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Hydrogeochemical characteristics and genetic implications of Edipsos thermal springs, north Euboea, Greece

Research Article

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Abstract: Edipsos area, situated in northern Euboea, has been well known since ancient times for the existence of thermal springs. In order to assess the hydrogeochemical conditions, thermal and cold water samples were collected and analyzed by ICP method for major and trace elements. The results revealed the direct impact of seawater, a process which is strongly related to the major tectonic structures of the area. Seawater impact was confirmed by the Cl/Br and Na/Cl ionic ratios, as well as from statistical processing and graphical interpretation of the analytical results, which classified the sampled waters into three groups (two for cold waters and one for the thermal ones). Trace element ranges for thermal waters are: As (44-84 ppb), Pb (23-154 ppb), Ag (1-2 ppb), Mn (31-680 ppb), Cu (61-97 ppb), Cs (66-244 ppb), Se (0-76 ppb), Li (732-3269 ppb), Fe (0-1126 ppb), Sr (14000-34100 ppb), B (4300-9600 ppb).

Compared with the chemical composition of other thermal springs from the Hellenic Volcanic Arc, Edipsos thermal waters are enriched in Ca^{2+}, Na^{+}, Cl^{-}, $SO_4{}^{2-}$, Li, B and K^{+}, reflecting the influence from seawater. Cold waters are free of heavy metals compared with other natural waters and are characterized by good quality based on the major element chemistry. Finally, several geothermometers were applied in order to assess the reservoir temperatures, but none of them appear to be applicable, mainly due to the impact of seawater on the initial hydrogeochemistry of the geothermal fluids.

Keywords: thermal springs • hydrogeochemistry • Edipsos, Euboea

1. Introduction

The specific geological background of Greece created favorable conditions for the formation of many thermal springs. The major tectonic movements in macroscale gave rise to a dynamic geological evolution which is expressed through volcanic activity, orogenetic processes and active tectonism. Volcanic activity in the Aegean Sea commenced in the Oligocene and continues to the present day [1, 2]. Two major phases took place. The first one was the Oligocene-Miocene volcanic phase during which the volcanic activity occurred in an East to West orientated zone from Thrace to the central Aegean. Many places of the central Aegean region (North Euboea, Tinos, Sikinos,

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Figure 1. Map of Euboea Island showing the study area.

Patmos and Samos Islands) were affected by this activity. The above conditions together with the existing major faulting zones were the fundamental causes for the warming and the uplift of deep thermal waters, resulting in their discharge at the surface as thermal springs.

The thermal springs of North Euboea are located near the city of Edipsos (Figure 1) which lies about 38°51'N and 23°02'E. Edipsos has been well known for the healing attributes of its thermal waters since ancient times, as Strabo, Pausanias, Aristotle and others recognised and described this. The famous Edipsos baths have been developed along the shoreline in a slightly inclined surface, while a short distance to the west lays Telethrio Mountain and Edipsos plain. According to the local population, these springs are said to be effective in curing diseases such as rheumatoid and inflammatory arthritis, degenerative arthritis, spondylo-arthritis, myalgia, neuralgia, lumbago, neuritis, backaches, tendonitis, vessel diseases, diseases of the endocrine cycle and post traumatic inflammation.

The aim of the present paper is to define the exact hydrogeochemical characteristics of Edipsos thermal springs through extended chemical analyses, and the determination of the genetic processes which affect their formation and characteristics.

2. Study area

2.1. Geological setting

The geology of northern Euboea [3–8] includes at the lower series a Permian–Triassic volcanoclastic complex with low-grade metamorphic rocks and rift volcanics [9, 10]. This is overlaid by Upper Triassic to Upper Jurassic limestones (the "Sub-Pelagonian" unit) [11] and finally an ophiolitic nappe is tectonically imposed over the limestones, which was emplaced in the Late Jurassic to Early Cretaceous [12–14]. These Mesozoic formations were also folded during the main phase of the Alpine orogeny (Paleocene–Eocene in this part of the Hellenide units) [8, 15].

The Permian-Triassic volcanic rocks are best developed at the southeast part of Edipsos, where they occur in a thick series of thrust slices [16]. The dominant lithology is bedded tuff, fine-grained agglomerate and rare ignimbrite. The colour of the tuffs is usually purple, indicating subaerial oxidation. Basaltic pillow lavas are interbedded with the tuffs, indicating that parts of the sequence are of submarine origin [16].

Post-Alpine formations are dominated by Lower Miocene to Upper Pliocene fluvio-lacustrine deposits, which were formed during the earlier neotectonic phases of the region [12, 17]. The graben of the north Euboic gulf, which is one of the most prominent active tectonic features in the area, was formed during the last geological periods by NW–SE to WNW–ESE normal fault zones [17–21].

3. Formation of Edipsos thermal springs

The formation of Edipsos thermal springs can be attributed to both intense tectonic activity and volcanism. The presence of volcanic rocks found in all isopic zones of continental Greece and the Greek Islands indicates considerable volcanic activity in this area. From Tertiary times, the Aegean area has been dominated by orogenic volcanism due to the relative advance of the African plate into the Eurasian mass. This volcanic activity is closely related to fault systems that favour the displacement of thermal springs, such as those of Edipsos.

According to previous researchers [22] the major tectonic processes which caused the back arc basin of Maliakos Ocean seem to be the predominant factor of their structural origin. In more detail, the northern part of this tectonic structure which defines the Euboic Gulf as well, formed the Edipsos thermal springs, while its southern part gave rise to the formation of Sperchios thermal springs, which lie to the west in the region of Eastern Greece [22]. Apart from the tectonic activity, the magma body associated with the volcanic center of Lichada (Figure 1) (northwards of the study area) is likely a principal factor for the elevated values of geothermal gradient in the wider area.

The functional processes of the thermal springs are firstly expressed by the descent of seawater, to greater depths, through the existing tectonic structures. The depth of descent is related to temperature. The high temperatures of Edipsos thermal springs together with the elevated values of CO_2 (1044 – 1620 mg/L) [23] denote that during the underground circulation, the thermal waters are in contact with recently crystallized magmatic bodies [22].

As a result, they become heated and enriched in dissolved gasses, such as CO_2 and H_2S.

Table 1. Major element analyses and physicochemical parameters of Edipsos thermal (S1-S11) and cold (S12-S16) water samples.

			Physicochemical Parameters				Major Cations				Major Anions		
Samples	coordinates (x,y)	pH	T	EC	TDS		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	HCO_3^{-}	SO_4^{2-}
			°C	μS/cm	mg/L		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
S1	38°51.47N 23°02.94E	6.5	81	11370	5680		2157	416	12475	366	18761	343	2745
S2	38°51.22N 23°02.94E	7.5	57	11440	5710		2365	474	13053	400	21510	62	1865
S3	38°51.13N 23°07.74E	7.0	65	7830	3910		2005	317	8036	225	12339	410	1912
S4	38°51.11N 23°59.16E	7.0	45	11330	5650		2183	799	11961	340	19339	206	2008
S5	38°51.30N 23°03.18E	6.9	74	11140	5560		2277	433	12202	351	19596	514	1688
S6	38°51.41N 23°02.96E	6.5	69	10990	5480		2209	426	11593	357	19375	318	1580
S7	38°51.28N 23°02.94E	6.5	79	11580	5780		2285	452	12888	387	20339	347	2150
S8	38°51.24N 23°03.03E	6.4	83	11480	5730		2376	454	12794	389	20646	408	2233
S9	38°51.33N 23°02.90E	7.1	78	11430	5700		2207	414	12142	377	18523	378	2197
S10	38°51.42N 23°03.10E	7.0	33	10220	5100		1480	883	11365	340	17649	325	1468
S11	38°51.57N 23°02.80E	6.8	82	11200	5590		2252	437	12015	394	19849	244	1851
S12	38°51.73N 23°04.18E	7.2	18	430	210		67	35	17	3	24	268	7
S13	38°54.19N 23°02.81E	8.0	19	620	300		112	33	58	2	100	222	7
S14	38°54.12N 23°02.42E	7.1	20	530	260		110	27	48	3	71	218	27
S15	38°52.65N 23°02.44E	7.0	18	670	330		101	44	49	1	89	190	59
S16	38°41.47N 23°22.94E	7.0	18	530	860		71	36	8	1	18	272	1.5

Table 2. Trace elements analyses of Edipsos thermal (S1-S11) and cold (S12-S16) water samples (* bdl: below detection limit).

Samples	Type	Ag ppb	Al ppb	As ppb	Au ppb	B ppm	Ba ppb	Be ppb	Br ppb	Cs ppb	Cr ppb	Cu ppb
S1	Thermal	2	313	55	11	8.3	391	4	72	214	bdl	61
S2	Thermal	2	287	79	5	9.6	380	bdl	84	244	bdl	78
S3	Thermal	1	306	53	2	8.8	261	4	45	229	bdl	42
S4	Thermal	2	292	84	4	4.3	99	bdl	72	66	bdl	74
S5	Thermal	1	152	57	2	8.2	299	2	12	212	bdl	70
S6	Thermal	1	411	63	2	8.4	334	2	71	203	bdl	97
S7	Thermal	1	91	73	1	8.7	383	bdl	76	222	bdl	69
S8	Thermal	1	126	64	1	9.2	435	bdl	78	221	bdl	66
S9	Thermal	1	178	60	2	8.4	335	bdl	69	206	1	60
S10	Thermal	2	205	44	2	5.8	111	bdl	65	95	bdl	71
S11	Thermal	1	171	58	2	8.9	368	bdl	73	221	bdl	65
S12	Cold	bdl*	10	bdl	bdl	bdl	17	bdl	bdl	bdl	bdl	4
S13	Cold	bdl	45	1	bdl	0.4	300	bdl	bdl	1	1	10
S14	Cold	bdl	23	1	bdl	0.3	252	bdl	bdl	bdl	bdl	6
S15	Cold	bdl	28	1	bdl	0.2	68	bdl	bdl	bdl	1	43
S16	Cold	bdl	43	bdl	bdl	bdl	20	bdl	bdl	bdl	bdl	7
Detection Limit		0.05	1	0.5	0.05	0.005	0.05	0.05	5	0.01	0.5	0.1

Samples	Type	Fe ppb	Hg ppb	Li ppb	Mn ppb	Ni ppb	Pb ppb	Se ppb	Si ppm	Sr ppm	Zn ppb	Zr ppb
S1	Thermal	166	10	1542	48	bdl	73	48	34	18.3	bdl	53
S2	Thermal	bdl	3	1864	54	bdl	51	35	39	20.4	bdl	1
S3	Thermal	1126	1	3269	680	bdl	23	bdl	66	34.1	bdl	1
S4	Thermal	503	1	732	31	bdl	97	bdl	14	17.6	1	bdl
S5	Thermal	958	bdl	1638	219	bdl	129	16	33	18.9	bdl	bdl
S6	Thermal	962	bdl	1608	82	bdl	41	29	34	18.1	1	bdl
S7	Thermal	bdl	bdl	1652	58	bdl	103	29	39	19.2	bdl	bdl
S8	Thermal	40	bdl	1714	63	bdl	90	bdl	36	18.8	bdl	bdl
S9	Thermal	bdl	bdl	1602	105	bdl	69	76	34	14	3	bdl
S10	Thermal	303	bdl	954	408	bdl	154	6	21	14	9	bdl
S11	Thermal	200	bdl	1688	104	bdl	74	24	35	19.8	bdl	bdl
S12	Cold	bdl	bdl	1	1	bdl	2	bdl	3	0.7	13	bdl
S13	Cold	10	bdl	11	12	1	4	1	14	0.4	24	bdl
S14	Cold	bdl	bdl	22	2	1	2	1	14	0.7	28	bdl
S15	Cold	bdl	bdl	5	2	bdl	3	bdl	11	0.3	100	bdl
S16	Cold	14	bdl	4	1	bdl	2	bdl	3	0.1	384	bdl
Detection Limit		10	0.1	0.1	0.05	0.2	0.1	0.5	0.4	10^{-6}	0.5	0.02

The ascent of thermal waters can be attributed to several factors, such as the hydrostatic pressure, gas pressure (such as CO_2), and to the difference in density between cold and warm waters. During their ascent, thermal waters leach the calciferous formations of the area and become enriched in $Ca(HCO_3)_2$. The high amounts of $CaCO_3$in the calciferous formations become more soluble when gaseous CO_2 is present, forming $Ca(HCO_3)_2$according to the following reaction: $CaCO_3 + H_2CO_3 \leftrightarrow Ca(HCO_3)_2$. Calcium bicarbonate is an unstable compound in descending temperature and water pressure [22]. As a result, it dissolves and precipitates as $CaCO_3$ with the form of calcite or aragonite accompanied by gaseous CO_2. It should be noted that during field studies, the presence of travertine and Fe-oxides were frequently located near thermal spring discharges.

4. Sampling and analysis

Eleven water samples were collected from the representative thermal springs of the study area. Five samples of cold water were also collected from boreholes, in order to be used as reference samples. During sampling, all the necessary precautions were taken in order to avoid any possible contamination. General physicochemical parameters (pH, Electrical Conductivity, Total Dissolved Solvents and Temperature) were measured in situ. Samples were collected in polyethylene bottles. The quantity of sample (approximately 50ml) which was intended to be analyzed for trace elements was micro-filtered through a 0.45 μm pore size membrane in situ and then acidified to a final concentration of about 1% HNO_3. The remaining sample intended to be analysed for major ions was vacuum filtered in the lab and stored in cool conditions.

Totally 33 chemical parameters were determined, including major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, Cl^- and HCO_3^-), trace elements (Ag, Al, As, Au, B, Ba, Be, Br, Cs, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Si, Sr, Zn and Zr) and general physicochemical parameters (pH, EC, TDS and Temperature). The analyses were performed at the Laboratory of Economic Geology & Geochemistry (Faculty of Geology & Geoenvironment-University of Athens) and at the ACME Analytical Laboratories Ltd, Canada. The parameters of SO_4^{2-} and Cl^- were measured photometrically using DR/4000 apparatus, the parameter of HCO_3^- by titration, while the rest of the chemical parameters were analyzed by Inductively Coupled Plasma Mass Spectrometry method (ICP-MS). Results are shown in Tables 1 and 2. Data quality was assured by introduction of internal reference samples and by analysing duplicates of four samples. The precision was calculated from these duplicates and was found to be within the international standards.

5. Graphical process of data

Water samples were classified according to measured temperatures and their main chemical constituents (Tables 1 and 2). The Piper diagram in Figure 2 illustrates the composition of three main groups of waters: groups A (S16 and S12) and B (S13, S14 and S15) correspond to cold waters collected from boreholes, while group C corresponds to thermal springs. As it can be deduced from Figure 2, the A group consists of waters with low milliequivalent percentages of Cl^- and SO_4^{2-}, but enriched in the relative milliequivalent percentage of HCO_3^- compared to the other groups. The above classification shows that the major influence in hydrogeochemistry of these waters is the dissolution of the carbonate formations through the process of karstification, and that the presence of seawater has no influence. The same is assessed by increased milliequivalent percentages of major cations (Ca^{2+} and Mg^{2+}), denoting influence from the substrate formations (Mesozoic dolostones and limestones). Matching influences appear to be involved in group B, which has similar anionic and cationic milliequivalent percentages to group A. It indicates a potential trend for salinity due to overexploitation or mixing with the geothermal waters of high Cl^- values. The third group C, includes hydrothermal waters with high milliequivalent percentages of Na^+, $Cl^-$and SO_4^{2-}. In more detail, group C shows elevated values for TDS (Table 1), denoting the impact of seawater, a fact which is confirmed also by the elevated milliequivalent percentages of Cl^- and SO_4^{2-}, while cations are enriched in the alkaline members (Na+K). According to the above, the waters which belong to groups A and B are classified as $Ca\text{-}HCO_3$ type, while the waters of group C as Na-Cl type.

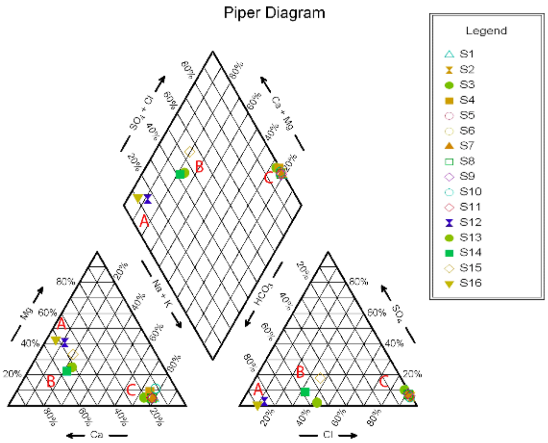

Figure 2. Piper diagram for the 16 water samples. Groups A, B correspond to cold waters while C corresponds to thermal. Values are meq/L.

As it can be deduced from Figures 3 and 4, there is almost a linear correlation between Cl-Br (Figure 3) and Na-Cl (Figure 4). There are two clearly distinguished groups of samples, corresponding to cold (group 1) and thermal waters (group 2) respectively. Cold waters (S12-S16) are plotted near the intersection point of the axis (close to zero values), while thermal waters are plotted

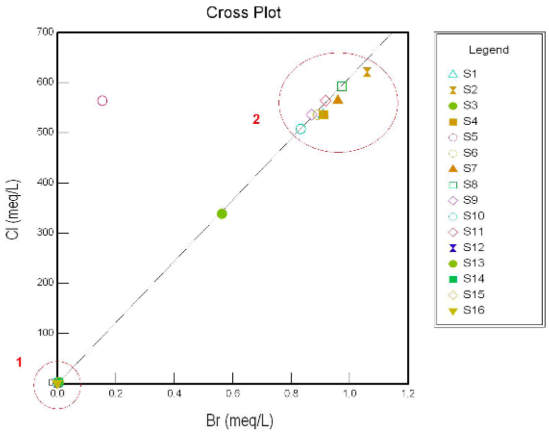

Figure 3. Cross plot of Cl and Br with the addition of the theoretical regression line. Groups 1 and 2 correspond to cold and thermal waters respectively.

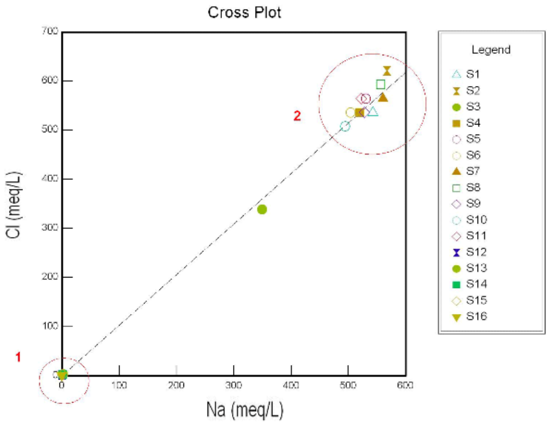

Figure 4. Cross plot of Na and Cl with the addition of the theoretical regression line. Groups 1 and 2 correspond to cold and thermal waters respectively.

away, including high milliequivalent values for Na^+ and Cl^-, and for Br compared with cold waters. The ionic ratios of Cl/Br and Na/Cl enhance the hypothesis of the influence of seawater and the possible correlation of thermal spring discharges with saline water. In more detail, the elemental ratios of Cl/Br (in meq/L) range between 580 and 650 for the most of thermal water samples, denoting direct impact from saline water, as the elemental value for seawater is about 655 [24]. The minor decrease in the values of the elemental ratio might be interpreted as the mixing of saline and meteoric water. The same can be determined for the elemental ratios of Na/Cl, which range between 0.7 and 1.0 for the majority of the samples, close to that of seawater (0.84) [23].

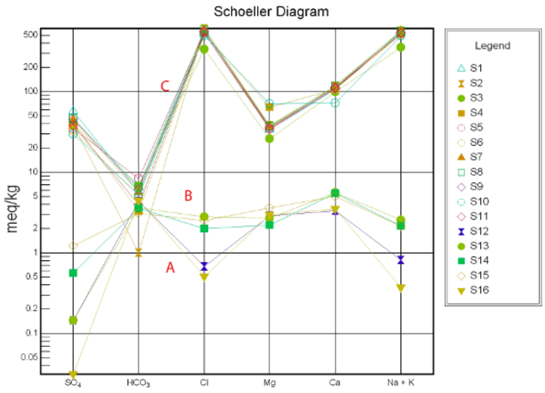

Figure 5. Schoeller diagram for the collected water samples. Groups A, B correspond to cold waters while C corresponds to thermal.

The different origin of the waters as well as their hydrogeochemical variations is also shown in the Schoeller diagram of Figure 5, where the aforementioned differentiation is depicted through the plotted linear trend of the analysed samples. It is obvious that thermal waters are characterised by similar inclinations and linear trends, while cold waters are significantly different.

6. Statistical processing of data

The analytical results of both thermal and cold waters were treated statistically, in order to examine potential correlations between the parameters and to assess the predominant geochemical processes and sources affecting their hydrogeochemistry. For this purpose, correlation analysis was applied for 21 selected parameters whose concentrations appeared to show significant variation. Initial data have been standardised in order to eliminate the influence of different units. Results are shown in Table 3.

The high positive intercorrelations between seawater related parameters [25], such as the correlations between Ca^{2+}, Cl^-, Na^+, K^+, SO_4^{2-}, Mg^{2+}, Br and EC, which are in all cases higher than +0.96, shows that the impact from seawater is profound. Furthermore, the high positive correlation of temperature (T) with the aforementioned parameters clearly shows the linkage between hydrothermal and saline waters. More specifically, the high positive relationship between Ca^{2+} and T (+0.94) reflects the dissolution of calcite at elevated temperatures and its probable deposition in the form of aragonite. As previously mentioned, sulfates are connected with marine water, no correlation between SO_4^{2-} and Fe (+0.31) suggesting that alternative origins such as pyrite oxidation is not possible.

Table 3. Correlation analysis for the 21 selected parameters of Edipsos thermal water samples.

	Ca	Cl	K	Mg	Na	HCO_3^-	SO_4^{2-}	Al	As	B	Ba	Br	Cs	Cu	Fe	Mn	Pb	Se	Si	EC	T
Ca	1																				
Cl	0,99	1																			
K	0,99	0,98	1																		
Mg	0,96	0,97	0,97	1																	
Na	0,99	1	0,99	0,97	1																
HCO_3^-	0,2	0,19	0,21	0,18	0,19	1															
SO_4^{2-}	0,97	0,98	0,95	0,94	0,98	0,18	1														
Al	0,9	0,9	0,87	0,88	0,89	0,08	0,84	1													
As	0,9	0,92	0,86	0,84	0,92	0,09	0,93	0,82	1												
B	0,9	0,92	0,86	0,83	0,92	0,12	0,93	0,82	1	1											
Ba	0,7	0,71	0,65	0,53	0,71	0,08	0,7	0,61	0,85	0,88	1										
Br	0,99	0,99	0,98	0,98	0,98	0,19	0,95	0,92	0,87	0,87	0,65	1									
Cs	0,96	0,96	0,95	0,92	0,96	0,21	0,9	0,89	0,88	0,89	0,74	0,95	1								
Cu	0,9	0,92	0,85	0,9	0,91	0,09	0,92	0,85	0,89	0,88	0,62	0,89	0,85	1							
Fe	0,41	0,4	0,39	0,44	0,39	0,44	0,31	0,58	0,31	0,32	0,17	0,42	0,47	0,35	1						
Mn	0,89	0,9	0,88	0,86	0,9	0,33	0,86	0,84	0,84	0,86	0,67	0,88	0,92	0,79	0,53	1					
Pb	0,96	0,97	0,96	0,98	0,96	0,25	0,93	0,83	0,86	0,85	0,61	0,95	0,93	0,89	0,42	0,86	1				
Se	0,48	0,5	0,5	0,41	0,5	-0,03	0,45	0,42	0,52	0,55	0,64	0,46	0,52	0,41	-0,04	0,45	0,49	1			
Si	0,73	0,73	0,7	0,62	0,74	-0,19	0,74	0,73	0,76	0,78	0,78	0,71	0,73	0,67	0,12	0,63	0,62	0,58	1		
EC	1	0,99	0,99	0,98	0,99	0,2	0,96	0,9	0,88	0,88	0,66	1	0,96	0,91	0,41	0,88	0,97	0,48	0,71	1	
T	0,94	0,92	0,92	0,85	0,92	0,31	0,9	0,79	0,81	0,83	0,74	0,92	0,91	0,8	0,33	0,8	0,87	0,49	0,72	0,93	1

7. Discussion of the hydrogeochemical results

From Table 1 it is shown that all thermal water samples are enriched in major ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}) and have abnormal EC values (7830-11580 μS/cm). Considering the specific genetic characteristics of the studied thermal springs and the results of correlation analysis, it is obvious that the thermal water chemistry is influenced by seawater intrusion and the intermixing with the hydrothermal fluids. This is confirmed by the elemental ratios of Cl/Br and Na/Cl, and the isotopic enrichment in ^{18}O and ^{2}H, which ranges from -0.37 to 0.00 for $\delta^{18}O\leq$ and -0.9 and 2.2 for $\delta^{2}H\leq$ respectively [23]. The above assessment is in accordance with previous research in the area which implies direct seawater involvement [23, 26]. Cold waters are not affected by sea water, so the origin of the influence should be attributed to the descent of seawater to great depths through the existing tectonic structures, and their ultimate discharge as thermal springs on the surface. An additional enrichment factor for Ca^{2+} and SO_4^{2-} could be the hydrothermal activity. The elevated values of temperature, increase the dissolution of calcite, which is the principal mineral in the limestones of the Alpine substrate. The general increase in oxidizing conditions which occur as the thermal waters ascend from anoxic depths to the surface, may result in some cases to the oxidation of H_2S which is present due to past volcanic activity, and enrichment of waters in SO_4^{2-}. This may be the case for the elevated values of SO_4^{2-} in springs which are located far from the shoreline, so the impact from seawater is minimal. Finally, temperatures vary between 33°C and 81°C, with the majority of the samples having temperatures around 70°C.

From Table 2, the following assessments can be made. Values of Ag are present even in trace quantities (1-2 ppb) in all samples of thermal water. Au is also present, especially in samples 1, 4 and 5 where its concentrations are 4, 5 and 11ppb respectively. Ba ranges between 99 and 435 ppb, Br between 45 and 83 ppb, Cs between 66 and 244, Se between 0 and 76 ppm, and Cu ranges between 42 and 97 ppb. Furthermore, As ranges between 44 and 84 ppb, Pb between 23 and 154 ppb and Mn ranges between 31 and 680 ppb. The above concentrations are probably correlated with the hydrothermal activity, likewise for Hg, Be and Zr, which are present only in trace quantities. The elements of Cr and Ni have almost negligible concentrations, while Zn is absent in all thermal samples, probably due to precipitation. As it can be judged from these results, metals such as Fe, Pb, Zn, Cu show low concentrations (ppb class order) compared with those of the metallogenic hydrothermal solutions, which in the case of Cu-Zn and Fe reach 100-500 ppm and 300 ppm respectively [27]. The above confirms that hydrothermal fluids are not metallogenic and also that the substrate which

Table 4. Temperatures (°C) estimated from chemical geothermometers.

	Geothermometers					
Samples	Quartz	Chalcedony	Na-K	Na-K-Ca	Mg-Li	Na-Li
S1	> 250°C	> 250°C	< 150°C	154.67°C	60.615°C	66.089°C
S2	> 250°C	> 250°C	< 150°C	158.74°C	63.373°C	70.688°C
S3	156.48°C	132.06°C	< 150°C	144.15°C	81.339°C	108.18°C
S4	79.339°C	82.99°C	< 150°C	153.28°C	38.608°C	45.343°C
S5	118.62°C	116.99°C	< 150°C	156.29°C	61.505°C	68.703°C
S6	120.15°C	118.29°C	< 150°C	158.21°C	61.277°C	69.751°C
S7	127.32°C	124.38°C	< 150°C	157.53°C	61.219°C	67.235°C
S8	123.11°C	120.8°C	< 150°C	154.54°C	61.985°C	68.639°C
S9	120.15°C	118.29°C	< 150°C	153.23°C	61.51°C	68.152°C
S10	96.885°C	98.296°C	< 150°C	162.91°C	42.786°C	54.346°C
S11	121.64°C	119.56°C	< 150°C	< 0°C	62.069°C	70.162°C

undergoes leaching by the fluids is poor in such metals.
Compared with the chemical composition of other thermal springs from the Hellenic Volcanic Arc [28] it can be seen that the Edipsos thermal waters are enriched in Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, Li, B and K^{+}, reflecting the influence of seawater. Relevant compositions of thermal waters are shown only in thermal springs of the Hellenic Arc which are closely related with saline influence (e.g. individual springs in the Islands of Santorini, Milos, kimolos, Nisyros and Kos). From all of the thermal springs that occur in the above islands, plus those of Methana and Korinthos (mainland, east Peloponnese), the Edipsos springs appear to have the highest temperatures. Finally, cold waters appear to be of high quality (2000/60/EU) [29], with the potential for use as drinking water.

Assessment of the reservoir temperatures was made through the use of silica and cation geothermometers. The geothermometers used were quartz [30], Na–K [31], Na–K–Ca [32], Na/Li [33, 34] and K–Mg [35], Li–Mg [36]. The results are given in Table 4.

The quartz and chalcedony geothermometers (applicable with higher systems above 150°C) [36] show different results. Particularly, the differences of samples S3-S11 vary between a range of 60°C for quartz and 50°C for chalcedony, while in samples S1 and S2 the temperature exceeds 250°C. Considering the fact that the temperatures of the springs are lower than 100°C, this suggests that dilution can seriously affect the silica geothermometers [37], and the estimates obtained here cannot be regarded as reliable.

Applied to thermal waters, the cation geothermometers Na-K gives temperatures below 150°C for all samples. The Na-K geothermometers is less sensitive to the secondary processes (e.g. mixing and boiling) that may change the original reservoir characteristics of waters [37], so this geothermometer may yield erroneous results when applied to low temperature spring waters. On the other hand, the Na-K-Ca geothermometer which is developed to eliminate the effects of high Ca [32], yields temperatures ranging between 144°C and 162°C degrees. Finally, the geothermometers of Mg-Li and Na-Li appear to give relatively similar results for the majority of the samples, but with the occurrence of some abnormal low or high values, such those of samples S3 and S4. Overall, it is not possible to select a single geothermometer as the best representative for the region, due to the temperature variances that exist in different geothermometers and in different samples of the same geothermometer. These changes may originate from the influence of seawater on the geochemistry of geothermal fluids, which alters their original characteristics [38].

8. Conclusions

The thermal springs of the Edipsos were formed as a result of the intense tectonic activity and volcanism of the North Euboea lithological structure. The major element chemistry of the thermal waters is influenced by the intrusion of sea water of Na–Cl type, found through the graphical classification, whilst cold waters belong to the Ca–HCO_3 group. Marine water is the primary factor for the composition of hydrothermal waters and it is expressed through the elevated values Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-},K^{+}, TDS and EC. Metals such as Fe, Pb, Zn, Cu show low concentrations compared with those of the metallogenic hydrothermal solutions. Cold waters are free of heavy metals compared with other natural waters and are characterised by being of good quality based on the major and trace element chemistry. Finally several geothermometers were applied in order to assess the reservoir temperatures, but none appear to be applicable, largely due to the impact of seawater on the initial hydrogeochemistry of the geothermal fluids.

References

[1] Fytikas M., Innocenti F., Manetti P., Mazzuoli R., Peccerillo A. and Villari L., Tertiary to Quarternary evolution of volcanism in the Aegean region, Geological Society of London, Special Publications, 1984, 17, 687-699
[2] Pe-Piper G., Piper D.J.W., Spatial and temporal variation in Late Cenozoic Back-arc volcanic rocks, Aegean Sea region., Tectonophysics, 1989, 169, 113-134
[3] Katsikatsos G., Les formations triassiques de l'Eubée

centrale, Annales Géologiques des Pays Helléniques, 1970, 22, 62-76

[4] Katsikatsos A.G., La structure tectonique d'Attique et de l'Ile d'Eubée, Proceedings of the 6th Colloquium of the Geology of the Aegean Region, 1977, 1, 211-228

[5] Katsikatsos A.G., Fytikas M., Koukis G., Geological map of Greece, Kymi sheet, 1:50000, IGME, Athens, 1981

[6] Katsikatsos A.G., Mettos A., Vidakis M., Geological map of Greece, Istiea sheet, 1:50000, IGME Athens, 1984

[7] Vardaki C., Kelepertis A., Environmental impact of heavy metals (Fe, Ni, Cr, Co) in soils, waters and plants of Triada Euboea from ultrabasic rocks and nickeliferous mineralisation, Environ. Geochem. Hlth., 1999, 21, 221-226

[8] Danelian T., Robertson A., Neotethyan evolution of eastern Greece (Pagondas Melange, Evia Island) inferred from radiolarian biostratigraphy and the geochemistry of associated extrusive rocks, Geol. Mag, 2001, 138, 345-363

[9] Christodoulou G., Tsaila-Monopolis S., Contribution to the knowledge of the stratigraphy of Triassic in the Eastern Hellenic zone, Bulletin of the Geological Society of Greece, 1972, 9, 109-118

[10] De Bono A., Cirilli S., Vachard D., Vavassis I., Stamplfli G.M., The Liri unit: an external unit at the base of Pelagonia terrane in central Evia Island. Evidence for a Paleotethyan suture in the Hellenides, Symposium DO6, Inter-Relations between Paleotehys and Neotethys in Eurasia, Journal of Conference Abstracts, 1999, 4

[11] Vavasis I., De Bono A., Valloton A., Stampfli G., Gosca M., Amelin Y., Geochronological data from the Pelagonian basement in Evia Island (Greece): Geodynamic implications for the evolution of Paleotethys, Symposium DO6, Inter-Relations between Paleotehys and Neotethys in Eurasia, Journal of Conference abstracts, 1999, 4

[12] Guernet C., Etudes géologiques en Eubée et dans les régions voisines (Grece) 1971, These Doctoral, Faculte de Sciences, Universite de Paris

[13] Katsikatsos G., Migiros M., Mettos A., Geological structure of internal Hellenides (E. Thessaly-SW Macedonia, Euboea-Attica-northern Cyclades Island and Lesvos), Geological and Geophysical Research, Special Issue, IGME, Athens, 1986, 191-212

[14] Scherreiks R., Platform margin and oceanic sedimentation in a divergent and convergent plate setting (Jurassic, Pelagonian Zone, NE Evvoia, Greece), Int. J. Earth Sci., 2000, 89, 90-107

[15] Palyvos N., Bantekas I., Kranis H., Transverse fault zones of subtle geomorphic signature in northern Evia Island (central Greece extensional province): An introduction to Quaternary Nileas graben, Geomorphology, 2006, 76, 363-374

[16] Tsikouras B., Pe-Piper G., Piper D.J.W., Hatzipanagiotou K., Triassic rift-related komatiite, picrite and basalt, Pelagonian continental margin, Greece, Lithos, 2008, 104, 199-215

[17] Mettos A., Rondogianni T., Ioakim C., Papadakis I. Evolution, géodynamique et reconstruction paleoenvironnmentale des Basins Neogenes-Quaternaires de la Grece centrale, Paleontologia i Evolucio, 1992, 24-25, 393-402

[18] Philip H., Etude néotectonique des rivages égéens en Locride et en Eubée nord orientale, These de 3eme cycle, Acad de Montpellier, Univ. De Languedoc, 1974

[19] Lemeille F., Etudes néotectoniques en Grece central nord-orientale (Eubée centrale, Attique, Béotie, Locride), These de 3eme cycle, XI-Centre d'Orsay, Universite de Paris, 1977

[20] Rondogianni T., Etude néotectonique des rivages occidentaux du canal d'Atalanti (Grece central), These 3eme cycle, Universite Paris XI, 1984

[21] Roberts S., Jackson J., Active normal faulting in central Greece: an overview. In: Roberts A.M., Yielding G., Freeman B. (Eds), The geometry of normal faults, Geological Society, London, Special Publication, 1991, 56, 125-142

[22] Orfanos G., Hydrogeological reconnaissance of the thermometallic springs of Killini, Kaifa, dipsos, Thermopylae, Ypati, I.G.M.E., technical report, 1976 (in Greek)

[23] Kallergis N., Lambrakis G., Contribution to the study of greek thermal springs: hydrogeological and hydrochemical characteristics and origin of thermal waters, Hydrogeol. J., 2005, 13, 506-521

[24] Alcala F., Custodio E., Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal, Journal of Hydrology, 2008, 359, 189-207

[25] Hem J., Study and interpretation of the chemical characteristics of natural water, U.S. Geological Survey, Water Supply Paper 2254, 1985

[26] Minissale A., Duchi V., Kolios N., Totaro G., Geochemical characteristics of Greek thermal springs, J. Volcanol. Geoth. Res., 1989, 39, 1-16

[27] Gill R., Chemical fundamentals of Geology, Unwin Hyman, London, 1989

[28] Minissale A., Duchi V., Kolios N., Nocenti M., Verrucchi C., Chemical patterns of thermal aquifers in the volcanic islands of the Aegean arc, Greece, Geothermics, 1997, 26, 501-518

[29] European Water Directive. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy, European Union, 2000

[30] Fournier R.O., Application of water geochemistry to geothermal exploration and reservoir engineering. In: Rybach L., Muffer L.J.P. (Eds.), Geothermal Systems: Principles and Case Histories, J.Wiley, New York, 1981, 109-143

[31] Arnorsson S., Gunnlaugsson E., Svavarson H., The chemistry of geothermal waters in Iceland: III. Chemical geothermometry in geothermal investigations, Geochim. Cosmochim. Ac., 1983, 47, 567-577

[32] Fournier R.O., Truesdell A.H., An empirical Na–K–Ca geothermometer for natural waters, Geochim. Cosmochim. Ac., 1973, 37, 515-525

[33] Fouillac C., Michard G., Sodium/lithium ratios in water applied to geothermometry of geothermal reservoirs, Geothermics, 1981, 10, 55-70

[34] Kharaka Y.K., Lico M.S., Law L.M., Chemical geothermometers applied to formation waters, Gulf of Mexico and California basins (sbs), Am. Assoc. Pet. Geol. B., 1982, 66, 588

[35] Giggenbach W.F., Confiantini R., Jangi B.L., Truesdell A.H., Isotopic and chemical composition of Parbati valley geothermal discharges, north-west Himalaya, India, Geothermics, 1983, 12, 199-222

[36] Kharaka Y.K., Mariner R.H., Chemical geothermometers and their application to formation waters from sedimentary basins. In: Naeser N.D., Mc Collon T.H. (Eds.), Thermal History of Sedimentary Basins, Springer-Verlag, New-York, 1989, 99-117

[37] Mutlu H., Gulec N., Hydrogeochemical outline of thermal waters and geothermometry applications in Anatolia (Turkey), J. Volcanol. Geoth. Res., 1998, 85, 495-515

[38] Dotsika E., Leontiadis I., Poutoukis D., Cioni R., Raco B., Fluid geochemistry of the Chios geothermal area, Chios Island, Greece, J. Volcanol. Geoth. Res., 2006, 154, 237-250