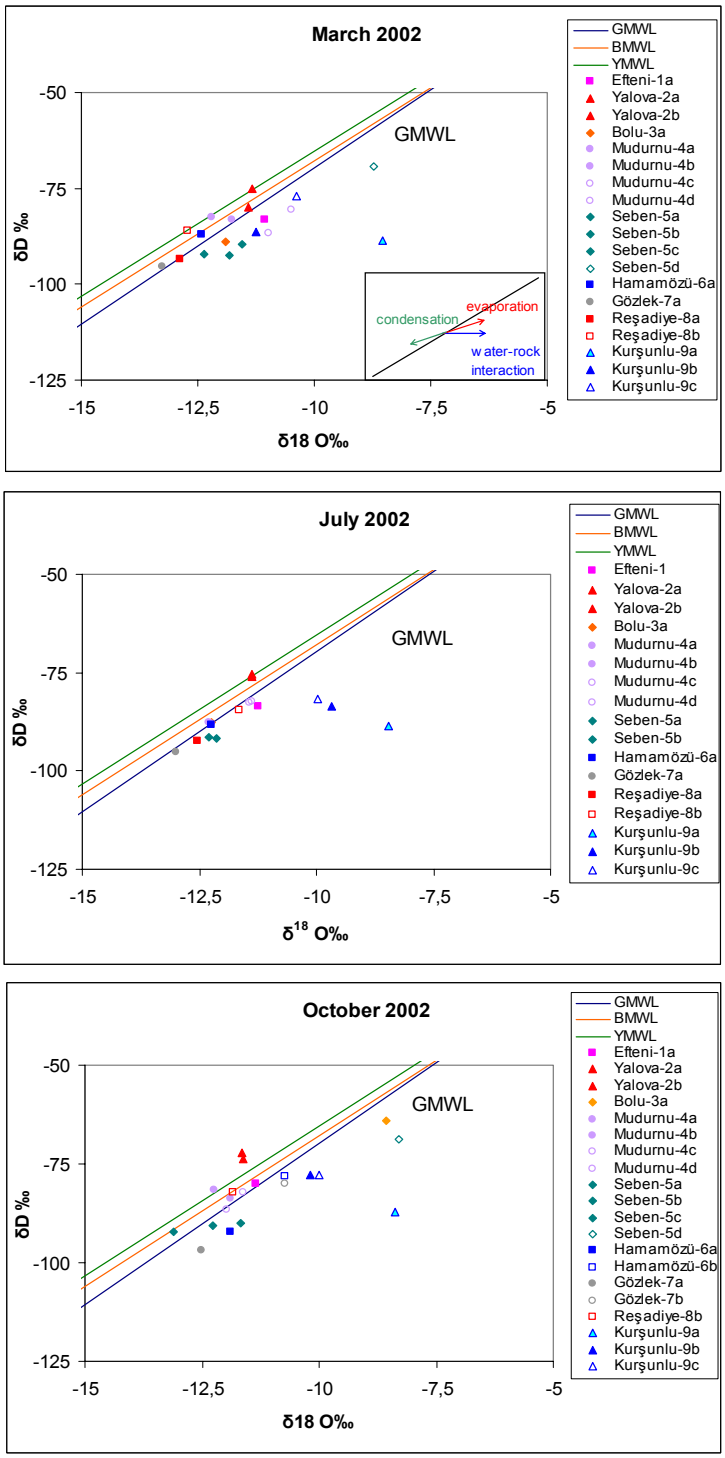


Figure 7.1.a. $\delta^{18}O$-δD diagrams of the sampled waters for 2002 sampling periods (GMWL: Global Meteoric Water Line (Craig,1961), BMWL: Bursa Meteoric Water Line (Öztürk, 2001), YMWL: Yozgat Meteoric Water Line (Şimşek, 1995)).

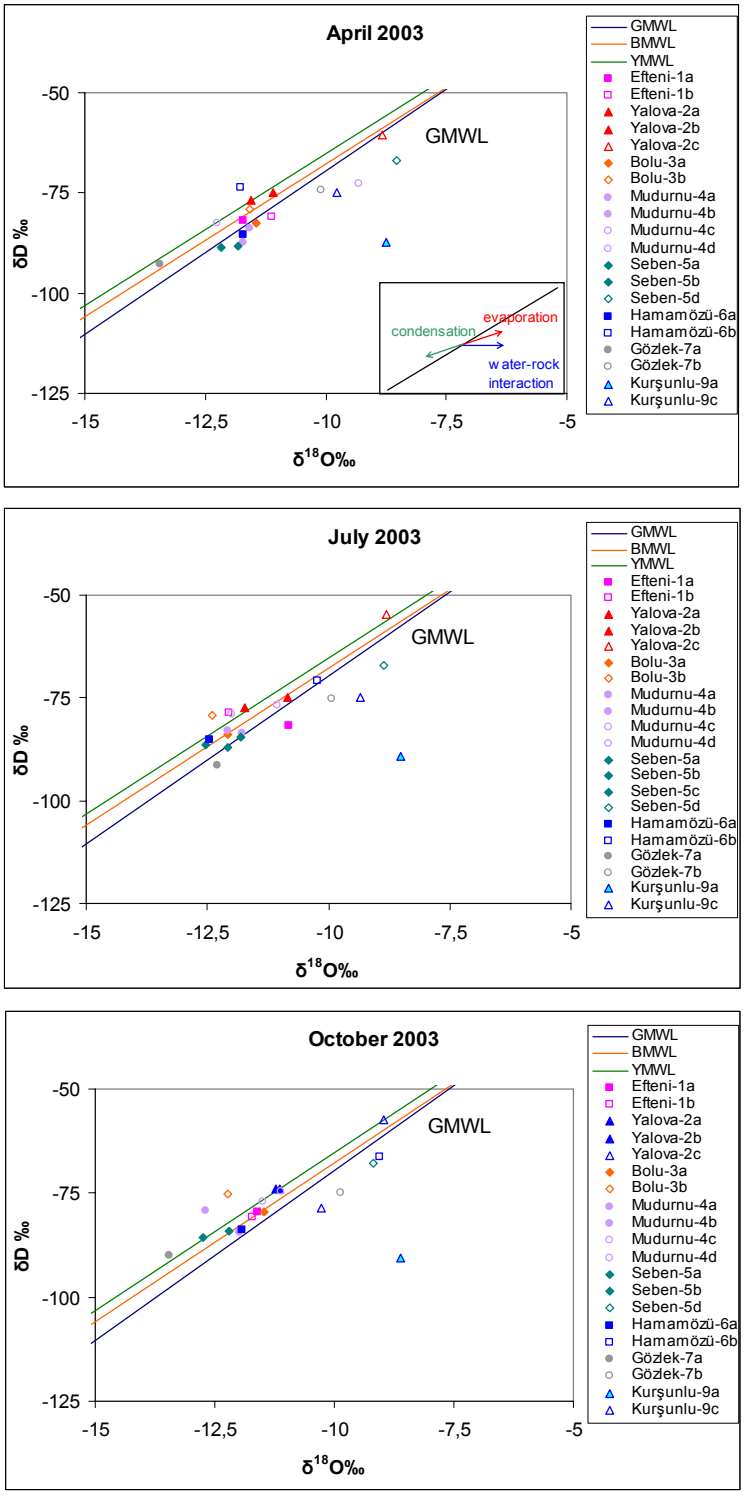


Figure 7.1.b. $\delta^{18}O$-δD diagrams of the sampled waters for 2003 sampling periods (GMWL: Global Meteoric Water Line (Craig,1961), BMWL: Bursa Meteoric Water Line (Öztürk, 2001), YMWL: Yozgat Meteoric Water Line (Şimşek, 1995)).

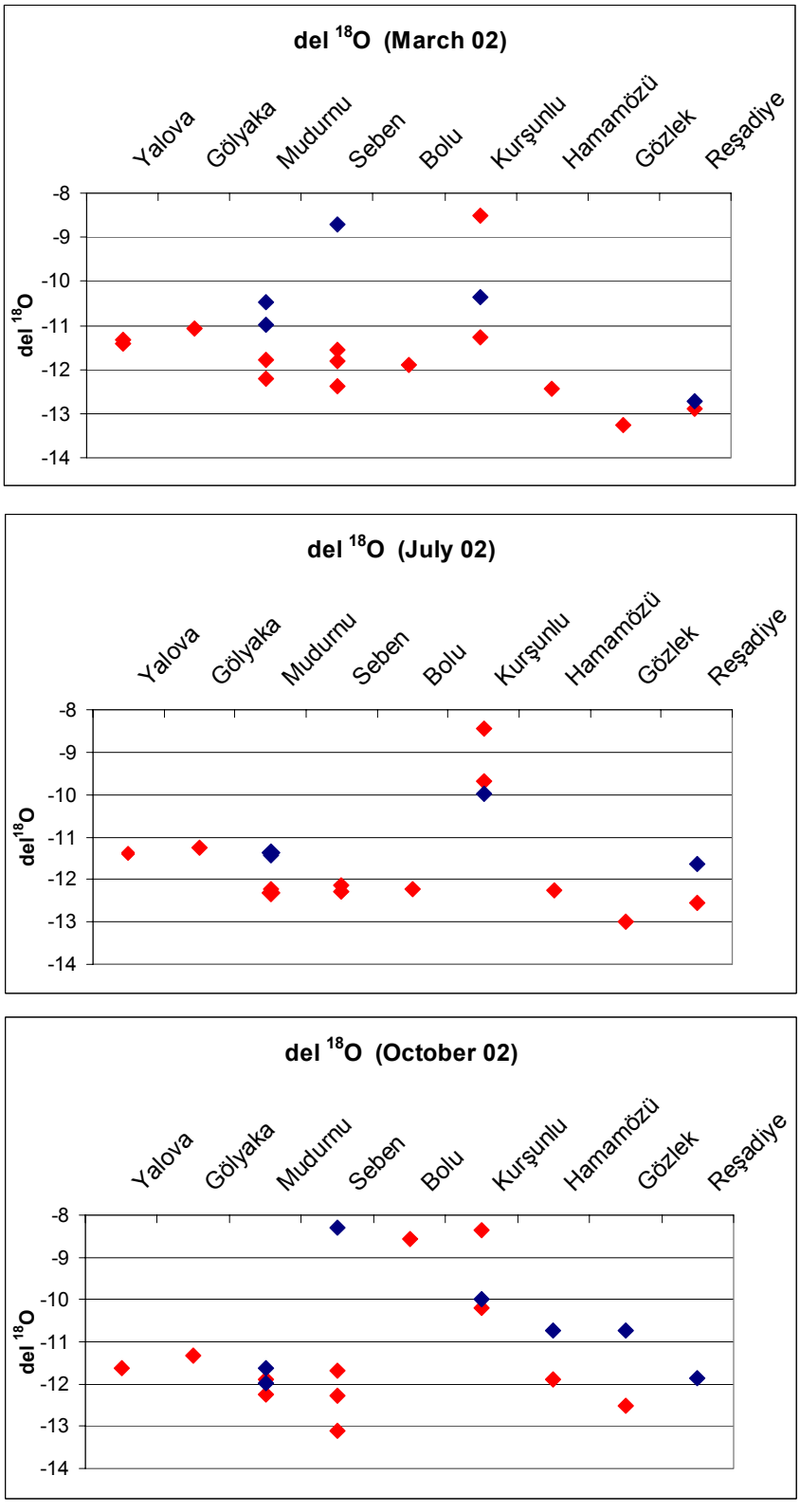


Figure 7.2.a. $\delta^{18}O$ vs locality diagrams covering 2002 sampling periods (red dots show hot, blue dots show cold waters).

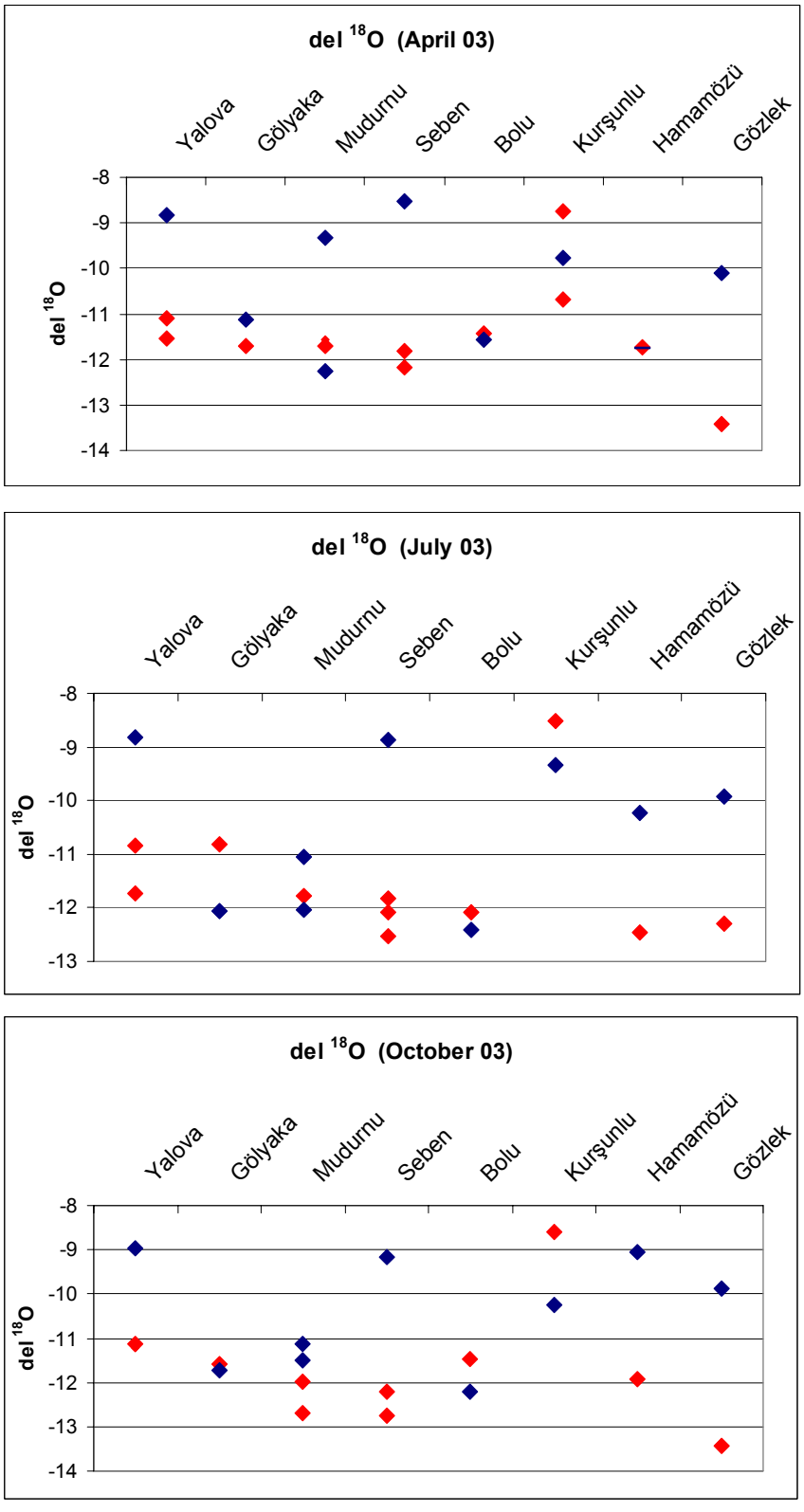
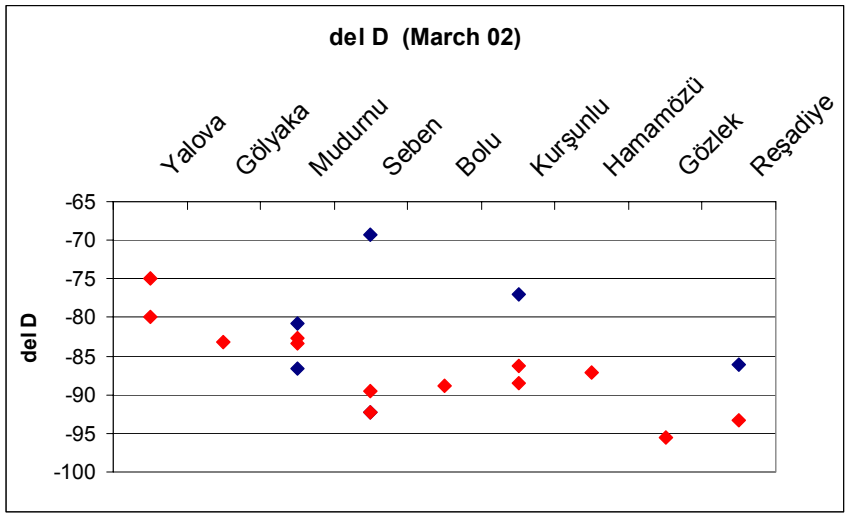
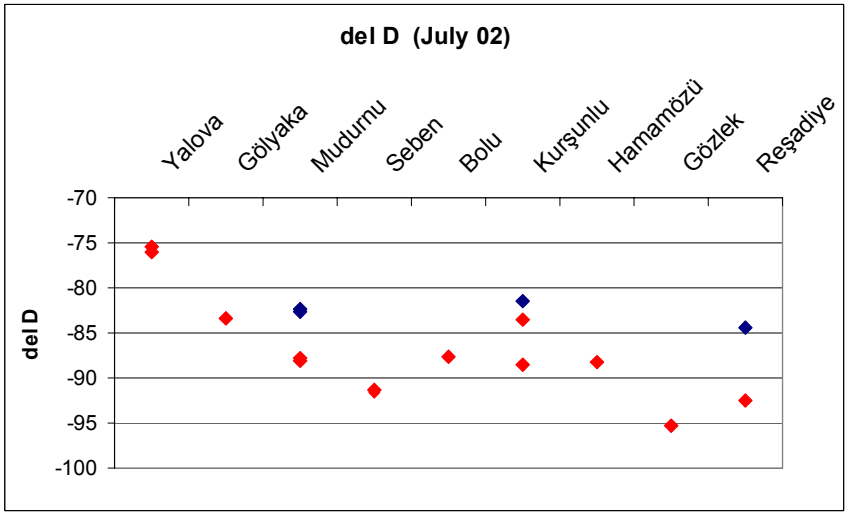


Figure 7.2.b. $\delta^{18}O$ vs locality diagrams covering 2003 sampling periods (red dots show hot, blue dots show cold waters).





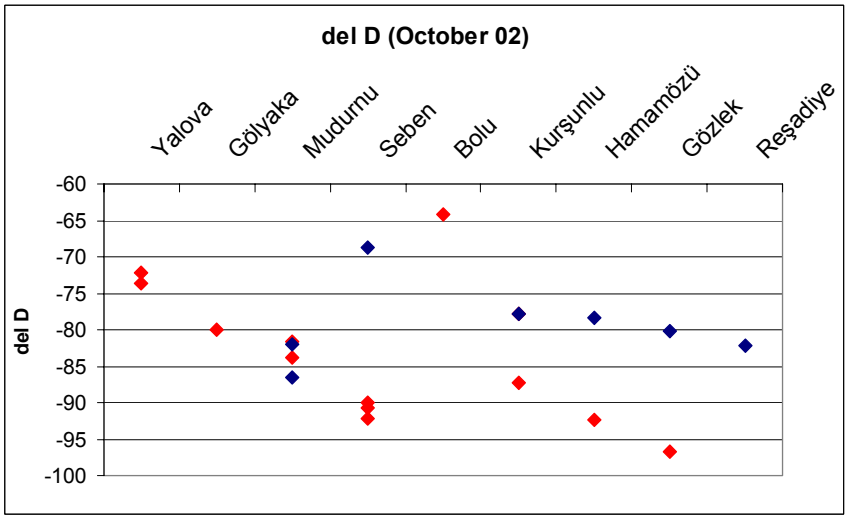


Figure 7.3.a. δ D vs locality diagrams covering 2002 sampling periods (red dots show hot, blue dots show cold waters).

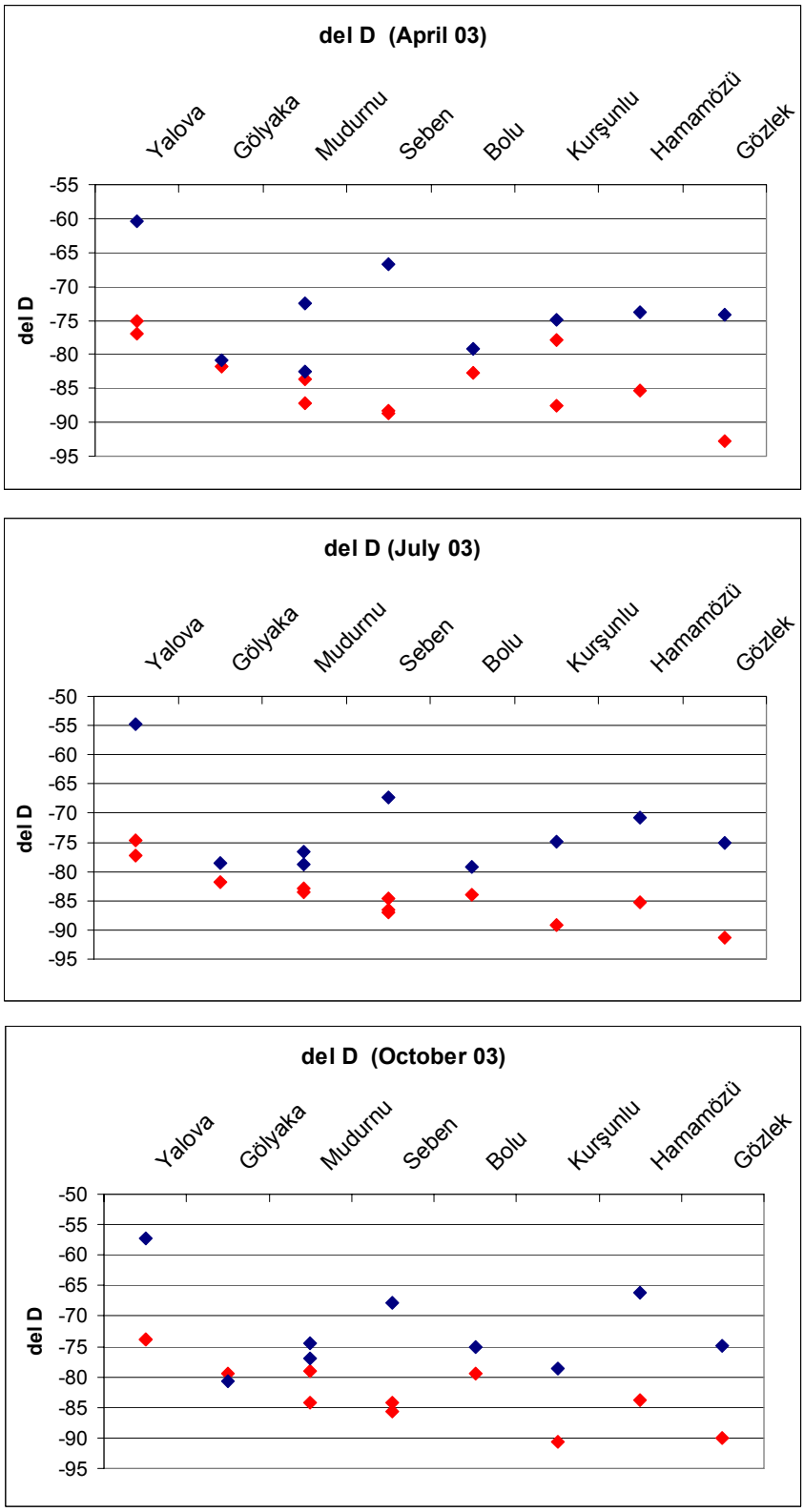


Figure 7.3.b. δD vs locality diagrams covering 2003 sampling periods (red dots show hot, blue dots show cold waters).

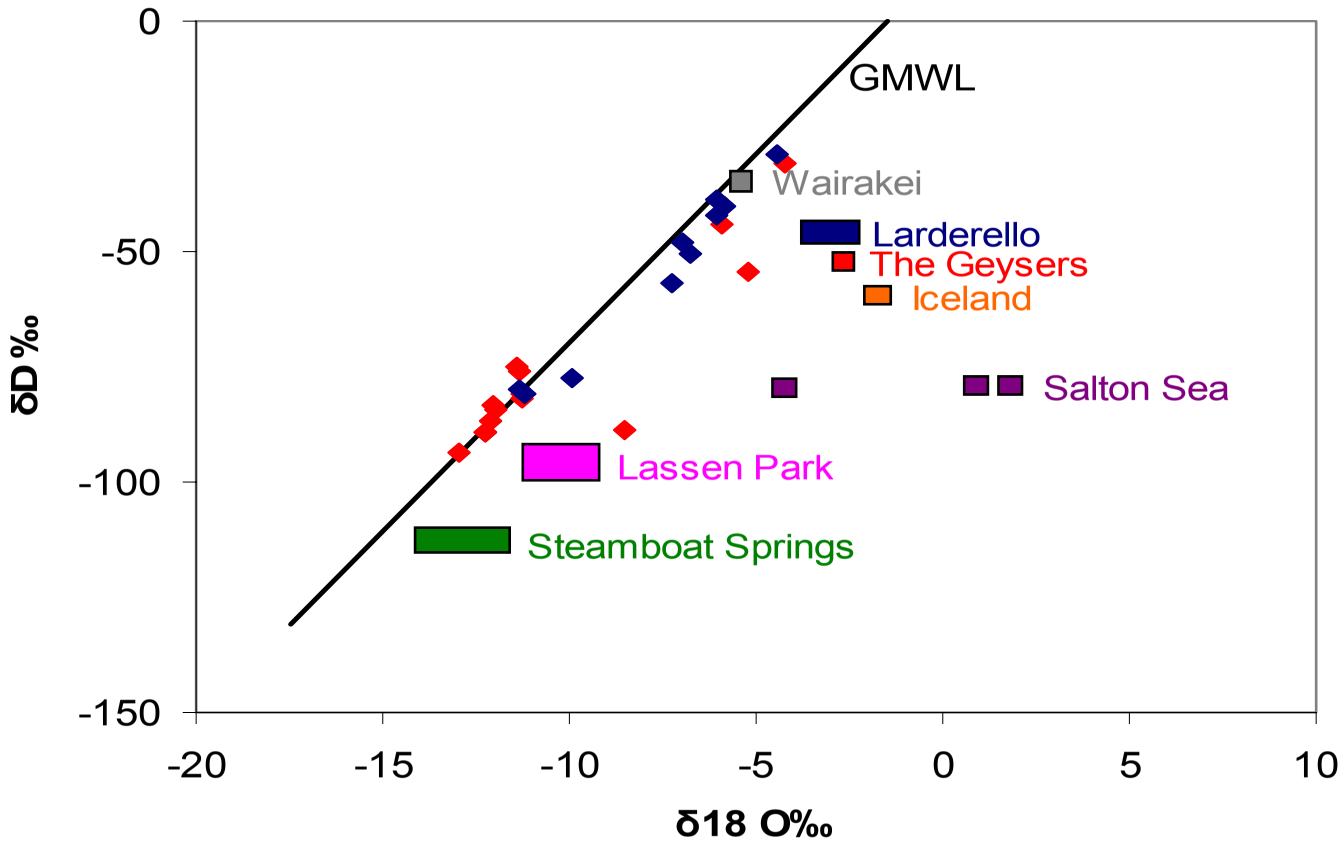


Figure 7.4. Comparison of the $\delta^{18}O$ and δD values of the NAFZ waters with those from various geothermal fields (averages of all sampling periods are taken to represent $\delta^{18}O$ and δD values; red symbols show hot, blue symbols show cold waters, rectangles represent the $\delta^{18}O$ and δD range of the famous geothermal fields, as taken from Ellis and Mahon, 1977).

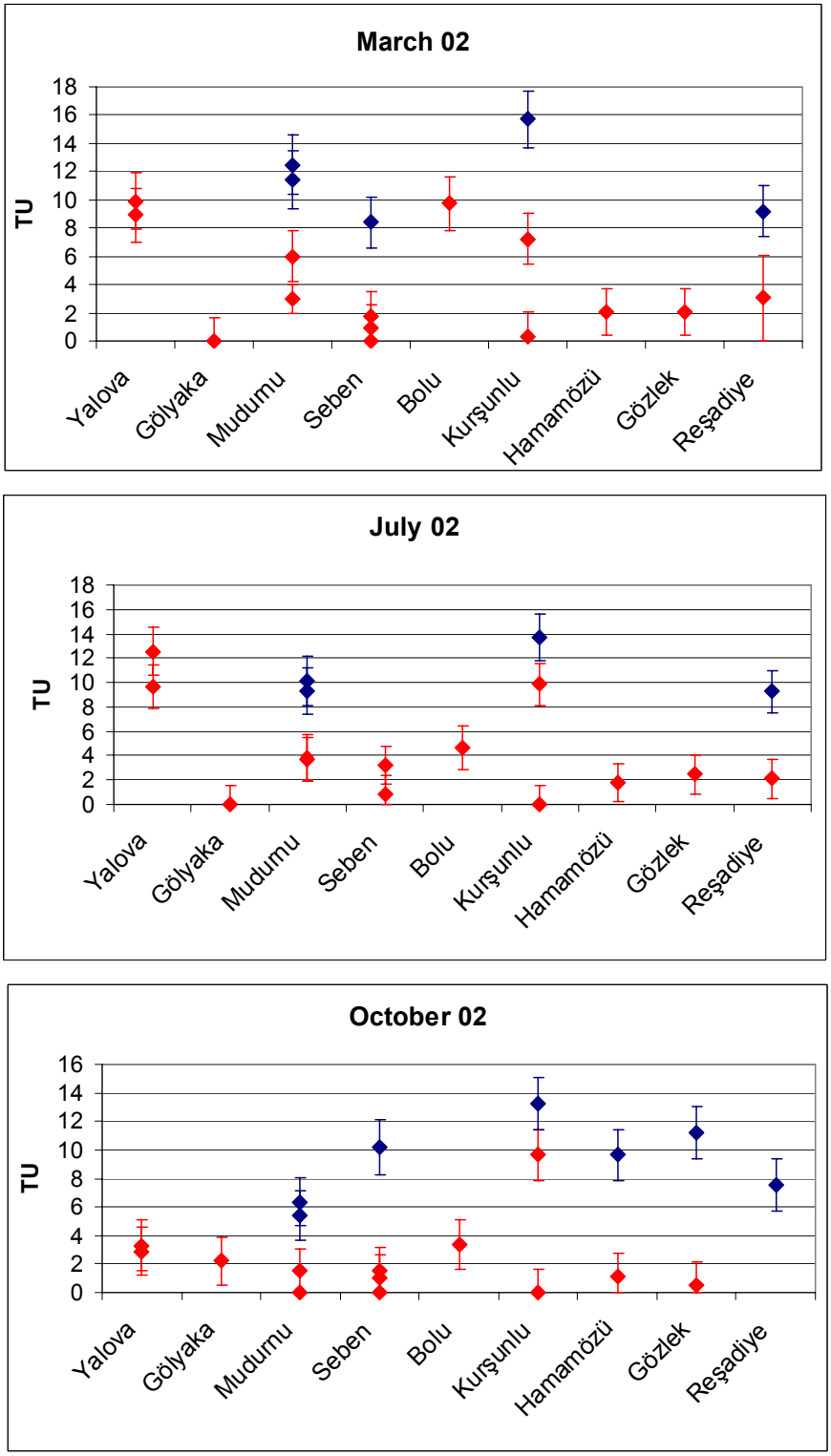


Figure 7.5.a. Tritium content vs. locality diagrams for 2002 sampling periods (red dots showing hot, blue dots showing cold waters; the bars represent the errors associated with the analyses).

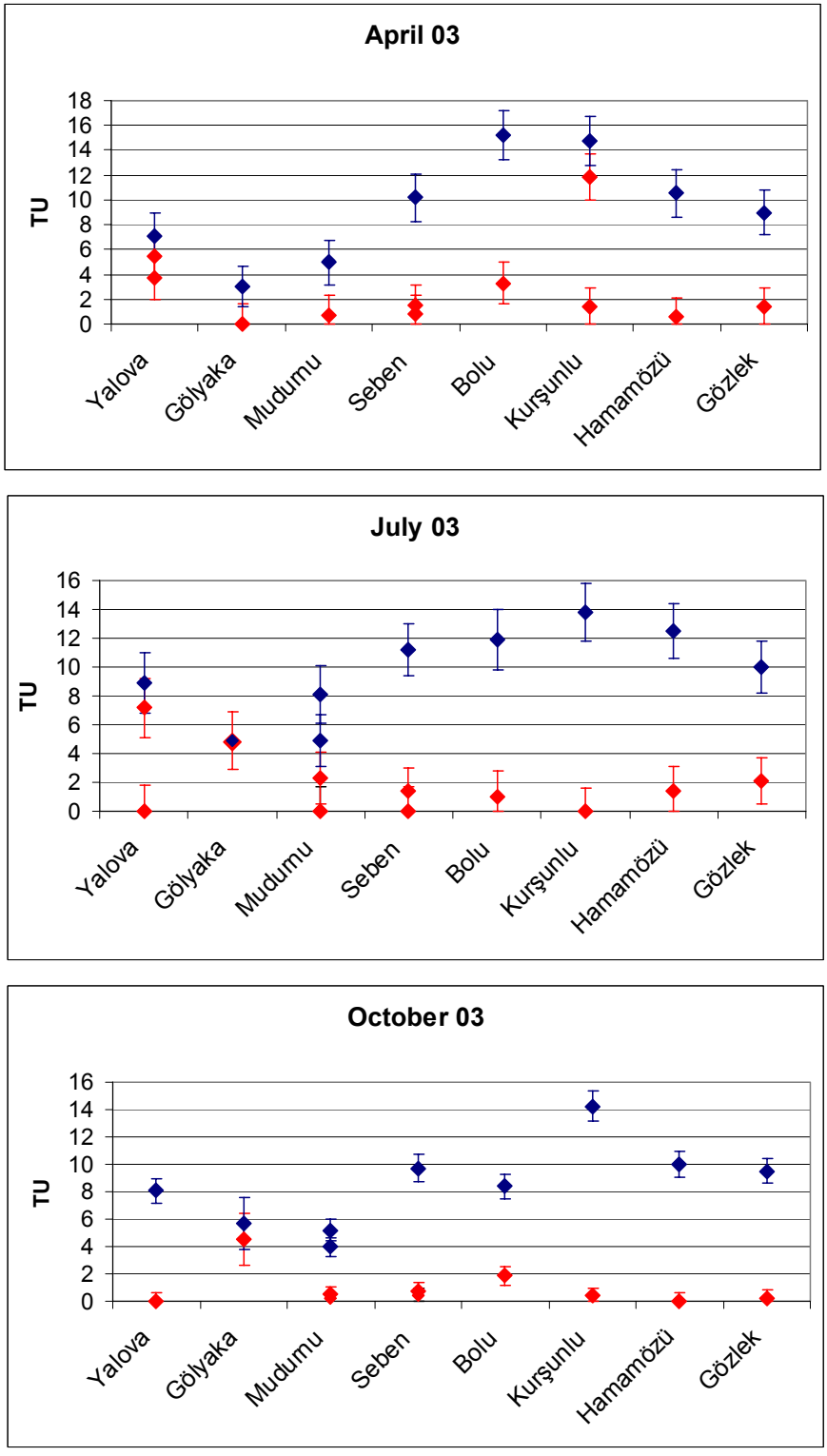


Figure 7.5.b. Tritium content vs. locality diagrams for 2003 sampling periods (red dots showing hot, blue dots showing cold waters; the bars represent the errors associated with the analyses).

CHAPTER 8

TEMPORAL VARIATIONS AND RELATION TO SEISMICITY

8.1. Temporal Variations in Temperature and pH Values

The temporal variations in temperatures of the NAFZ waters are presented in Figure 8.1. In Efteni, Yalova, Bolu, Mudurnu, Hamamözü and, to a lesser extent, in Kurşunlu, temporal variations in temperatures of the cold waters are better recorded since in these fields, especially in summer periods, increase in temperatures are detected, pointing to cold water aquifers which respond to seasonal variations. In Gözlek and Seben cold waters, on the other hand, variations could not be observed and a constant trend is identified suggesting less affected cold water aquifers by seasonal variations.

When the hot waters are concerned, constant trends are observed in Efteni, Bolu, Seben, Hamamözü, Gözlek and Kurşunlu fields. In Yalova samples two different trends are observed: in sample 2a variation is detected on a period base, that is, increasing temperature in summer and decreasing temperature in winter periods, whereas in sample 2b, an almost constant behaviour is detected. It can be commented that sample 2a is responding to seasonal variations more intensely than 2b, and sample 2b can be coming from a deeper reservoir that is less affected by seasonal variations. In Mudurnu 4a sample, an increase only in October 2002 period is observed, whereas in sample 4b, a constant trend is seen.

These variations in temperatures are not much significant to be correlated with seismic activities.

In Figure 8.2 temporal variations in pH of hot and cold waters are presented. As can be seen from Figure 8.2, the cold waters have higher pH values than the hot waters. Regarding the temporal variations, cold waters show rather constant values except for the small variations in Yalova, Gözlek and Kurşunlu fields, which may reflect the effects of seasonal variations. On the other hand, constant trends in pH are observed for most of the hot waters except for Efteni and Bolu fields. In Efteni, in July 2002, an increase is observed in pH (by a factor of 1.2), which can be a result of CO_2 gas escape from the water. In fact, the studies in progress (Güleç et al., in press) report an increase in the CO_2/He ratios (in July 2002) of the gas phase associated with the geothermal fluids in Efteni. Although the reason for CO_2 escape can not be adequately assessed, it seems to be correlated with 14th July 2002 Yığılca and Akçakoca (M: 3.1. and 2.6, respectively) and 15th July 2002 Yığılca (M: 2.8) earthquakes. In Bolu, in March 2002, the pH value is higher (by a factor of 1.2) than the values recorded in the other periods. Since no anomalies are observed in the CO_2 gas content in Bolu in March 2002 period (Güleç et al., in press), this increase in pH may stand from mixing with cold waters (which have relatively high pH values) and this mixing could have been induced by the 23rd March 2002 Sea of Marmara earthquake (M: 4.7).

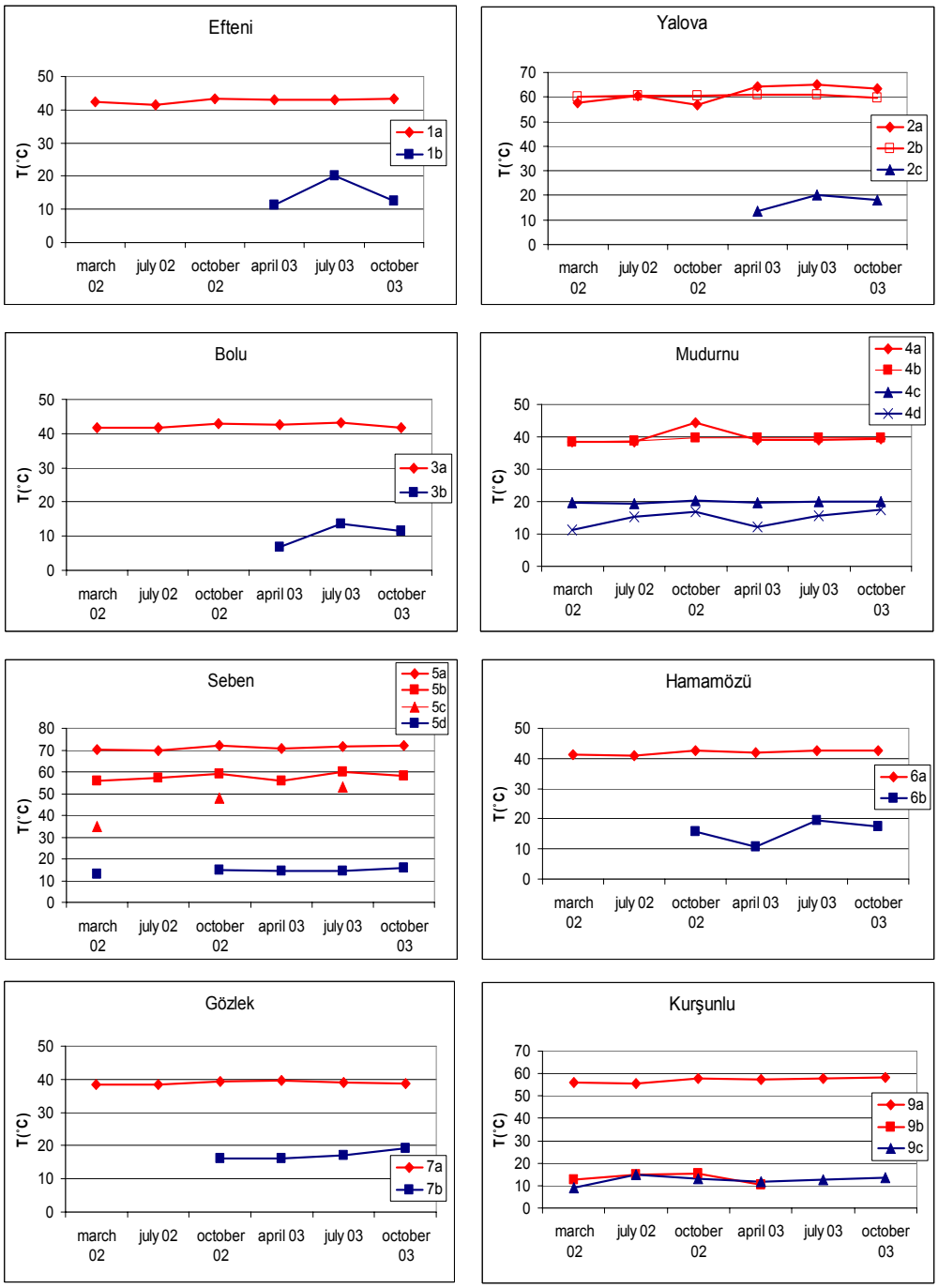


Figure 8.1. Temporal variations in temperature for all fields.

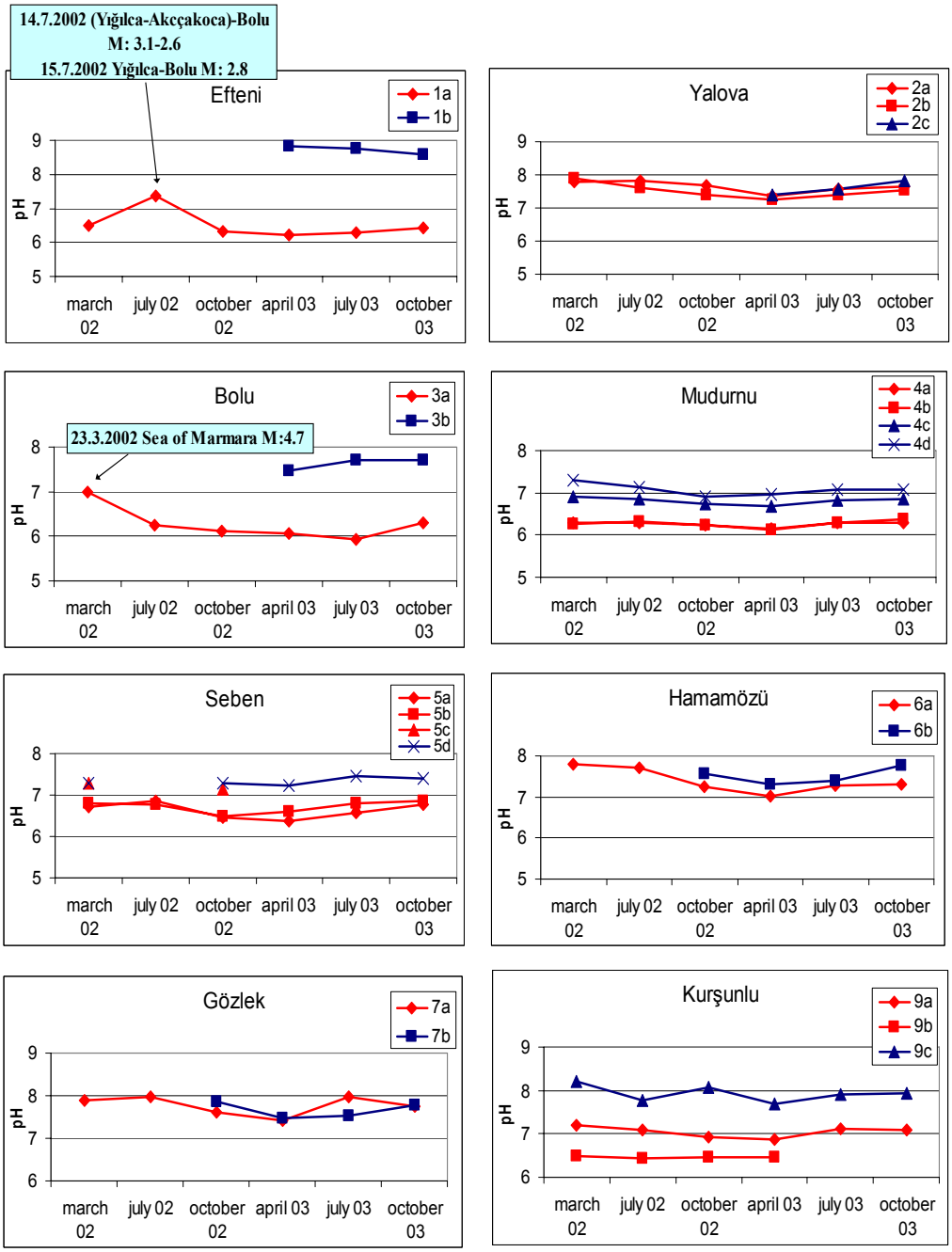


Figure 8.2. Temporal variations in pH for all fields.

8.2. Temporal Variations in Chemical Compositions

Temporal variations in chemical compositions are shown in Figure 8.3 as plots of concentration versus sampling periods. Regarding the hot waters, the most striking features in Figure 8.3 can be summarized as follows:

- About 1.5-fold decrease in the Ca content of Efteni hot water, in July 2002, which is correlated with the pH increase noted in Section 8.1. Since any pH increase in waters is accompanied by a decrease in the calcite dissolution, this Ca decrease in water is not only coupled with, but also in confirmity with the pH increase in July 2002 period in Efteni. As has been noted above, July 2002 pH increase (and the accompanying Ca decrease) is also coupled with an increase in the CO_2/He gas ratio (Güleç et al., in press) and appear to be correlated with the seismic activities on 14th and 15th July 2002 in the vicinity of Düzce (epicenters Yığılca; M: 2.8-3.1).

- About 1.5-fold increase in Ca contents in Efteni in April 2003, and in Yalova, Hamamözü and Gözlek in July 2003 periods. Since the dominant cation of the hot waters in the concerned fields is Na, whereas that of the cold waters is Ca, this increase in Ca content suggests mixing of the hot waters with the shallow, cold waters. It is interesting to note that the period of mixing appear to precede the seismic activities of 22nd and 24th of July 2003 (M:3.5 and 3.3, respectively) in Yalova, and 11th of May 2003 (M:2.8) in Gölyaka-Düzce. In this respect, the Ca anomalies in Yalova and Efteni fields can probably be correlated with the above mentioned seismic activities. Similarly, the Ca anomalies in Hamamözü and Gözlek in July 2003 can be correlated with the 26th June 2003 Gümüşhacıköy-Amasya (M: 3.4) earthquake.

- About 1.5-fold decrease in Cl content in Yalova in July 2002 period. Since Cl is considered to be a conservative constituent used as tracer, the decrease in the Cl content points to a hot-cold water mixing process which can be

correlated with the seismic activities occurred on 3rd and/or 13th of July 2002 in Armutlu-Yalova (M: 3.1). Since the sampling date in Yalova is 9th of July, it is difficult to decide, however, whether the above mentioned Cl decrease is the precursor of the 13rd July 2002 seismic activity or if it is the post-earthquake signature of the 3rd July 2002 activity. It is interesting to note here that in July 2002 period there is a concomitant increase (again about 1.5-fold) in SO_4 content of Yalova hot waters which suggests that the seismic activities (responsible for hot-cold water mixing) were also associated with degassing of sulphur probably from the young organic sediments in the İzmit Bay to the north of the Yalova field.

- About 1.5 fold increase in Mg content of Mudurnu 4a and 4b samples in July and October 2003, compared to the previous periods. Since Mg contents of hot and cold waters are almost similar in Mudurnu field (Table 6.1), this increase in Mg content of the hot waters can not be related to a mixing process that could be induced by seismic activities. In fact, a similar increase in Mg contents are also recorded in Mudurnu cold waters (Figure 8.4). Although the actual mechanism involved is difficult to assess, the Mg increase in Mudurnu samples may be reflecting the effects of seasonal variations.

- High SO_4 contents of Bolu-3a and Seben-5a, 5b hot waters in March and July 2002 periods compared to the other periods (Figure 8.3). Since the SO_4 content of cold water in Bolu is lower than that of hot water, and since the SO_4 content of Seben cold water (5d) (Figure 8.4) also seems to be high in March 2002 period, it is difficult to comment on the origin of these SO_4 increases. A possible emission of deep origined H_2S gas (and its dissolution in water) may explain the high SO_4 content in Seben (in relation to the 14th and 15th July 2002 Yığılca earthquakes). It is important to note, at this stage, that the depth of the 14th July 2002 Yığılca earthquake is 9.6 km which may be taken as a support for the release of deep origined H_2S gas. In fact, deep origined gas releases are reported by Güleç et al. (in press) in Seben area,

although not in the same period (mantle-He emissions in October 2002 period). The same mechanism, however, can not be applicable for Bolu as there is also an increase in pH in the same period, as opposed to the expections (increase in SO_4 from H_2S dissolution should be accompanied by a decrease in pH).

- A continuous decrease in the Cl content of Kurşunlu 9b sample. This sample, despite its low temperature (<20 ºC), has a high TDS (Total Dissolved Solid) value ("*mineral water*") and is treated here in the category of hot waters. Its Cl content displays a continuous decrease from 210 mg/l in March 2002 to 82 mg/l in April 2003 period. This situation can be attributed to either i) an anomaly in March 2002, with the return of Cl contents to their original values in time, or ii) a hot-cold water mixing process triggered by seismic activities following March 2002, with an increase in the cold water component in time. As can be seen from the previously presented Table 3.1 in Chapter 3, both the frequency and the magnitute of the seismic activities in the Çankırı region starts to increase in the periods following April 2002 and, hence, the second alternative above seems to be more likely.

- Chemical variations in hot water compositions are also observed in the other fields (and in constituents apart from Cl and Ca) but these do not seem to be significant (less than 1.5-fold).

In case of cold water compositions (Figure 8.4), Kurşunlu-Çavundur, Mudurnu and to some extent Reşadiye fields are the ones where temporal variations are better recorded. Variations in the concerned fields are probably seasonal, related to changes in the amount of precipitation and/or evaporation.

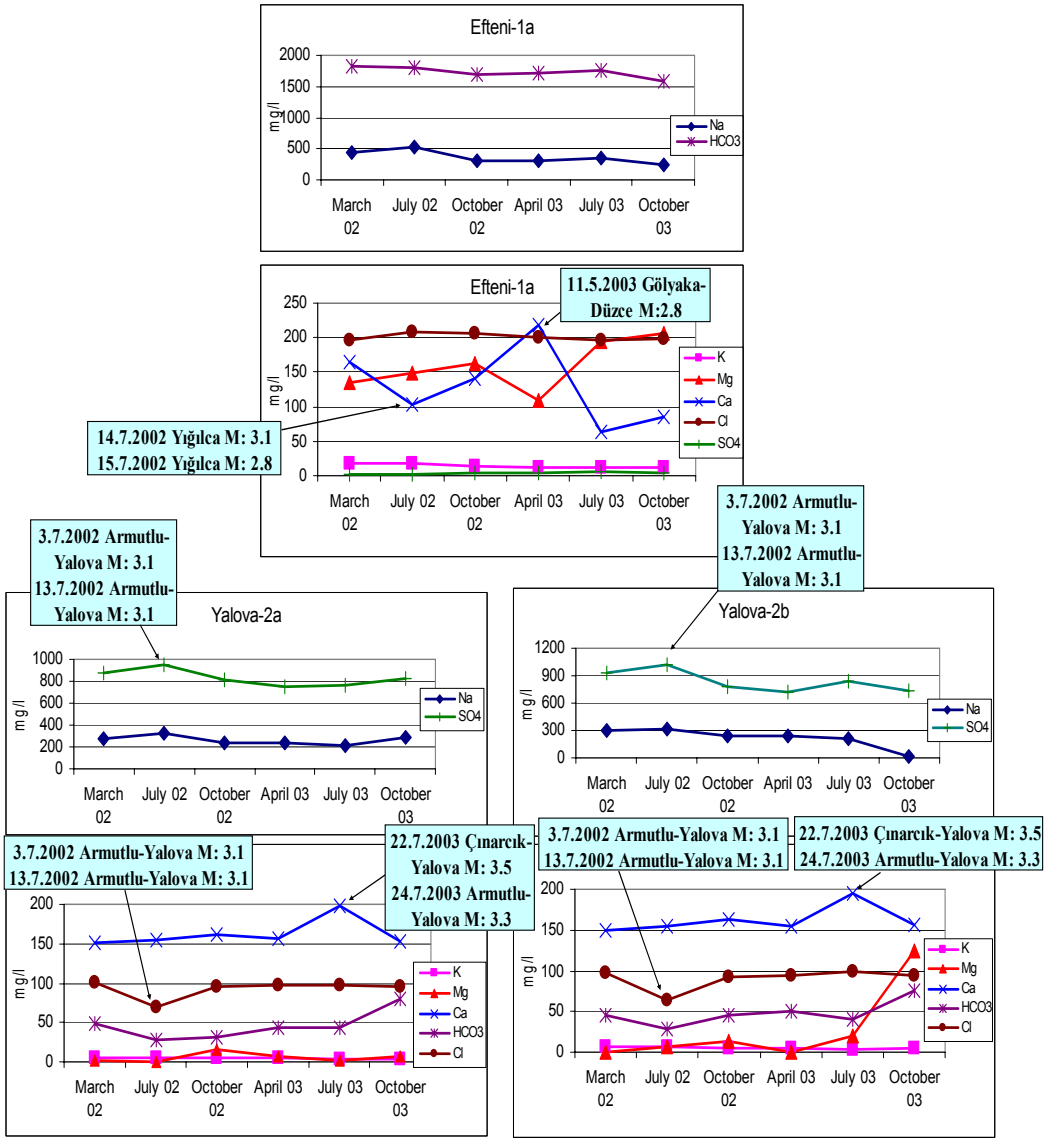


Figure 8.3. Temporal variations in the ionic compositions of the hot waters.

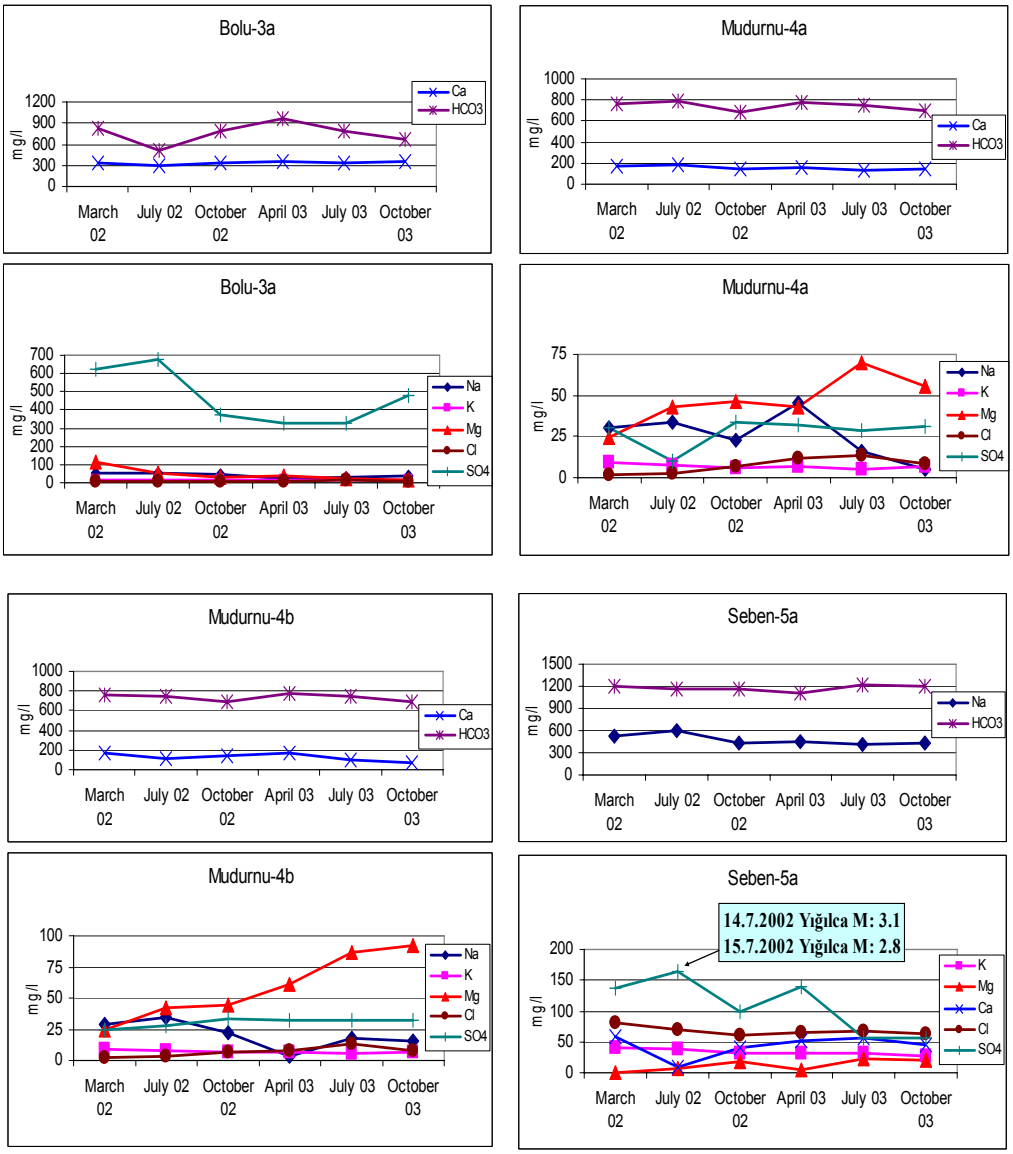


Figure 8.3. (continued).

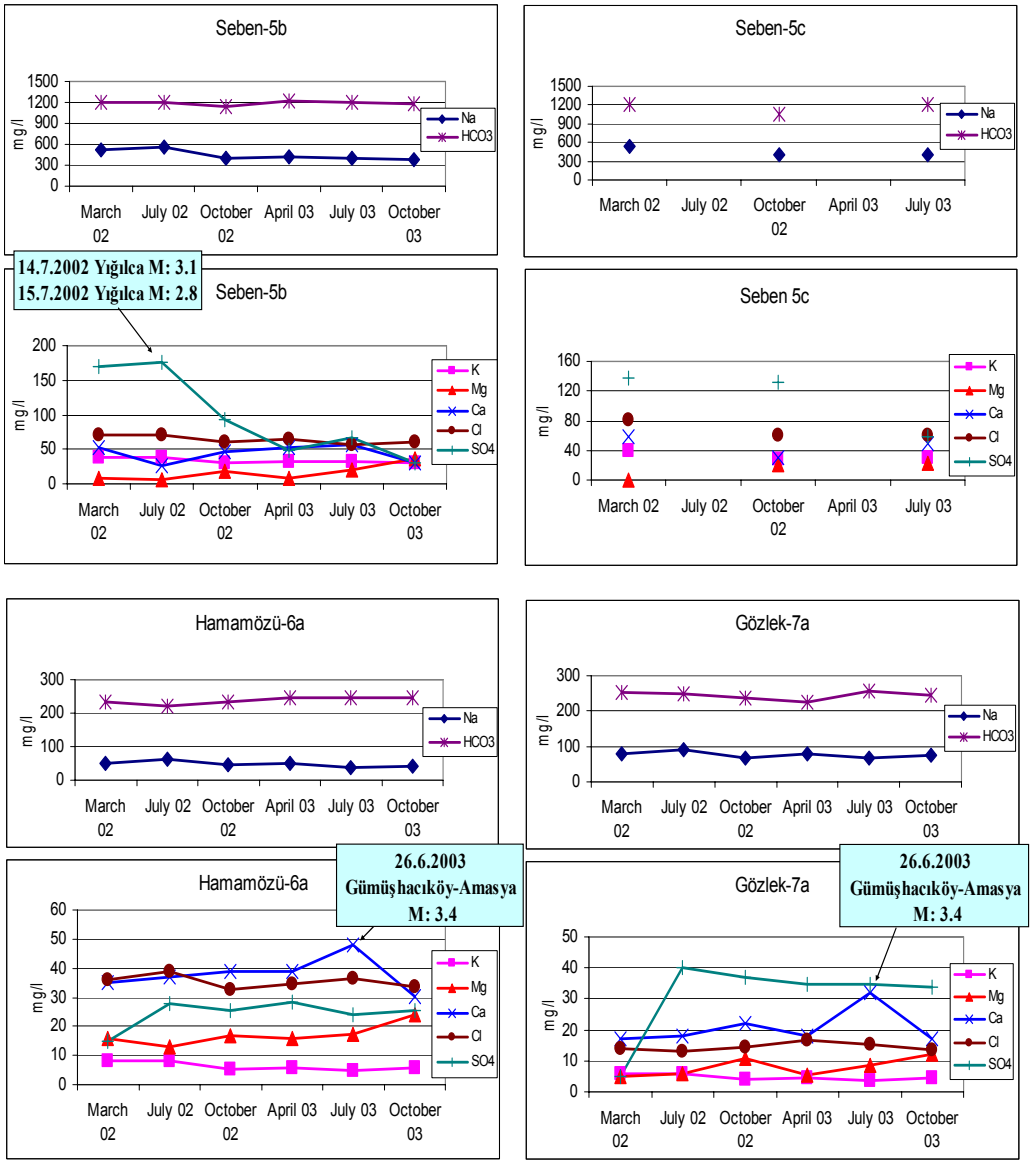


Figure 8.3. (continued).

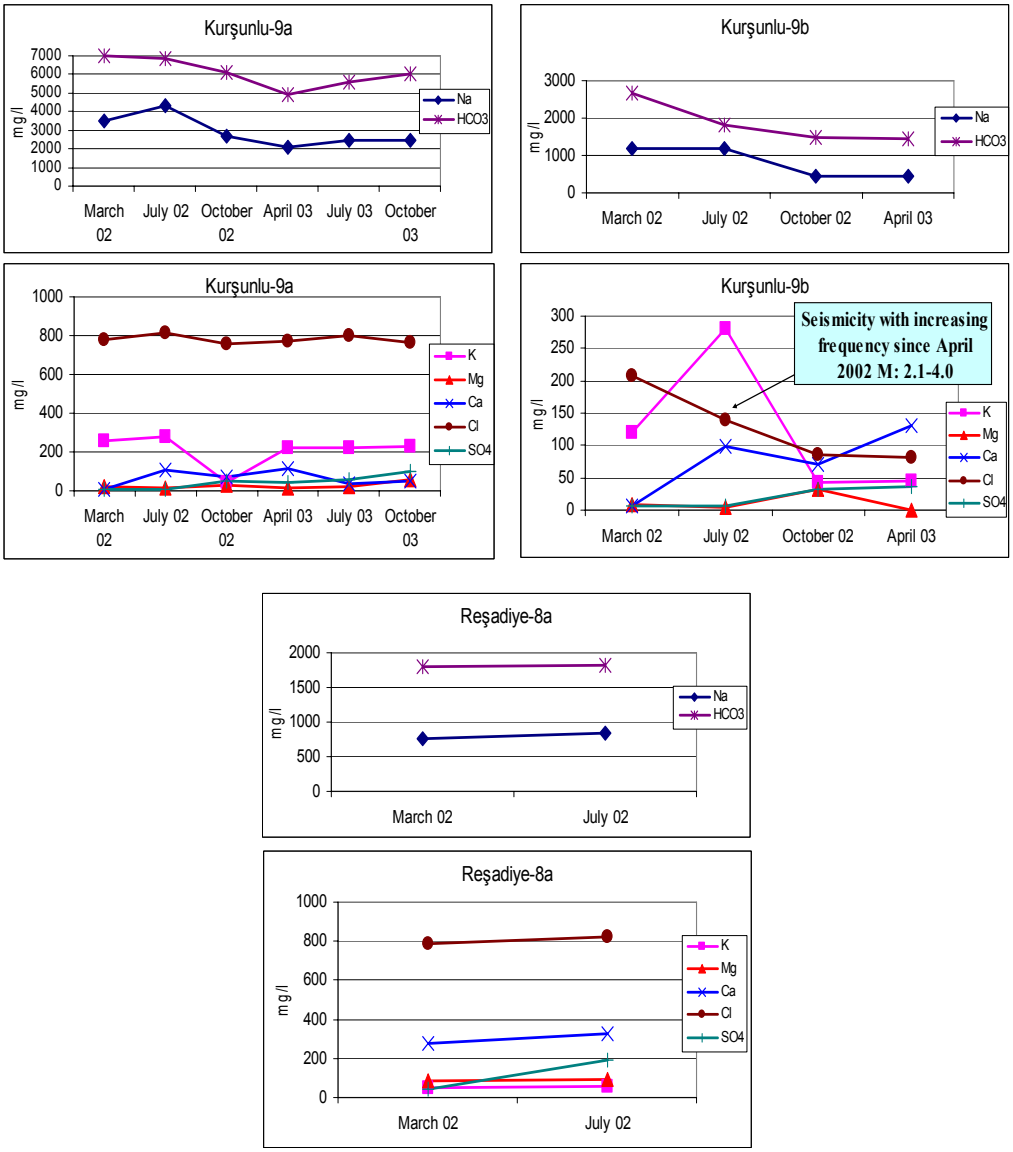


Figure 8.3. (continued).

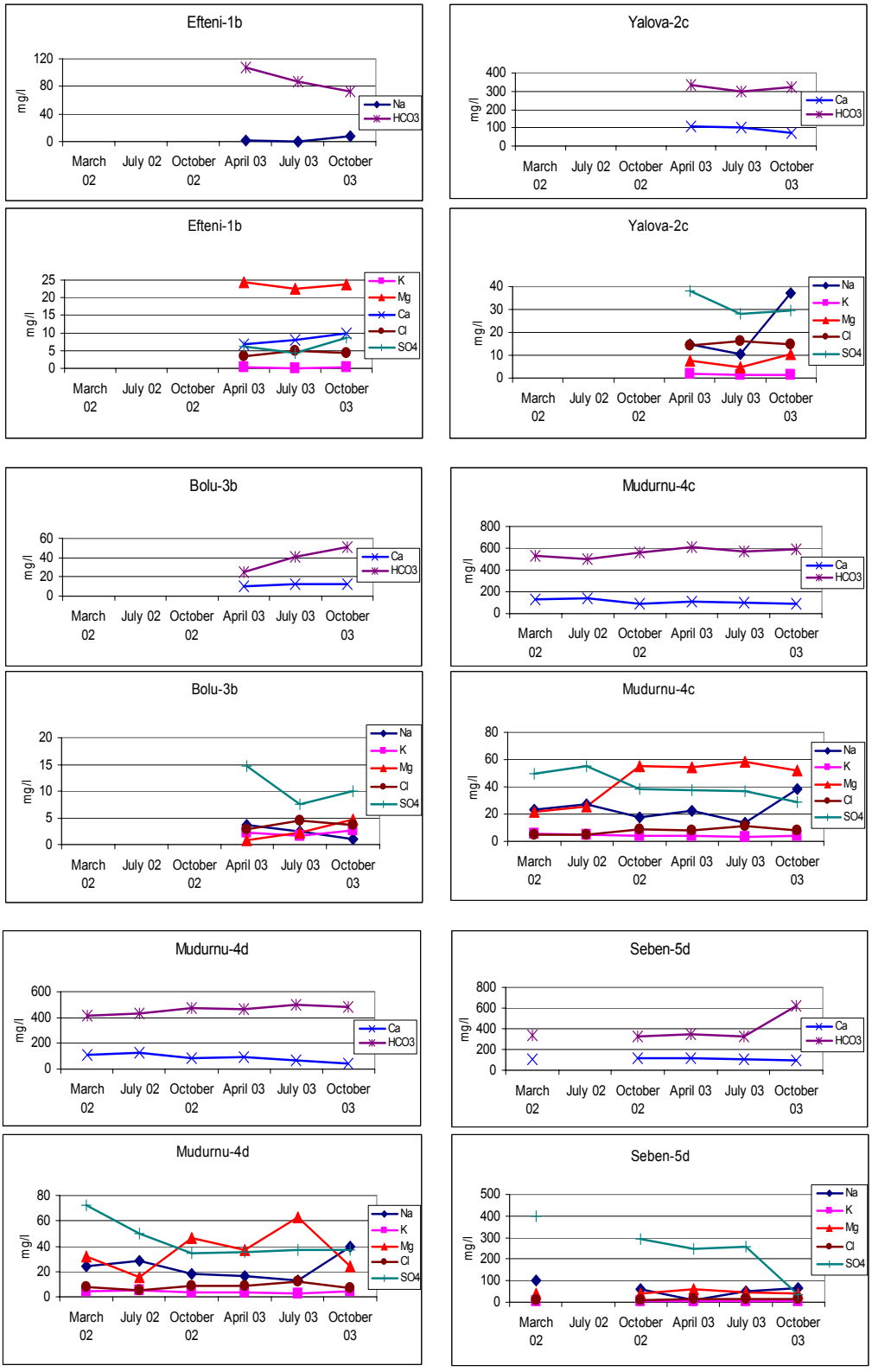


Figure 8.4. Temporal variations in the ionic compositions of the cold waters**.**

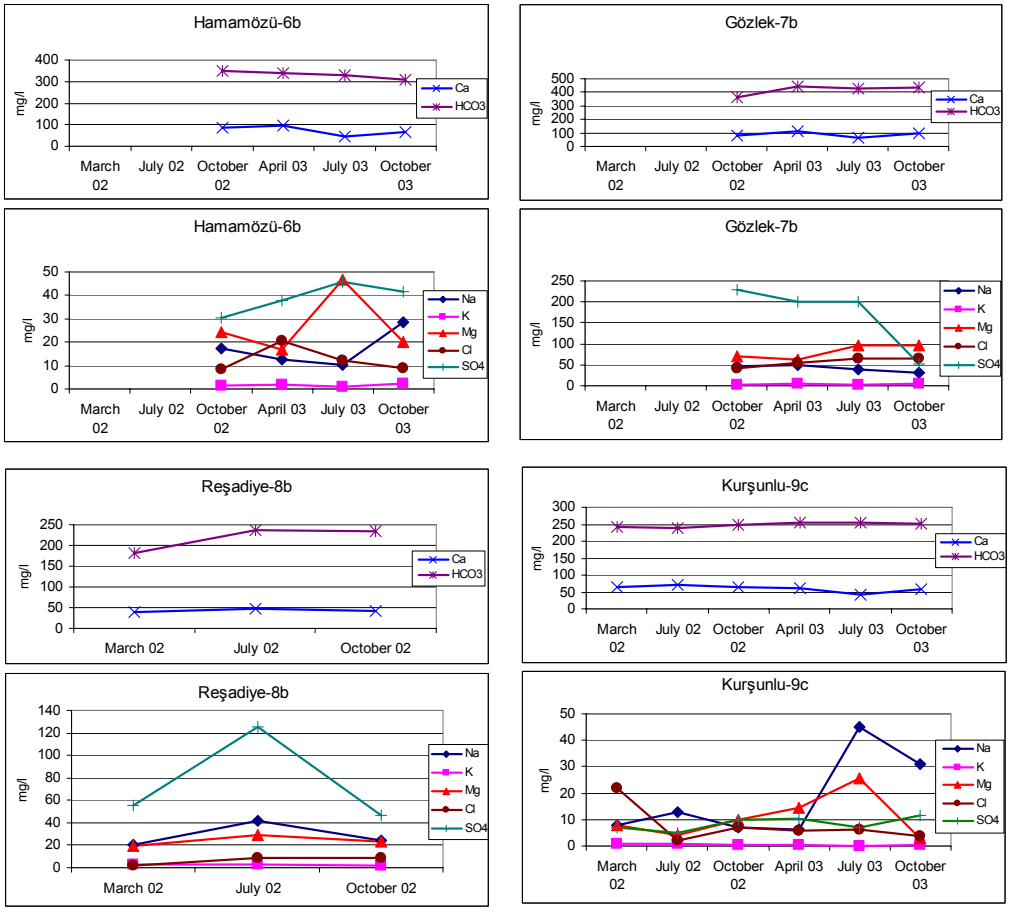


Figure 8.4. (continued).

8.3. Temporal Variations in Oxygen-18 and Deuterium Compositions

The temporal variations in $\delta^{18}O$ and δD values, shown in Figures 8.5 and 8.6 respectively, are generally outside the limits of analytical errors (0.1‰ for $\delta^{18}O$ and 1‰ for δD) and appear to be more prominent in Bolu and Mudurnu fields. These variations and are observed i) in October 2002 in the hot water sample from Bolu, and ii) in April 2003 in the cold water sample from Mudurnu. The increase in Mudurnu cold water sample is likely to reflect seasonal effects (precipitation and/or evaporation), while in Bolu, the variations in hot water is probably a result of hot-cold water mixing process triggered by a

seismic activity. Although there appears to be two seismic activities in Bolu on 21st October 2002 and 1st November 2002 (M: 2.6 and 3.4, respectively) that can be related to this mixing process, the effects of these seismic activities are not observed on the other parameters (i.e. in anion-cation-tritium contents).

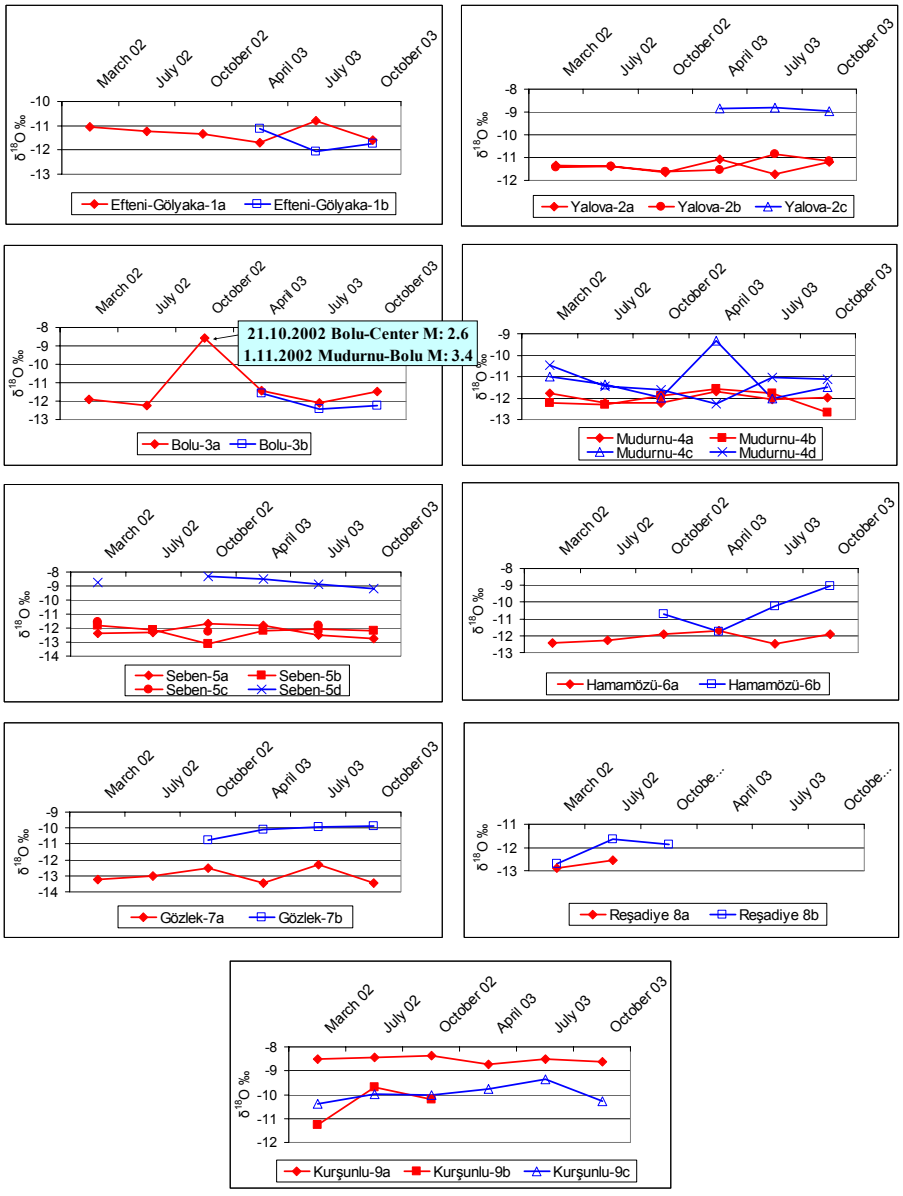


Figure 8.5. Temporal variations in oxygen isotope compositions (red symbols represent hot, blue symbols represent cold waters).

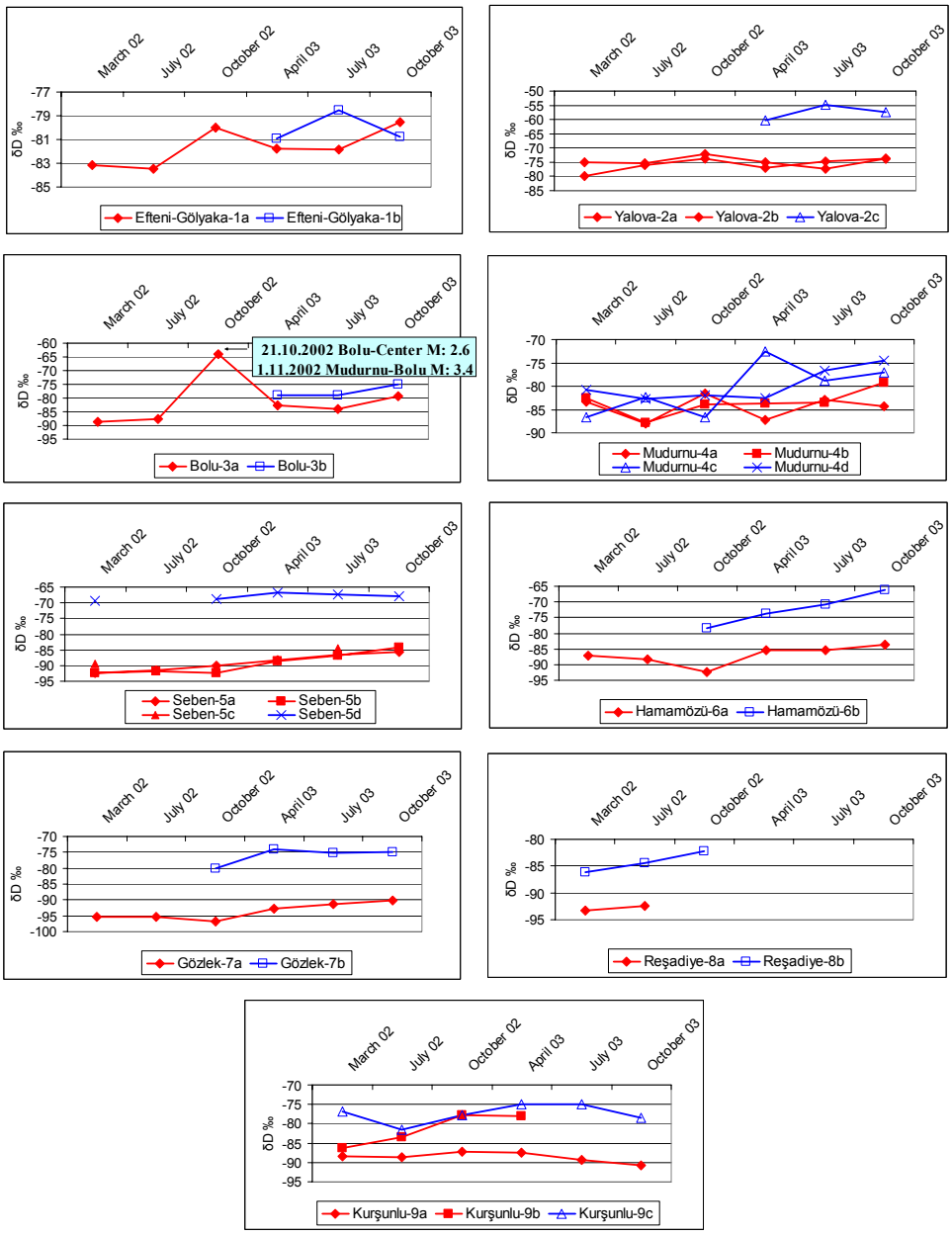


Figure 8.6. Temporal variations in hydrogen isotope compositions (red symbols represent hot, blue symbols represent cold waters).

8.4. Temporal Variations in Tritium Contents

Temporal variations in tritium contents are shown in Figure 8.7 (a, b). An inspection of Figure 8.7.a reveals increase in tritium content of the Efteni hot water (1a) in October 2002, and July-October 2003 periods. The increase in October 2002 does not seem to be significant as it is within the limits of analytical errors associated with this sample for the preceding periods. On the other hand, the increases in July and October 2003 periods can be significant, as, although the values are within the limits of analytical error for October 2002 analysis, they are outside the error limits recorded for the other periods. Since tritium is low in deep circulating hot waters and high in shallow reservoirs fed by recent recharges, this increase in tritium contents in July-October 2003 periods may point to the effects of a mixing with the cold shallow waters, and the mixing could have been induced by the earthquake swarm in July to August 2003 period (epicenters: Kaynaşlı-Düzce, Yığılca –Düzce and Gölyaka-Düzce) with magnitutes ranging between 2.3-4.0 (Table 3.1). It should be noted, however, that this tritium increase in Efteni sample, in July-October 2003 periods, is not accompanied by any anomaly in anion and/or cation contents (see section 8.2). In fact, the recorded chemical anomaly (Ca increase) for Efteni belongs to the April 2003 period (section 8.2) which is not reflected in tritium contents in the same period.

In Bolu field, the tritium content of March 2002 period is considerably higher than those recorded for the other periods (pointing to mixing with cold waters), and the closest seismic activitiy in this period is the earthquake with epicenter Sea of Marmara and Magnitute: 4.7. This tritium anomaly in March 2002 seems to be coupled with the high SO_4 content in the same period (Section 8.2).

In Mudurnu field, the tritium content of hot water sample 4a is significantly higher in March 2002 and July 2002, compared to the other periods (Figure 8.7.a). Since tritium content of cold water (Figure 8.7.b) is also high in March-July 2002 periods, these increases in tritium contents are

probably related to seasonal precipitations which affected both hot and cold aquifers.

In Kurşunlu field, tritium content of sample 9b displays an increasing trend with time. This is correlated with the decreasing Cl trend (Figure 8.3 and 8.8) mentioned in section 8.2 and supports the idea of mixing whereby the cold water component increases in time in relation to the increasing frequency and magnitude of seismic activities in Çankırı since April 2002.

In Yalova Field, significant increase (outside the limits of analytical errors) in tritium contents of hot waters (particularly sample no.2a) is detected in July 2002 period (Figure 8.7.a). The interpretation of this anomaly requires particular attention as during the course of monitoring high background levels were sometimes encountered in the DSİ laboratory (personal communication with C. Çifter, 2003). However, it is important to note that this increase in tritium content is accompanied by a decrease in Cl content in the same period (as noted in section 8.2) in Yalova (Figure 8.8). Since deep penetrating hot waters have high Cl and low tritium, whereas the shallow circulating cold waters have low Cl and high tritium contents, the increase in the cold water component in any hot-cold water mixing process is characterized by an increase in tritium and a concomitant decrease in Cl content. In other words, the tritium increase observed in Yalova may indicate a mixing process, possibly triggered by seismic activities occured in Armutlu-Yalova on the 3rd and 13th of July 2002. Apart from July 2002, high tritium contents are also recorded in March 2002 in Yalova hot water samples. Although they are not coupled with any significant variations in anion-cation contents, these high tritium contents can be correlated with the seismic activity occurred in the Sea of Marmara (M: 4.7) on 23rd March 2002.

Regarding the overall tritium variations, it is important to note that the effects of the March and July 2002 seismic activities are recorded in Yalova and Bolu, whereas those of July 2003 are recorded in Efteni field. This suggests

that the March and July 2002 earthquakes seem to have affected the southern, while the July 2003 earthquakes affected the northern strand of the NAFZ.

In addition to the recorded variations in tritium and chloride, there exist some seismicity related variations in other geochemical parameters reported by other studies (Güleç et al., in press), such as those in CO_2/He gas ratios and $\delta^{13}C$ values in the CO_2 gas of the geothermal fluids. In March 2002, an anomalous value of +5.79‰ was recorded in Yalova geothermal field in $\delta^{13}C$ values, which were recorded as below zero for almost all the other sampling periods. This was accompanied by high CO_2/He ratio in the same period. Such high values in both parameters can probably be attributed to thermo-metamorphic decay of marine carbonates, which may be induced by the seismic activity on the 23rd of March 2002 in the Sea of Marmara (M: 4.7), which is the same day of sampling from Yalova.

8.5. Comparison of Thermal Waters from Springs and Wells

Spring waters tend to react chemically with the wall-rocks through which they pass along their journey to the surface and deviate from reservoir water composition from which they originate. This is due to the fact that spring waters actually represent an open system, that is, they carry the effects of the processes they have gone through such as adiabatic cooling, conductive cooling, water-rock interaction and mixing with different waters. Since spring waters are closer to the surface, they can present more intense effects of mixing with cold waters due to their shallow circulation when compared with the well waters.

Well waters, on the other hand, are more likely (although not necessarily) to represent a closed system and are sampled without being intensely contaminated by outer sources, and hence they are more likely to reflect the original reservoir composition. In this respect, any seismicity-induced mixing is more likely to be reflected in the composition of spring, rather than well waters. In fact the chemical variations noted in Section 8.2

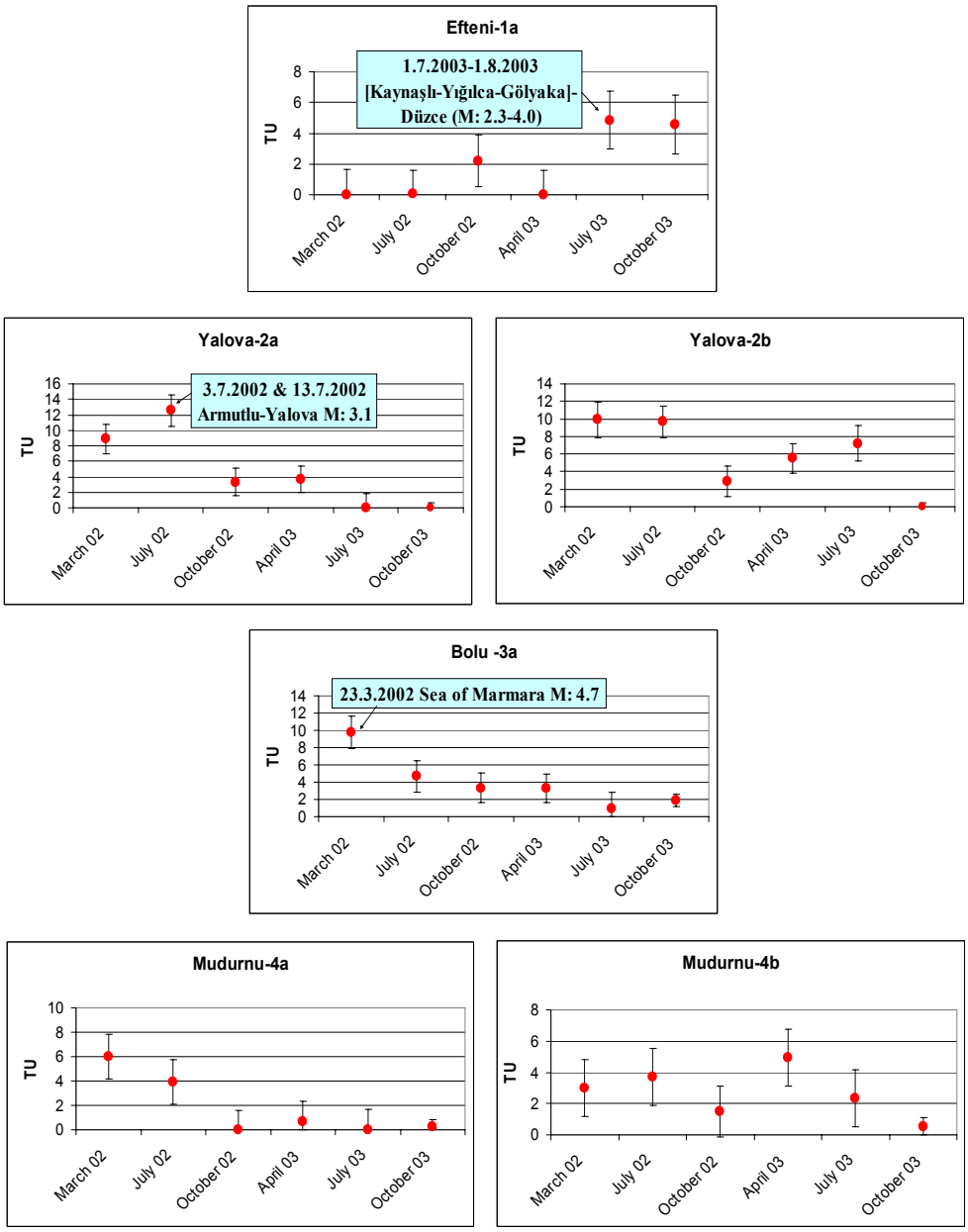


Figure 8.7.a. Tritium vs sampling periods for the hot waters.

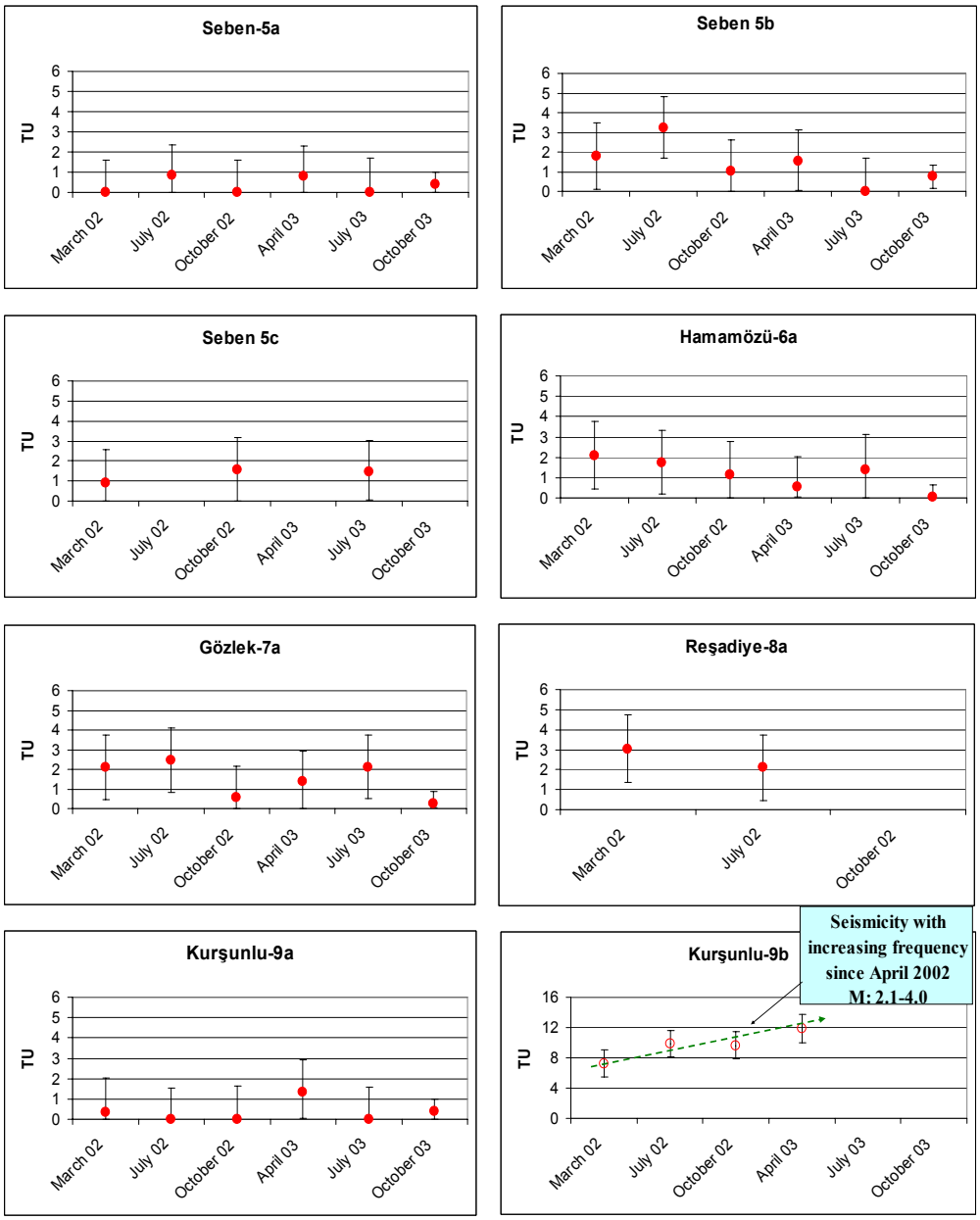


Figure 8.7.a. (continued).

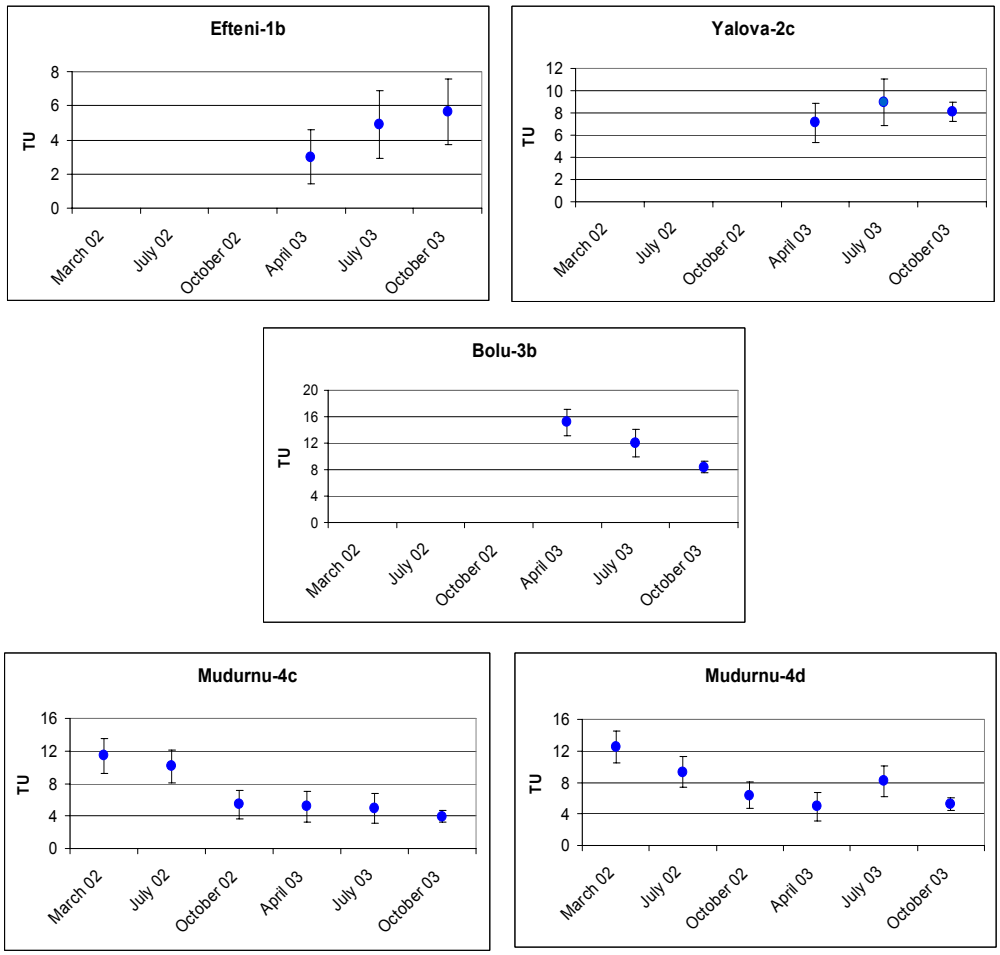


Figure 8.7.b. Tritium vs sampling periods for the cold waters.

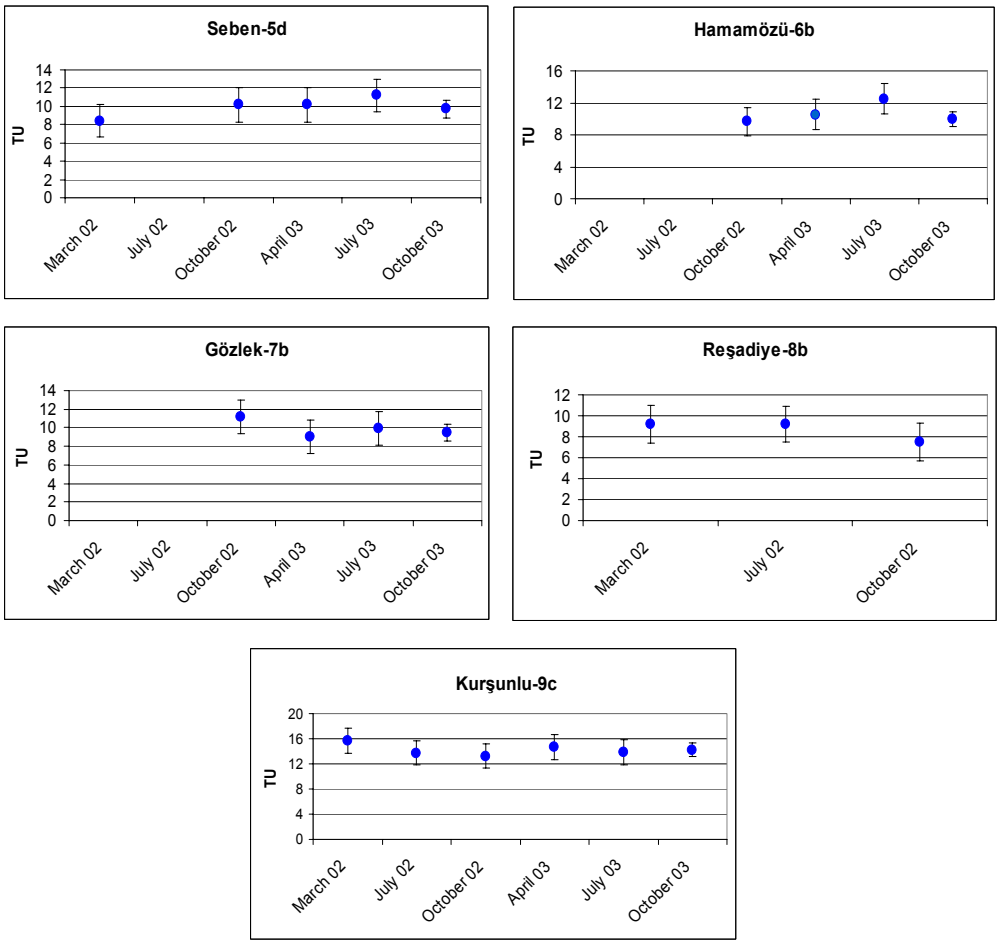
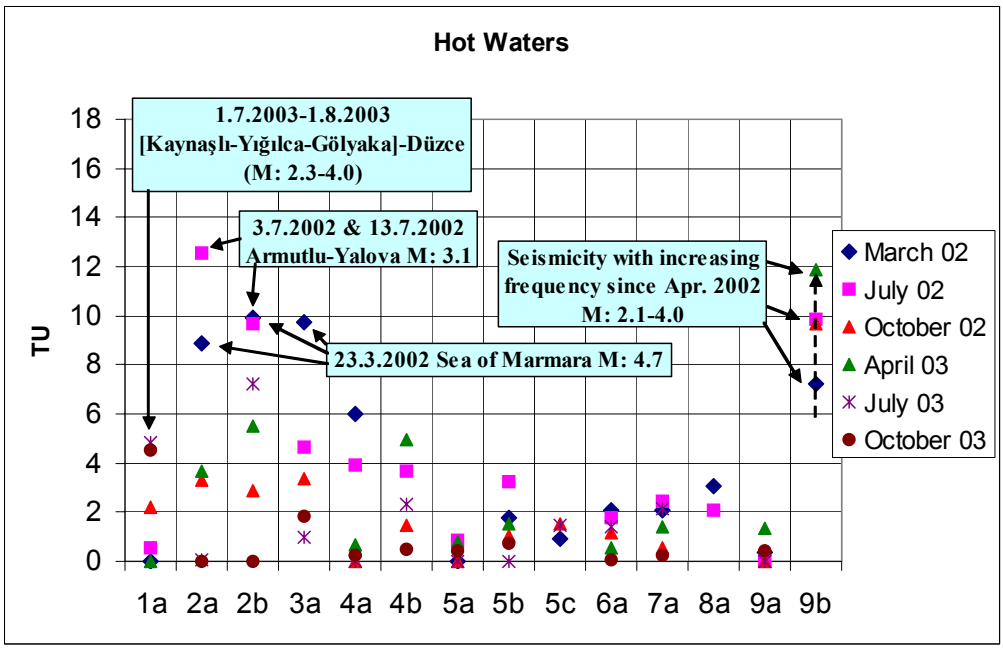


Figure 8.7.b. (continued).

a)



b)

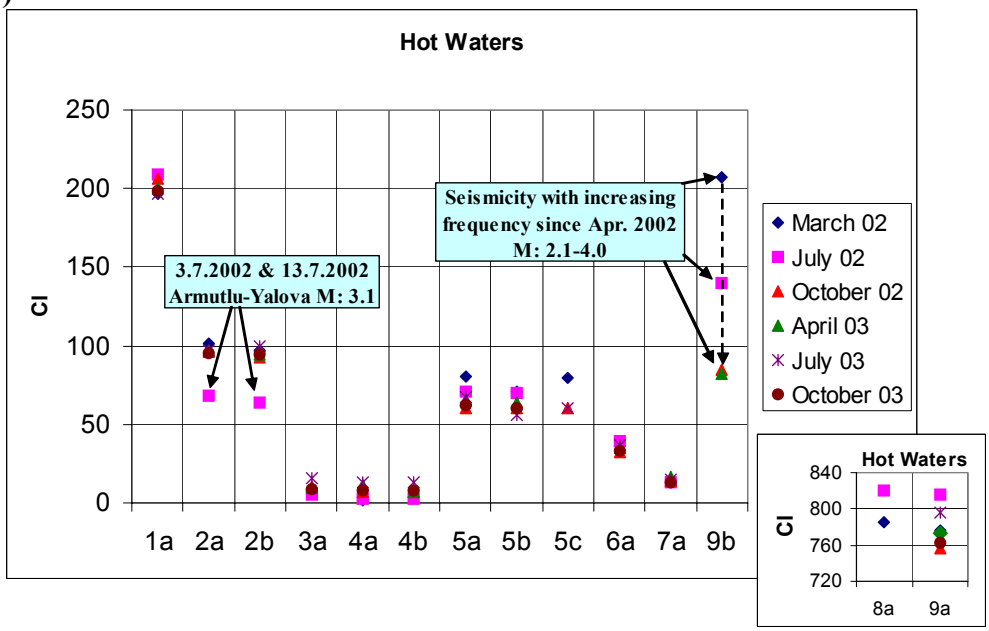


Figure 8.8. Concentration vs. Sample number plots depicting the temporal variations in a) TU contents, b) Cl contents of the hot waters.

(particularly Ca and Cl anomalies), which are likely to be the result of seismicity-induced mixing, are observed in spring samples of Efteni, Yalova and Kurşunlu. The SO_4 anomaly in Bolu in March-July 2002, and the Mg anomaly in Mudurnu in July and October 2003 periods, on the other hand, are those observed in the well samples. As has been noted in Section 8.2, the mechanism of the SO_4 increase in Bolu is yet to be resolved. The Mg anomalies in Mudurnu, on the other hand, are already noted (Section 8.2) to be rather independent of mixing as the increase in Mg contents are also observed in cold waters.

In reality, hot waters sampled from deep penetrating wells should have lower tritium contents than the hot spring samples, since they represent deep aquifer systems which are hardly affected by recent precipitations. Hot springs, on the other hand, should have higher tritium contents than those of the waters discharging from wells since they are open to both surface and subsurface influences. When this case is concerned, Kurşunlu hot water sample (9a) best fits this situation, since it is sampled from a well and gives the lowest TU values, that is, it is the field which is least affected by surface conditions. This is also coupled with high Cl content suggesting a deep hot water reservoir for the Kurşunlu field.

The hot water samples collected from wells from the other fields (Mudurnu, Bolu, Hamamözü and Gözlek) have relatively higher tritium contents than the Kurşunlu hot water, suggesting shallower reservoir conditions carrying the effects of recent precipitations. When the depth of producing zones in the wells are concerned, the Kurşunlu hot water reservoir is indeed deeper (165 m) than those in Bolu (83 m) and Mudurnu (80 and 125 m). Hamamözü (500 m) and Gözlek (398.5 m) reservoirs, although deeper than that in Kurşunlu, have higher tritium contents, ranging between 0.1 - 2.1 TU and 0.3 – 2.5 TU, respectively, compared to 0.0 – 1.4 TU in Kurşunlu. This suggest that although the reservoir is not as deep as those in Hamamözü and Gözlek, the waters in Kurşunlu have rather long residence times.

Regarding the spring samples, the tritium contents are lower in Seben and Efteni fields, pointing to deeper reservoir conditions and/or longer residence times of waters compared to the Yalova field.

Regarding the open system characteristics of spring waters, the variations in tritium contens (resulting from hot-cold water mixing) are expected in spring water samples, rather than well waters. In fact, the significant tritium variations (outside the limits of analytical errors) are observed in this study in spring waters (Efteni, Yalova, and Kurşunlu mineral water springs).

8.6. Concluding Remarks

The foregoing discussion reveals correlation between the seismic activities and the compositional variations of the NAFZ geothermal waters which are recorded essentially from the spring waters. These variations could have been induced by mixing of the hot waters with the cold waters, as a result of a change in the circulation path of the former caused probably by permeability variations due to rock fracturing in response to seismic energy release during or prior to the earthquakes.

In this section, the correlation between the seismic activities and the compositional variations is further examined in terms of a possible relation of the variations to the epicentral distance and the depth of the earthquakes in the vicinity of the studied geothermal fields. Since Yalova appears to be a field where seismicity-related variations are better recorded, in Figure 8.9, seismicity in the vicinity of Yalova is presented in a *earthquake distance vs. date* diagram. This diagram reveals that the earthquakes with epicenters closest to Yalova are mainly concentrated in October 2002-April 2003 periods. Since significant chemical/isotopic variations in Yalova waters are recorded in March 2002 (tritium), July 2002 (tritium and Cl) and July 2003 (Ca) periods, there does not seem to be an apparent trend characterizing the relation between the compositional variations and the epicentral distance of earthquakes.

Figures 8.10 and 8.11 depict the relationship between earthquakes and compositional variations in terms of *earthquake depth vs. date* diagrams. Figure 8.10 presents this relation for the Yalova field. It appears from Figure 8.10 that the July 2002 period (when significant Cl decrease, coupled with tritium and SO_4 increase, is recorded from Yalova) is characterized by earthquakes with shallower depths. On the other hand, in July 2003 (which is another period of seismicity-induced variations), the depth of earthquakes are variable. Therefore, seismicity induced variations can not be exactly correlated with the depth of seismicity.

In Figure 8.11, the relation to earthquake depths are shown for Bolu, Efteni, and Seben, which are the fields (apart from Yalova) where most of the compositional variations are observed. As can be seen from Figure 8.11, although for most of the sampling periods the earthquakes in the vicinity of the concerned fields have shallow depths, the July 2002 period is characterized by earthquakes with variable depths. Although the variations in SO_4 contents (Seben field – March and July 2002 periods) can be the result of deep origined H_2S emissions induced by deep earthquakes, whereas the variations in the other constitutents may be related to shallower earthquakes, it is not possible with the available data to construct a well-defined relation between the compositional variations and the depth or epicentral distance of the earthquakes.

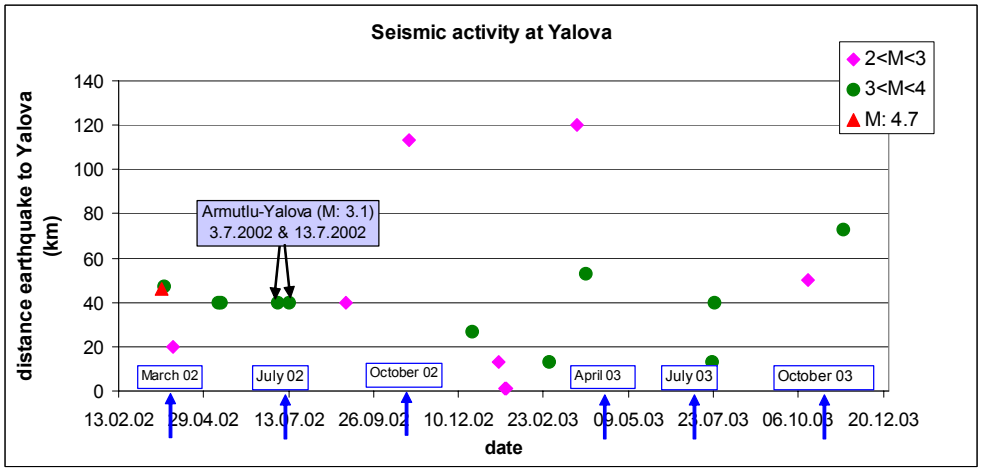


Figure 8.9. Earthquake distance versus date diagram, depicting the seismic activity around Yalova.

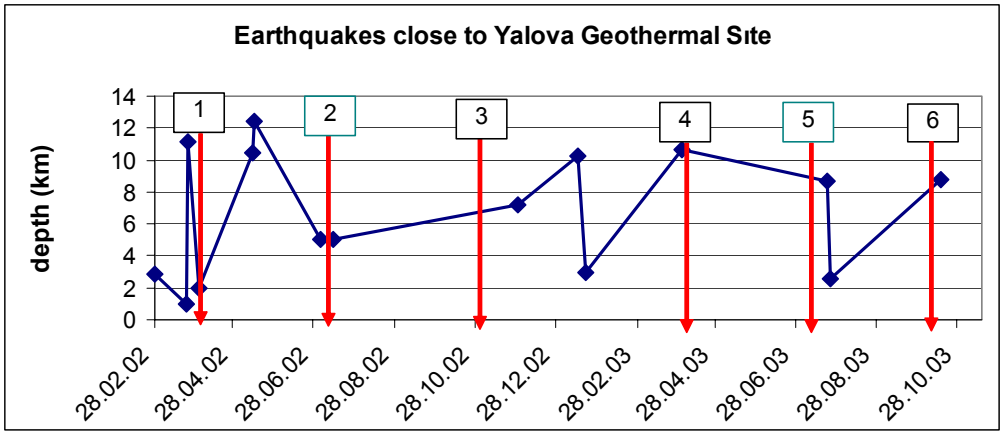


Figure 8.10. Earthquake depth vs. date diagram for Yalova field (numbers in boxes represent the sampling periods, 1: March 2002, 2: July 2002, 3: October 2002, 4: April 2003, 5: July 2003, 6: October 2003; coloured boxes correspond to the periods with significant compositional variations)

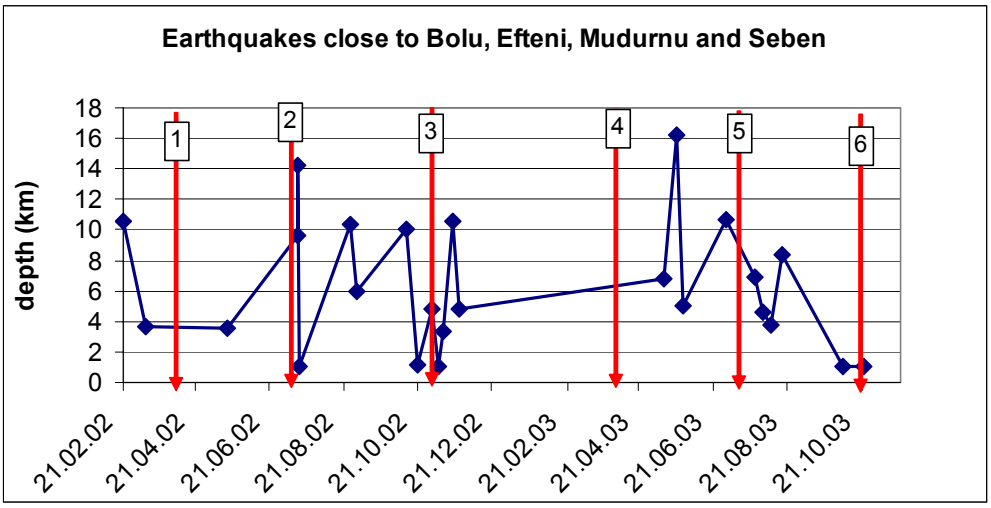


Figure 8.11. Earthquake depth vs. date diagram for Bolu, Efteni, Mudurnu and Seben fields (numbers in boxes represent the sampling periods, 1: March 2002, 2: July 2002, 3: October 2002, 4: April 2003, 5: July 2003, 6: October 2003).

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

The main conclusions drawn from the thesis study can be summarized as follows:

- The geothermal waters along the NAFZ are mostly Na-HCO_3 in character with the exceptions of Na-SO_4 type Yalova and Ca-HCO_3 type Bolu and Mudurnu waters, whereas the cold waters are mostly Ca-HCO_3 type. The water types for most of the fields reflect the reservoir lithology which is dominated by limestone.

- The hot waters together with their cold water companions show meteoric origin since they all plot on/or along the Global Meteoric Water Line. The only exception is seen in Kurşunlu-9a hot water sample which gives a more positive $\delta^{18}O$ value, probably related to the scaling encountered in the well. The hot water samples for most of the fields show more negative $\delta^{18}O$ and δD values when compared with the cold waters and this situation suggests higher recharge altitudes for the hot waters than those for the cold waters.

- The cold water samples are characterized by higher tritium contents, compared to the hot waters, suggesting that the cold water aquifers are recharged with more recent precipitation. The low tritium contents of the hot waters suggest a deep circulation system which is less affected by recent precipitation.

- Temporal variations are recorded in both chemical and isotopic compositions of the hot and the cold waters. The temporal variations observed in the cold water samples are probably seasonal, related to change in the amount of precipitation and/or evaporation. For the hot waters, on the other hand, the situation is more complex. The temporal variations are mostly recorded in the spring, rather than the well, waters which are subject to mixing with shallow cold waters during their free circulation to the surface. The variations observed in hot-spring waters are probably seismicity induced changes, resulting in hot-cold water mixing process responsible for the variation in the sensitive parameters. Of all the studied geochemical parameters, Cl and ^{3}H, and to a lesser extent Ca and SO_4, seem to be the most sensitive parameters in terms of temporal variations. Cl which is high in deep hot waters due to intense water-rock interaction at high temperatures, can be used together with tritium, which is higher in cold waters recharged with recent precipitation. Ca, on the other hand, has decreasing solubility with increasing temperature. Therefore, any decrease in Cl contents of the hot waters accompanied by an increase in tritium and/or Ca content, can point to the effects of mixing of the hot and the cold waters in the subsurface. SO_4 variations are likely to reflect the effects of deep origined H_2S releases into the aquifers, a process probably governed by seismic activities.

- Of all the studied geothermal fields, Yalova seems to be the field that deserves particular attention in terms of seismicity induced temporal variations. The decrease in Cl content of Yalova hot water in July 2002 period is accompanied by an increase in tritium in the same period, which reflects the mixing of the high Cl-low tritium hot, and the low Cl-high tritium cold waters, possibly triggered by the seismic activities occurred in Armutlu-Yalova on 3rd and 13th of July 2002. These seismic activities appear to be also responsible for degassing of sulphur from young organic sediments which resulted in an increase in the SO_4

content. However, since the sampling date from Yalova is the 9th of July, it is not possible at this stage to decide whether the variations are pre-earthquake signatures of 13th of July 2002 or if they are the post-earthquake signs of the 3rd July 2002 earthquake.

- In addition to Yalova, Seben geothermal field also seems to be important in the sense that rather than hot-cold water mixing, the emission of deep origined gases (probably induced by seismic activities) appear to be responsible for the temporal variations in water compositions. The high SO_4 content in July 2002 period, inferred to be related to deep H_2S emission, can in fact be correlated with the 14th July 2002 Yığılca earthquake (M: 3.1, depth 9 .6 km).

- $\delta^{18}O$ and δD compositions did not appear to be potential tracers for the geothermal waters along the North Anatolian Fault Zone, during the course of monitoring. Since both the hot and the cold waters are meteoric in origin, no indication as to mixing of different waters triggered by seismic activities can be inferred from $\delta^{18}O$ and δD compositions of the studied geothermal waters.

- Although there exist some significant correlations between the compositional variations in the NAFZ geothermal waters and the nearby seismic activities, it is still not possible at this stage to define an exact relation between magnitude-epicentral distance-depth of earthquakes and the respective compositional variations.

- A resolution of these relations requires long-term monitoring with frequent sampling, which can be more useful to highlight seismicity induced variations. Moreover, immediate sampling of waters after a high magnitude earthqauke is required to highlight possible pre- and post-earthquake signatures. Also in every monitoring study a background level of chemical and isotopic compositions of waters

should be established to easily identify the seismicity related anomalies associated with the waters. In fact, this thesis study stands essentially as a baseline construction, as no earthquakes with M>5 has ocurred during the course of the monitoring programme.

- The correlation of the results of this study with the results of other studies utilizing other geochemical parameters suggest that, for such monitoring programmes it is ideal to combine water chemistry with gas chemistry (e.g. gas ratios such as CO_2/He, and isotope ratios such as $^{3}He/^{4}He$, $^{13}C/^{12}C$).

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