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Isotope Composition of Geothermal Fluids along the North Anatolian Fault Zone: Spatial and Temporal Variations in Relation to Seismic Activities

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ABSTRACT

This study presents results of an on-going monitoring programme aimed at characterizing compositional variations in geothermal fluids along the North Anatolian Fault Zone (NAFZ). The study was initiated through a preliminary He-isotope survey in 2000 in response to 2 catastrophic earthquakes in 1999 (see results in Chem. Geol. 2002). The present programme was started in late 2001 and covers 9 geothermal sites which are monitored 3 times per year. The sites are located along an 800 km long segment of the NAFZ, from Yalova near the Sea of Marmara in the west, to Resadiye in the east. The data reported here cover the results obtained to date from the analyses of i) tritium contents and $^{18}O/^{16}O$ and D/H ratios of the hot and cold waters, along with their major anion-cation contents, and ii) CO_2/He gas ratios and $\delta^{13}C$ values of the CO_2 gas in geothermal fluids.

The geothermal waters associated with NAFZ are dominantly Na-HCO_3, whereas the cold waters are Ca-HCO_3 type. The $\delta^{18}O$ and δD values (-8.29 ‰ to -13.44 ‰ and -54.67 ‰ to -96.47 ‰, respectively) reveal meteoric origin for both hot and cold waters. Tritium contents range between 0-12.55 TU for the hot and 3.00-15.70 TU for the cold waters. The slightly higher $\delta^{18}O$ values and tritium contents of cold waters suggest recharge of cold water aquifers from higher altitudes with more recent precipitation.

CO_2 concentrations in geothermal fluids range between 0.02 – 3.02 cm^3 STP/g H_2O, and the $CO_2/^4He$ ratios fall between 3.85 x 10^3 - 3.72 x 10^8. $\delta^{13}C$ values cover the range - 4.51 ‰ to + 5.79 ‰, although most of the values are < 0 ‰. Low CO_2 concentrations tend to be associated with low $CO_2/^4He$ and high $\delta^{13}C$ values.

Although no major earthquakes (M>5) occurred along NAFZ over the monitoring period, the temporal variations observed in chemical and isotopic compositions appear to correlate with seismicity occurring close to sampling sites. Important to note is in this respect the prominent Cl decrease and concomitant tritium increase (by a factor of about 1.5 for both) in Yalova hot waters in July 2002, which correlate well with the earthquakes recorded on 3.7.2002 and 13.7.2002 (epicentre: Armutlu-Yalova, M: 3.1). Similarly, although $\delta^{13}C$ values in Yalova are < 0 ‰ in almost all sampling periods, an anomalous value (+ 5.79 ‰) is recorded in March 2002, on the same day (23.3.2002) as an earthquake (M: 4.7) occurred in the Sea of Marmara. Yet another point to note is the 0.5 – 2 ‰ drop in $\delta^{13}C$ values at most sampling sites in October 2002 which is one of the most seismically active months of the monitoring programme. These compositional variations in geothermal fluids probably reflect the effects of seismicity-induced changes in i) mixing ratios of hot waters with cold, shallow groundwaters, and ii) the balance between mantle-derived and crustal volatiles. Continuing monitoring of fluid compositions should lead to a better understanding of their relationship to seismic activities.

1. INTRODUCTION

Monitoring of the chemistry of geothermal fluids in seismically-active areas is a technique increasingly 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). Changes in the chemical and isotopic composition of the fluids are considered to reflect physical and chemical processes occurring at depth, such as fluid mixing, micro-fracturing and permeability modification. In this respect, the most widely-used geochemical parameters 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. A number of workers have reported success in their approaches with significant variations in gas and water chemistry observed either prior to or associated with earthquakes. Monitored observations include an increase in Rn (Wakita et al., 1980; Teng and Sun, 1986) and H_2 (Sato et al., 1986) emissions, large variations in $^3He/^4He$ and $^{13}C/^{12}C$ isotope ratios (Sano et al., 1986, 1998; Sorey et al., 1996; Hilton, 1996) as well as in gas ratios such as He/Ar, N_2/Ar, CH_4/Ar and CO_2/He (Sugisaki and Sugiura, 1986; Hilton, 1996), significant changes in tritium concentrations (Sano et al., 1998), anomalous increase in Pb concentrations with associated changes towards more anthropogenic Pb-isotope compositions (Poitrasson et al., 1999), and the anomalies detected in some of the major anion contents (Toutain et al., 1997; Nishizawa et al., 1998; Balderer et al., 2002).

The present study is concerned with monitoring chemical and isotopic compositions of geothermal fluids located along the North Anatolian Fault Zone (Figure1), in an attempt to determine the possible relation of compositional variations to seismic activities. We report here the results obtained so far from an on-going research project started in

late 2001 following a preliminary He-isotope survey (Güleç et al., 2002) in 2000 in response to 2 catastrophic earthquakes in 1999. Included in the project are a total of 9 geothermal sites which are monitored 3 times per year. The geothermal sites are located along an 800 km long transect extending from Yalova (near the Sea of Marmara) in the west, through Efteni, Mudurnu, Seben, Bolu, Kurşunlu, Hamamözü and Gözlek, to Resadiye in the east (Figure1).

2. TECTONIC SETTING AND RECENT SEISMICITY

North Anatolian Fault Zone (NAFZ) comprises one of the major structures in Turkey that developed during the neotectonic period in response to the intracontinental convergence following the Late Miocene collision of the Arabian promontory with Eurasia (McKenzie, 1972; Dewey and Şengör, 1979; Şengör et al., 1985; Barka, 1992). The NAFZ is a 1500 km long, few hundred meters to 40 km wide, dextral strike-slip fault system analogous to the San Andreas Fault System in California, and represents an intracontinental transform boundary between the Eurasian plate in the north and the Anatolian plate in the south (Koçyiğit et al., 1999 a, b). Along much of its length, the fault zone consists of shorter subparallel fault strands locally displaying an anastomosing fault pattern. The NAFZ extends from eastern Anatolia in the east to the Aegean Sea in the west. Just east of the Sea of Marmara, the fault zone bifurcates into two major strands towards the west. The northern strand traverses and the southern strand bounds the southern margin of the Sea of Marmara (Figure1). The age of dextral motion and the total off-set along the fault zone are controversial, covering the range of Middle Miocene-Early Pliocene and 20-85 km, respectively (see Bozkurt, 2001 for a review).

The NAFZ has a remarkable recent seismic activity, the most destructive effects of which was experienced by the 1999 İzmit (M: 7.4; 17 August 1999) and Düzce (M: 7.2; 12 November 1999) earthquakes, resulting in more than 25,000 fatalities in the region. The August and November earthquakes occurred, respectively, at depths of 11 km (with two successive shocks in 45 seconds at the centers of Gölcük and Arifiye) and 10 km (epicenter: Düzce) creating a total surface rupture length of 177 km from Gölcük eastwards (Koçyiğit et al., 1999a, b; Çemen et al., 2000). The most recent earthquakes along the NAFZ with magnitudes greater than 3 include: Orta-Çankırı (M: 5.9; 6 June 2000), the Sea of Marmara (M: 4.7; 23 March 2002), Armutlu-Yalova (M: 3.1; 3 July 2002 and M: 3.1; 13 July 2002), Yığılca-Düzce (M: 3.1; 11 October 2002 and M: 4.0; 25 July 2003), Sungurlu-Çorum (M: 3.3; 20 October 2002), Mudurnu-Bolu (M: 3.4; 1 November 2002), Çınarcık-Yalova (M: 3.5; 22 July 2003) and Bolu (M: 3.5; 7 August 2003 and M: 4.6; 14 April 2004).

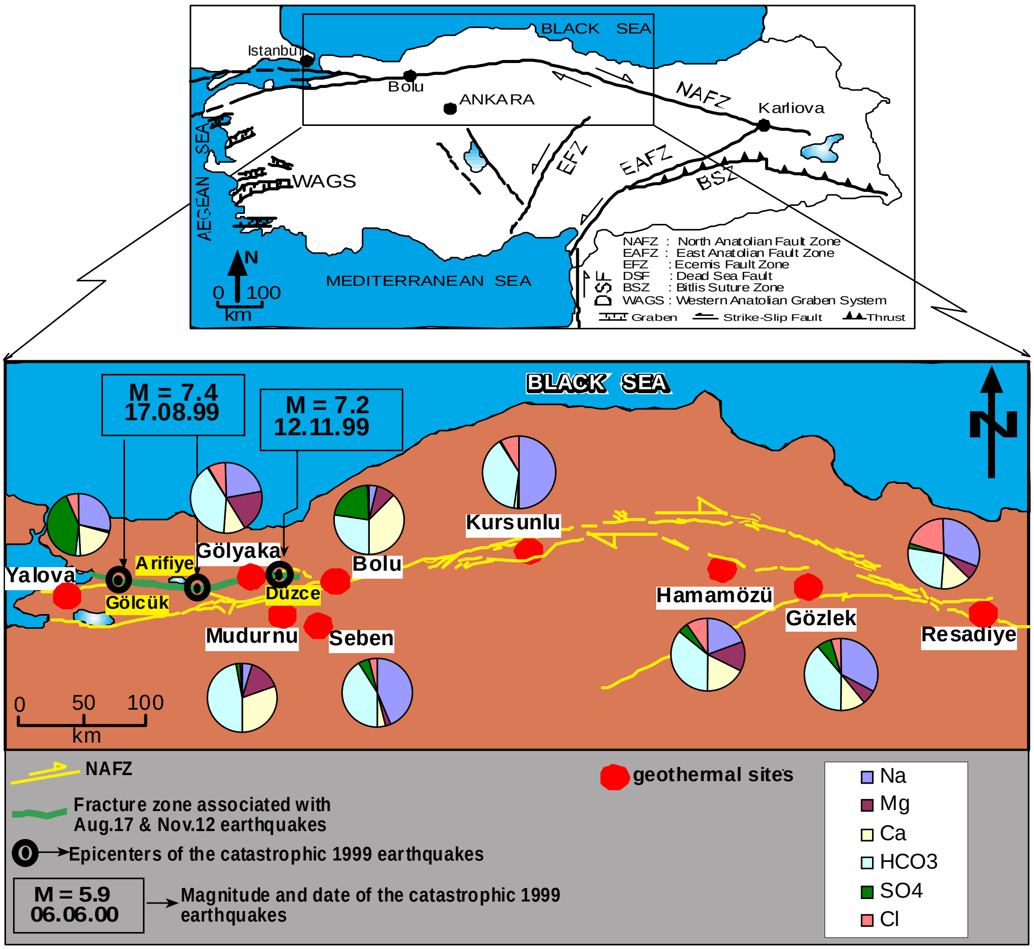

Figure 1: Distribution of the monitored geothermal sites along the NAFZ. Pie diagrams represent the hydrogeochemical facies of the hot waters.

3. REGIONAL GEOLOGY AND HYDROGEOLOGIC OUTLINE

The basement in all geothermal fields along the NAFZ is comprised of Paleozoic metamorphics (schists and marbles) which are unconformably overlain by Upper Jurassic-Lower Cretaceous limestones and Upper Cretaceous flysch consisting of intercalations of limestone, conglomerate, marl, sandstone, claystone and siltstone. Products of a widespread volcanic activity, extending from Late Cretaceous to Miocene and consisting of basaltic-andesitic lava flows, tuffs and agglomerates, are observed either as intercalated with, or as overlying the Upper Cretaceous flysch. The stratigraphic succession continues with Neogene clastics and lacustrine limestones (Şahinci, 1970; Canik, 1972; Koçak, 1974; Özcan and Ünay, 1978; Müftüoğlu and Akıncı, 1989; Erzenoğlu, 1991; Erişen et al., 1996). Plio-Quaternary fluviatile deposits form the youngest units of the succession and are accompanied, in the eastern-central segment of the NAFZ, by Plio-Quaternary volcanics of limited areal extent (Tatar et al., 1996).

Numerous hot-springs emerge in the geothermal fields along the fault and fracture zones which probably originated in association with the motion along the NAFZ. The temperature of the hot-springs range between 30 and 74 °C, and the flow rates range between 0.1 and 5.6 l/s. The reservoir rocks of the geothermal fields are dominantly Mesozoic limestones, although the Tertiary volcanics comprise the primary reservoir in the Yalova and Kurşunlu fields (Koçak, 1974; Erişen et al., 1996). Impervious clayey levels of the flysch facies and the Neogene sequence act as cap rocks of the geothermal systems.

4. SAMPLING AND ANALYSES

In late 2001 (time of commencement of sampling), sampling could be performed only at the Bolu and Efteni fields due to tough weather conditions. In 2002 and 2003, periodic sampling was performed at 9 geothermal sites (Yalova, Efteni, Mudurnu, Seben, Bolu, Kurşunlu, Hamamözü, Gözlek and Resadiye) in March-April, July and October-November periods, with the exception of Reşadiye where the hot-spring source had dried-up in October 2002. Both natural springs and production wells were utilized for sampling (Table 1).

For major anion-cation chemistry, tritium, $^{18}O/^{16}O$ and D/H isotopic analyses, water samples were collected via filtering into polyethylene bottles. For a better understanding of the compositional variations and evaluation of the possible subsurface processes like mixing and boiling, cold water samples were collected along with the hot waters, commencing in March-April 2002 for the Mudurnu, Seben, Reşadiye and Kurşunlu fields, and in March-April 2003 for the other sampling locations.

Table 1: Information relevant to sampling localities, sampling dates and sample types (samples were collected in March-April, July and October-November periods in 2002 and 2003. In late 2001, because of tough weather conditions, sampling could only be performed for gas samples and only at the Efteni and Bolu fields. Red rows in the table represent hot waters, and blue rows represent cold waters)

Locality	Samp. No.	*Sample Type	Sampling Dates						
Efteni-Gölyaka	1a	Spring	16/11/2001	23/3/2002	8/7/2002	27/10/2002	7/4/2003	9/7/2003	15/10/2003
Efteni-Gölyaka	1b	Spring	-	-	-	-	7/4/2003	9/7/2003	15/10/2003
Yalova-Termal	2a	Spring	-	24/3/2002	9/7/2002	28/10/2002	8/4/2003	10/7/2003	16/10/2003
Yalova-Termal	2b	Spring	-	24/3/2002	9/7/2002	28/10/2002	8/4/2003	10/7/2003	16/10/2003
Yalova-Termal	2c	Spring	-	-	-	-	8/4/2003	10/7/2003	15/10/2003
Bolu- Karacasu Termal	3a	Production well (P)	18/11/2001	24/3/2002	9/7/2002	28/10/2002	9/4/2003	10/7/2003	16/10/2003
Bolu- Karacasu Termal	3b	Spring	-	-	-	-	9/4/2003	10/7/2003	16/10/2003
Babas-Mudurnu	4a	Production well (A)	-	25/3/2002	10/7/2002	29/10/2002	9/4/2003	11/7/2003	17/10/2003
Babas-Mudurnu	4b	Production well (A)	-	25/3/2002	10/7/2002	29/10/2002	9/4/2003	11/7/2003	17/10/2003
Babas-Mudurnu	4c	Spring	-	25/3/2002	10/7/2002	29/10/2002	9/4/2003	11/7/2003	17/10/2003
Babas-Mudurnu	4d	Spring	-	25/3/2002	10/7/2002	29/10/2002	9/4/2003	11/7/2003	17/10/2003
Seben-Pavlu	5a	Spring	-	25/3/2002	10/7/2002	29/10/2002	9/4/2003	11/7/2003	17/10/2003
Seben-Pavlu	5b	Production well (P)	-	25/3/2002	10/7/2002	29/10/2002	9/4/2003	11/7/2003	17/10/2003
‡Seben-Pavlu	5c	Production well (P)	-	25/3/2002	-	29/10/2002	-	11/7/2003	-
‡Seben-Pavlu	5d	Spring	-	25/3/2002	-	29/10/2002	9/4/2003	11/7/2003	17/10/2003
Hamamözü-Arkutbey	6a	Production well (A)	-	26/3/2002	11/7/2002	30/10/2002	10/4/2003	12/7/2003	18/10/2003
Hamamözü-Arkutbey	6b	Spring	-	-	-	30/10/2002	10/4/2003	12/7/2003	18/10/2003
Gözlek-Amasya	7a	Production well (A)	-	27/3/2002	12/7/2002	31/10/2002	10/4/2003	12/7/2003	18/10/2003
Gözlek-Amasya	7b	Spring	-	-	-	31/10/2002	10/4/2003	12/7/2003	18/10/2003
‡‡Reşadiye-Tokat	8a	Spring	-	27/3/2002	12/7/2002	-	-	-	-
Reşadiye-Tokat	8b	Spring	-	27/3/2002	12/7/2002	31/10/2002	-	-	-
Kurşunlu-Çavundur	9a	Production well (A)	-	28/3/2002	13/7/2002	1/11/2002	11/4/2003	12/7/2003	19/10/2003
§Kurşunlu-Çavundur	9b	Spring	-	28/3/2002	13/7/2002	1/11/2002	11/4/2003	-	-
Kurşunlu-Çavundur	9c	Spring	-	28/3/2002	13/7/2002	1/11/2002	11/4/2003	12/7/2003	19/10/2003

*A: Artesian, P: Pumping

‡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 March-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.

For the measurement of gas ratios (CO_2/He) and the isotopic composition ($\delta^{13}C$) of the gases, geothermal fluids were collected in annealed copper tubes, which were sealed in the field using a cold welding tool.

Anion-cation chemistry, tritium, $^{18}O/^{16}O$ and D/H analyses of water samples were carried out at the laboratories of the Turkish State Hydraulic Works. 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). Tritium contents were determined by Liquid Scintillation Counting System (Packard Tri-Carb 2260 XL) after electrolytic enrichment. $\delta^{18}O$ and δD ratios were measured on a Micromass 602 C Mass Spectrometer.

CO_2/He gas ratios and $^{13}C/^{12}C$ ratios of the CO_2 gas in geothermal fluids were measured on VG Prism and quadrupole mass spectrometers at the Geosciences Research Division, Scripps Institution of Oceanography.

5. CHEMICAL COMPOSITIONS

The hot waters are almost all Na-HCO_3 type waters (Efteni, Seben, Gözlek, Reşadiye and Kurşunlu samples), except for the Ca-HCO_3 type (Bolu and Mudurnu), and Na-SO_4 type (Yalova) (Figure1). Additionally, Hamamözü hot water displays a mixed character with none of the ions exceeding 50 % of the total composition. The cold waters, on the other hand, are dominantly Ca-HCO_3 type. The bicarbonate character of 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 dominance of Na cation in the hot waters. The Na-SO_4 character of waters in Yalova probably has genetic connections with the young organic accumulations in the Izmit Bay (located to the north of Yalova).

Although hydrogeochemical facies defined by dominant anion-cation pairs stay fairly constant, temporal variations were recorded in the chemical composition of waters during the course of the monitoring period from March-April 2002 to October-November 2003. Of these, variations in Cl contents (Figure 2) appear to be particularly significant as Cl is considered to be a conservative constituent used as tracer. In this respect, a 1.5 fold decrease in the Cl content of Yalova hot water in 9 July 2002 (compared to March 2002 and October 2002 periods) deserves attention as it points to a hot water-cold water mixing that might have been induced by the seismic activities occurring on the 3rd and/or 13th of July 2002 in Armutlu-Yalova (M: 3.1). Additionally, the continuous decrease in the Cl content of Kuşunlu sample 9b (from 210 mg/l in March 2002 to 82 mg/l in April 2003) is also worth to note. This decrease 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. Since the seismic records following April 2002 indicate an increase both in the frequency and the magnitude of earthquakes in the Çankırı region, the second alternative seems to be more likely.

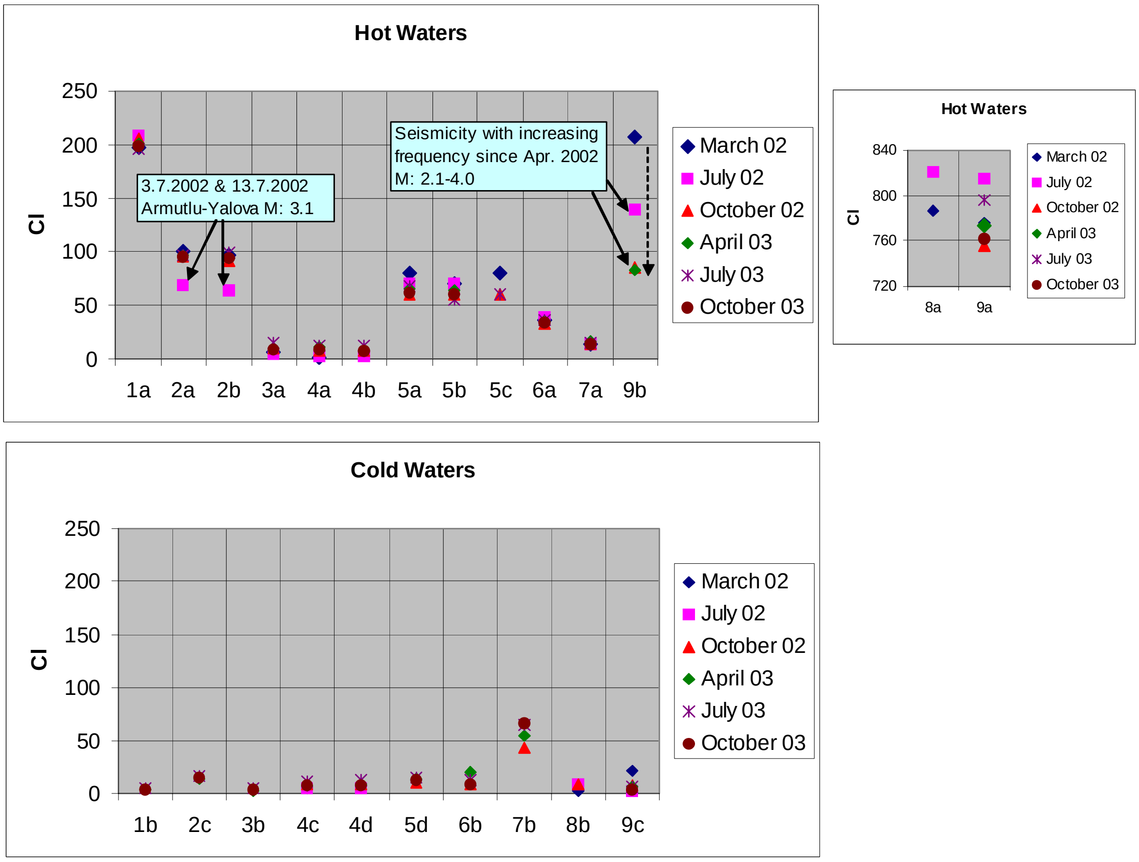

Figure 2: Concentration vs. Sample No. depicting temporal variations in Cl contents of hot and cold waters.

6. OXYGEN- AND HYDROGEN- ISOTOPE COMPOSITIONS

The $\delta^{18}O$ values of the hot waters recorded over the monitoring period range between -13.44 ‰ and -8.37 ‰, while the cold waters have values ranging from -12.71‰ to -8.29‰. The δD values have ranges between -96.47 ‰ and -64.15 ‰ for the hot waters, and between -86.7 ‰ and -54.67 ‰ for the cold waters. The isotope compositions of the waters are presented as $\delta^{18}O$ vs. δD diagram in Figure 3, where the data plotted represent the mean values of the measurements throughout the monitoring period (from March-April 2002 to October-November 2003). As can be seen from Figure 3, some of the samples lie along and/or close to the Global Meteoric Water Line (GMWL) (defined by Craig et al., 1961) whereas others plot away from it. The samples plotting away from the GMWL include not only the hot but also the cold waters whose aquifers are supposed to be recharged by meteoric precipitation. This suggests that local meteoric water lines are different from the GMWL). It is worth to note here that whether the cold waters define their own trends or whether they plot along the GMWL, their hot water companions also plot along the same trends (e.g. see Mudurnu, Yalova and Seben samples in Figure 3) suggesting a meteoric origin for both the hot and cold waters. Only in the Kurşunlu field, the hot water sample (no. 9a) has a relatively high $\delta^{18}O$ value, reflecting

An interesting point to note as to the isotope compositions of the samples is that in almost all geothermal fields (except Kurşunlu and Bolu), the hot waters have δD and $\delta^{18}O$ values lower than their cold water companions suggesting recharge of the hot water aquifers from higher altitudes (compared to the altitudes where cold water aquifers are recharged).

The temporal variations in $\delta^{18}O$ and δD values, exceeding the limits of analytical errors (0.1 ‰ and 1 ‰, respectively), appear to be more prominent in the Bolu and Hamamözü fields (Figure 4 and 5). These variations 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 the Mudurnu cold water sample is likely to reflect seasonal effects (precipitation and evaporation), while in Bolu the variations in hot water may be attributed to the effects of a possible hot-cold water mixing process. Although there appear to be two seismic events in Bolu on 21 October 2002 and 1 November 2002 (M: 2.6 and 2.4, respectively) that can be related to this mixing process, the effects of these events are not observed in the other parameters (e.g. Cl and/or tritium contents).

7. TRITIUM CONTENTS

Tritium (^3H) contents for the hot waters range between 0-12.55 TU, with the majority being less than 5 TU. For the cold waters, the range is 3.00-15.70 TU, although most of the samples have concentrations above 8 TU. The relatively high tritium contents of cold waters suggest recharge of cold water aquifers with more recent precipitation.

The temporal variations of tritium contents are shown in Figure 6. The interpretation of these variations requires particular caution since the analytical errors associated with tritium contents are high in some sampling periods (approaching ± 2 TU) depending on the high background level in the counter. Nevertheless, the high tritium content of the Yalova hot waters in July 2002 period deserves attention as it is accompanied by a decrease in Cl content (see section 5 and Figure2). Since deep circulating hot waters are characterized by high Cl - low tritium, and cold shallow waters by low Cl – high tritium contents, this positive tritium anomaly (and the associated negative Cl anomaly) in July 2002 may imply a hot water-cold water mixing process possibly triggered by the 3rd and/or 13th July 2002 earthquake(s) in Armutlu-Yalova (M: 3.1).

In the Kurşunlu field, the tritium content of sample no. 9b displays an increasing trend with time. Although the significance of this trend can be questioned, it is correlated with the decreasing Cl trend mentioned above (section 5) and appears to support the idea of mixing whereby the cold water component increased in time in relation to the increasing frequency and magnitude of seismic activities in Çankırı since April 2002.

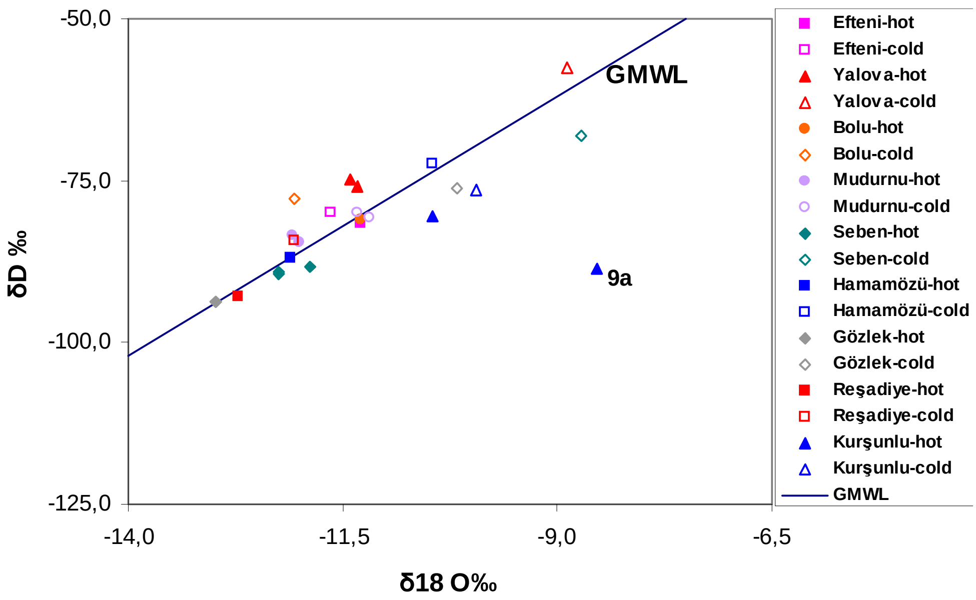

Figure 3: $\delta^{18}O$ vs. δD diagram. Data plotted represent the mean values of the measurements throughout the monitoring period from March-April 2002 to October-November 2003; GMWL: Global Meteoric Water Line from Craig et al. (1961).

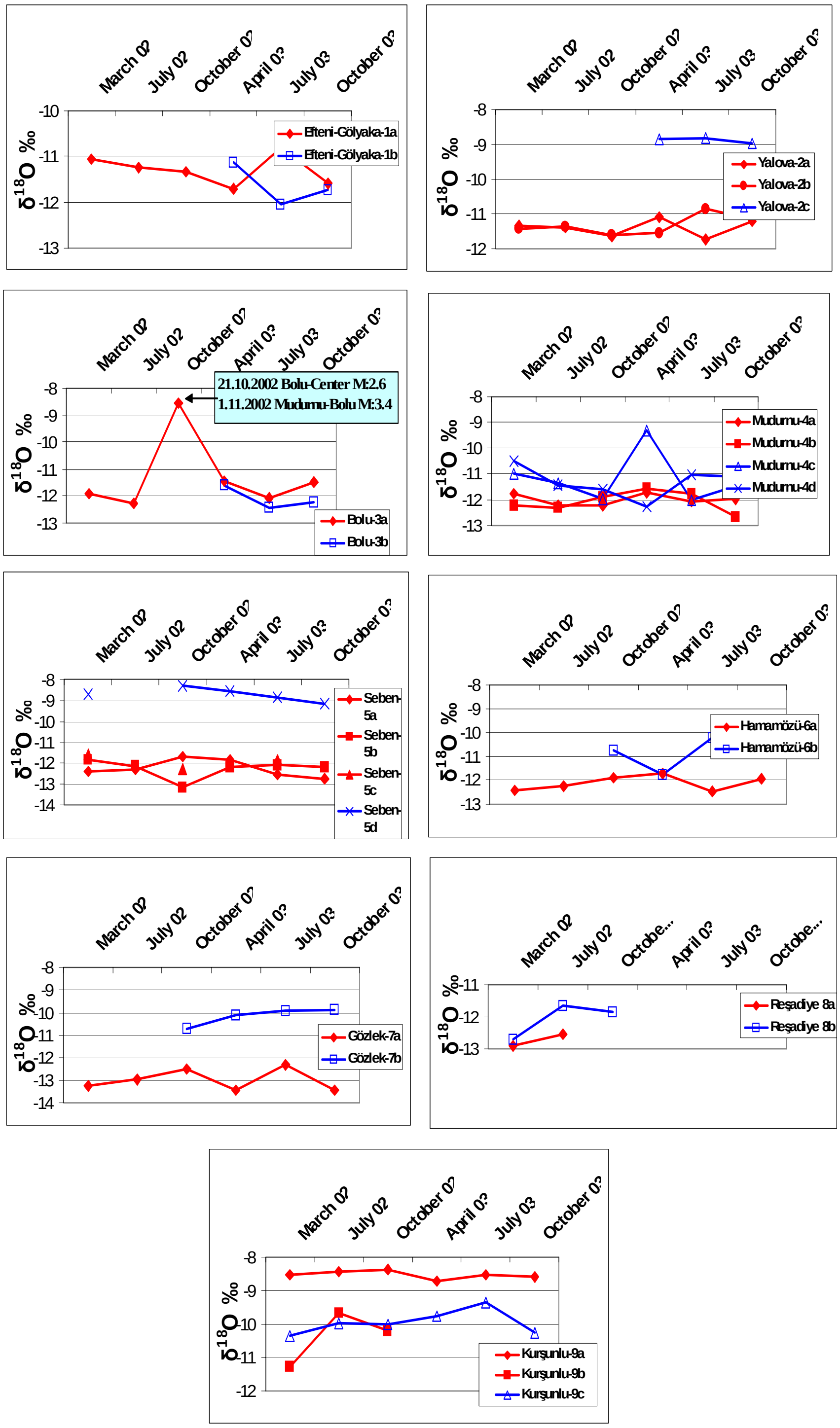

Figure 4: Temporal variations in oxygen-isotope compositions. Red symbols represent the hot, blue symbols represent the cold waters.

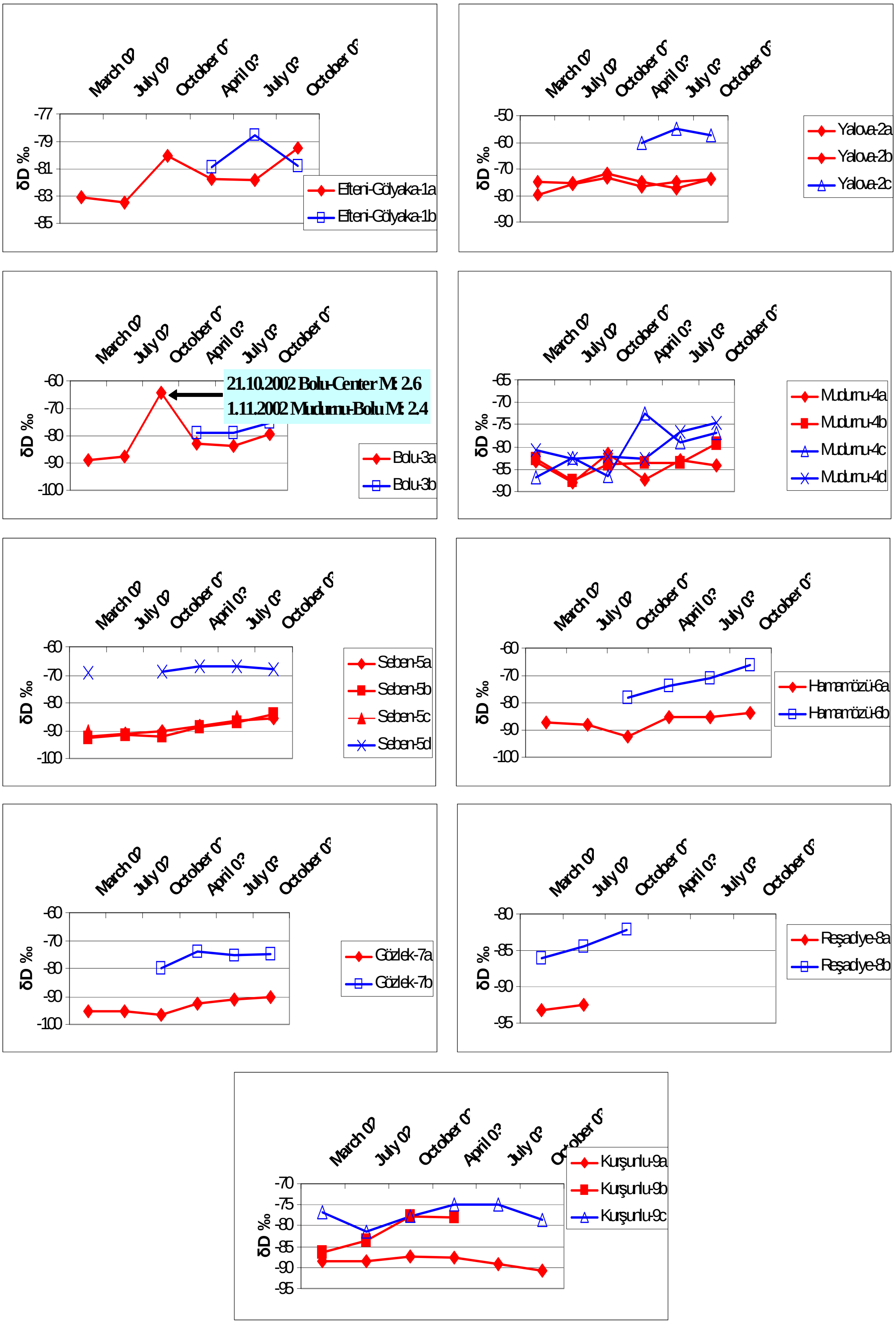

Figure 5: Temporal variations in hydrogen-isotope compositions. Red symbols represent the hot, blue symbols represent the cold waters.

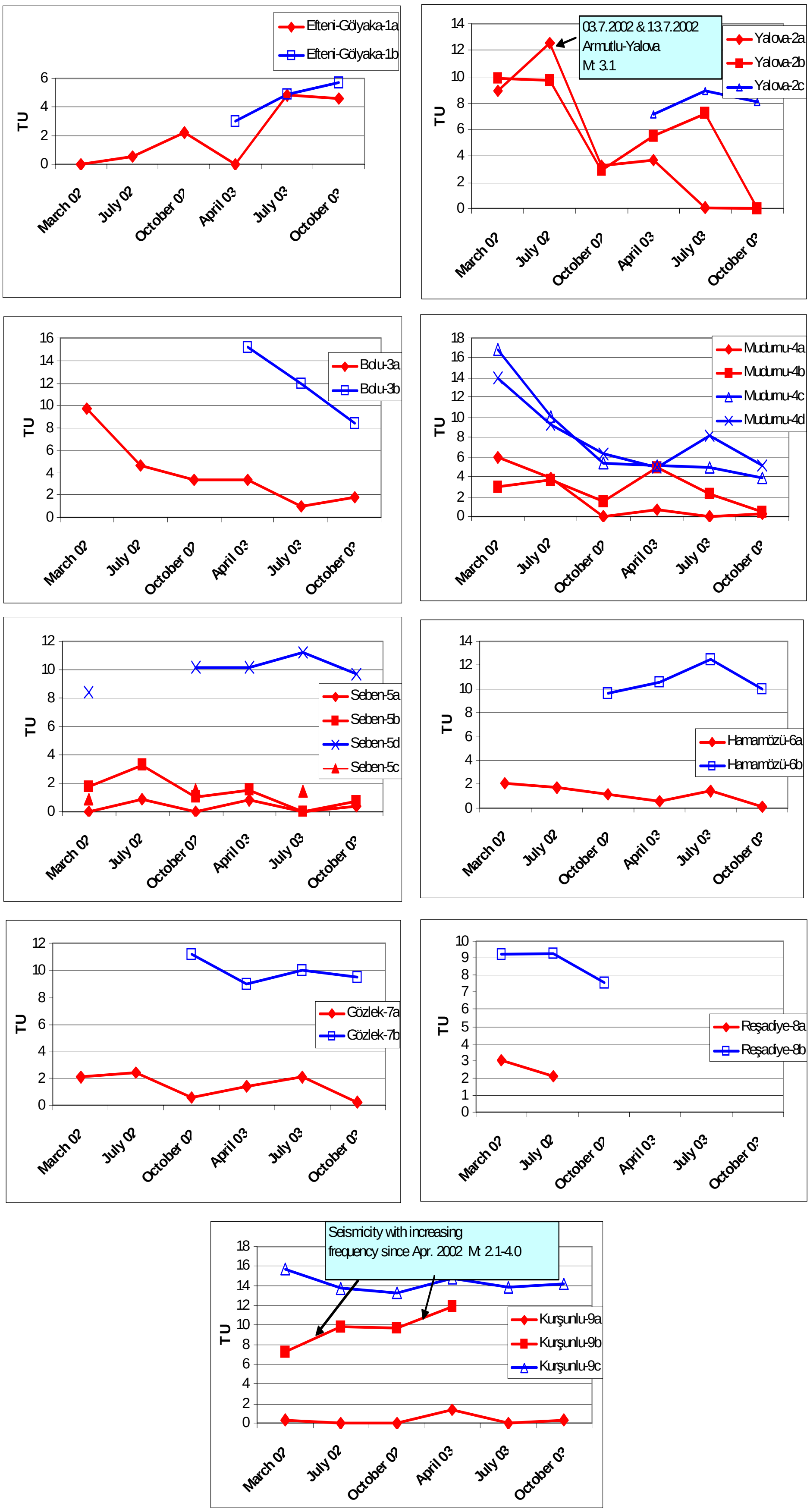

Figure 6: Temporal variations in tritium concentrations Red symbols represent the hot, blue symbols represent the cold waters.

8. CARBON ISOTOPE COMPOSITIONS

The $\delta^{13}C$ values of the CO_2 gas in the geothermal fluids are shown in Figure 7. As can be seen from the figure, except for the Yalova and – to some extent - Kurşunlu fields, the values are mostly below 0‰ and indicate mantle [$\delta^{13}C$: (-3‰)–(-8‰)] and/or marine carbonate [$\delta^{13}C$: (-1‰)–(+2‰)] contributions to the CO_2 gas. Regarding the Yalova sample, although $\delta^{13}C$ values are below 0 ‰ in almost all sampling periods, an anomalous value (+ 5.79‰) is recorded in March 2002. Such a high value can probably be attributed to the thermo-metamorphic decay of carbonates. It is worth to note here that the sampling in Yalova was performed on the 23rd of March 2002, on the same day as the seismic activity (M: 4.7) recorded in the Sea of Marmara. This seismic activity may be the triggering mechanism of the thermo-metamorphic process.

Another important point to note is the 0.5 – 2 ‰ drop in $\delta^{13}C$ values at the Seben, Mudurnu, Hamamözü and Gözlek fields in October 2002, which is one of the most seismically active months of the monitoring programme including the Yığılca-Düzce (M:3.1; 11.10.2002) and Sungurlu-Çorum (M: 3.3; 20.10.2002) earthquakes, and the earthquake swarm in Hendek-Sakarya (M: 2.5-2.9; 27.10.2002). These decreases in $\delta^{13}C$ values may indicate gas release from the mantle and/or marine carbonates in these geothermal fields which may have been induced by the above mentioned earthquakes.

9. CO_2 CONCENTRATIONS AND CO_2/He GAS RATIOS

CO_2 concentrations in geothermal fluids range between 0.02 – 3.02 cm^3 STP/g H_2O, and the $CO_2/^4He$ ratios fall between 3.85 x 10^3 - 3.72 x 10^8 (Figure 8). Low CO_2 concentrations tend to be associated with low $CO_2/^4He$ and high $\delta^{13}C$ values. In Yalova, however, the high $CO_2/^4He$ ratio in March 2002 period is associated with high $\delta^{13}C$ ratio which may be correlated with the seismic activity (M: 4.7) recorded on 23rd March 2003 in the Sea of Marmara. The seismic activity, as discussed in section 8, might have induced CO_2 gas escape from crustal levels (probably in connection with thermo-metamorphic processes).

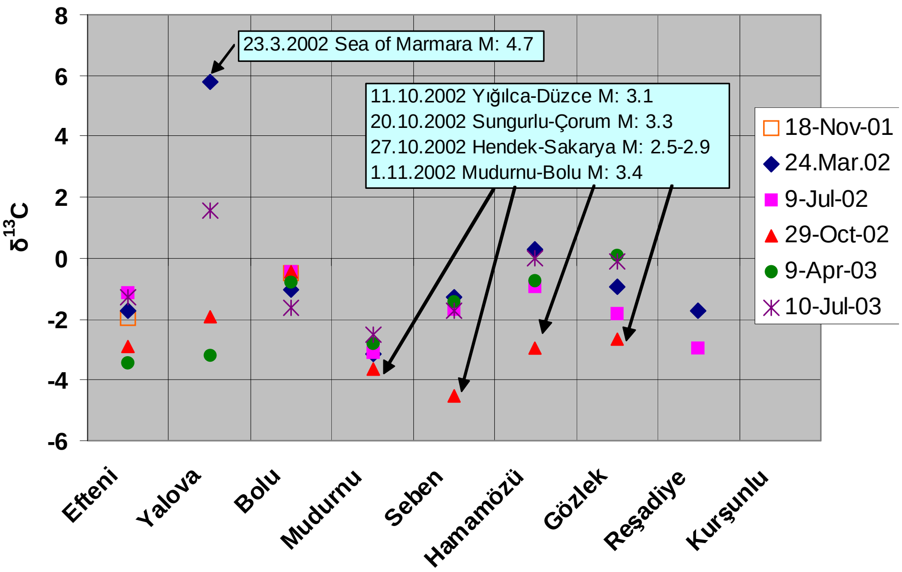

Figure 7: $\delta^{13}C$ vs. Locality diagram depicting temporal variations in $\delta^{13}C$ values of CO_2 gas. Since the Cu-tubes leaked, no measurements could be performed for sample no. 9a from the Kurşunlu field for the March 2002 period, and for sample no. 2a from Yalova for the July 2002 period.

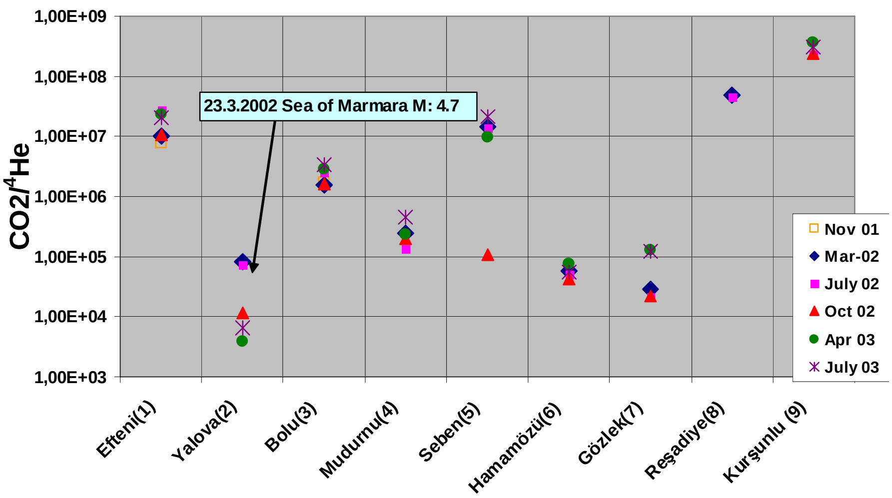

Figure 8: CO_2 / ^4He vs. Locality diagram depicting temporal variations in CO_2 / ^4He ratios. Since the Cu-tubes leaked, no measurements could be performed for sample no. 9a from Kurşunlu field for March 2002 period.

10. CONCLUSIONS

1. The geothermal waters associated with NAFZ are dominantly Na-HCO_3, whereas the cold waters are Ca-HCO_3 in character.

2. The oxygen- and hydrogen-isotope compositions point to a meteoric origin for both the hot and the cold waters. The slightly higher δ^{18}O- δD values and tritium contents of cold waters suggest the recharge of cold water aquifers from higher altitudes with more recent precipitation.

3. $^{13}C/^{12}C$ ratios of geothermal fluids suggest mantle and/or marine carbonate contributions to the CO_2 gas in geothermal fluids. High $\delta^{13}C$ values tend to be associated with low CO_2 concentrations and low $CO_2/^4He$ ratios.

4. Temporal variations in chemical and isotopic compositions of geothermal fluids appear to correlate with the seismic activities recorded during the course of the monitoring period from late 2001 to late 2003. $\delta^{13}C$ values, $CO_2/^4He$ gas ratios, Cl and tritium contents seem to be the most sensitive parameters, and Yalova geothermal field deserves particular attention in this respect.

5. The temporal variations in geothermal fluids' compositions probably reflect the effects of seismicity-induced changes in hot/cold water ratios in subsurface mixing processes, and the balance between mantle-derived and crustal volatiles. Continuing monitoring of compositions should lead to a better understanding of the relation to seismic activities.

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