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HYDROCHEMICAL CHARACTERISTICS AND GEOTHERMOMETRY APPLICATIONS OF HOT GROUNDWATER IN EDIPSOS AREA, NW EUBOEA (EVIA), GREECE

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Abstract

In Edipsos area many hot springs occur, as a result of both active tectonic of the area and recent volcanism (Lichades volcanic center). A geochemical study of Edipsos hot groundwaters was undertaken, in order to assess the hydrochemistry of hot springs from Edipsos and re-evaluate the geothermal situation of the area. For that purpose, 12 water samples were collected and analyzed by Spectrophotometry for the main ions and by AAS, ICP-OES and ICP-MS for major and trace elements. The interpretation of the analytical data showed that the geochemistry of Edipsos hot groundwaters is controlled by three factors i) a deep magmatic source, ii) the chemical composition of the local rocks (ultramafic and carbonates) and iii) sea water. The application of chemical geothermometers is problematic because of the chemical composition of the hot groundwaters and especially the high participation of the sea water. The temperature which derives from the use of Na-K-Ca geothermometer is greater than 160°C. Although, several studies have conducted in the area still remain unanswered questions concerning the underground circulation of the hot groundwater, in which only deep drilling data could give answers.
Keywords: *geothermal energy, groundwater geochemistry, major and trace element concentration, Edipsos (Aidipsos), NW Euboea (Evia).*

Περίληψη

Στην περιοχή της Αιδηψού υπάρχει πληθώρα θερμών πηγών, σαν αποτέλεσμα των ενεργών τεκτονικών διεργασιών και της σχετικά πρόσφατης ηφαιστειότητας (ηφαιστειακό κέντρο Λιχάδων) της περιοχής. Στα πλαίσια της παρούσας μελέτης πραγματοποιήθηκε γεωχημική έρευνα των υπογείων θερμών νερών της περιοχής, με σκοπό να αξιολογηθεί το γεωθερμικό δυναμικό. Για τον σκοπό αυτό 12 δείγματα θερμών νερών συλλέχθηκαν και αναλύθηκαν με φασματοφωτομετρία για κύρια ιόντα και με AAS, ICP-OES και ICP-MS για κύρια στοιχεία και ιχνοστοιχεία. Από την επεξεργασία των αποτελεσμάτων διαπιστώθηκε πως ο χημισμός των υπόγειων θερμών νερών της Αιδηψού ελέγχεται από 3 παράγοντες: α) μια βαθιά μαγματική πηγή, β) την χημική σύσταση των περιβαλλόντων πετρωμάτων (π.χ. υπερβασικά πετρώματα και ασβεστόλιθοι) και γ) το θαλασσινό νερό. Η εφαρμογή χημικών γεωθερμομέτρων πρέπει να γίνει με μεγάλη προσοχή στο εν λόγω πεδίο, εξαιτίας της χημικής σύστασης των θερμών νερών και κυρίως λόγω της μεγάλης συμμετοχής θαλασσινού νερού. Το πιο κατάλληλο χημικό γεωθερμόμετρο είναι του Na-K-Ca, βάσει του οποίου υπολογίστηκε ότι η θερμοκρασία ενός πιθανού γεωθερμικού ταμιευτήρα στην

περιοχή μπορεί να φτάνει έως τους 160ºC. Παρότι πολλές μελέτες έχον διεξαχθεί στην περιοχή, ακόμη παραμένουν αναπάντητα ερωτήματα σχετικά με υπόγεια κυκλοφορία του θερμού νερού, στα οποία μόνο ένα πρόγραμμα βαθιών γεωθερμικών γεωτρήσεων μπορεί να δώσει απαντήσεις.
Λέξεις κλειδιά: *γεωθερμική ενέργεια, γεωχημεία υπόγειων νερών, συγκεντρώσεις ιχνοστοιχείων και ανιόντων, Αιδηψός, ΒΔ Εύβοια.*

1. Introduction

In Greece occurs a large number of hot springs, which many of them are known since antiquity. The great number of hot springs in Greece is due to the geology of the country, which is located in the front line of the African - European tectonic plate collision-subduction zone. The combination of magmatic and volcanic processes and active fault systems favour the rise of deep waters that discharge at the surface as hot springs.

Hot waters exhibit a broad range of chemical compositions, from very dilute (a few hundred parts per million, by weight, of total dissolved constituents) to very concentrated (solutions containing tens of percent, by weight, of dissolved constituents). This dissolved load can provide important information about the characteristics of a reservoir including its temperature, mineralogy, and history. However, the dissolved load can also impact in the healing properties when is used for spa/bathing therapies and the performance of machinery in a geothermal power plant when is used in heating and cooling, as well as in generating power (Glassley, 2015).

From 1970-80`s, the Institute of Geological and Mineral Exploration in Greece (I.G.M.E.) performed the first systematic study on all known Greek hot springs (Orfanos, 1975; Sfetsos, 1988 etc.). Edipsos is known since ancient times for their hot springs and their healing properties. Aristotle at his study with tile Meteorology (II, 8.3) attempts to explain how hot springs of Edipsos works. Northern Euboea’s hot springs and their depositions were studied by many researches in the past (Gkioni, 1998; Shimizu *et al.*, 2005; Xatzis *et al.*, 2008; Kanellopoulos, 2006, 2011, 2013a, 2013b; D`Alessandro *et al.*, 2014; Dotsika, 2015).

The aim of this paper is to assess the hydrochemistry of hot springs from Edipsos and re-evaluate the geothermal situation of the area.

2. Geological setting

Euboea Island is located in the central part of Greece. The study area lies between the following coordinates X: 416400E, Y: 4301600N and X: 418000E, Y: 4300400N (EGSA `87). The greater area is characterized by rocky mountainous topography and some lowland areas.

Northwester part of Euboea Island belongs geologically to the western part of the internal geotectonic units of Greece, more specifically the Pelagonian and Sub-Pelagonian units (Mountrakis, 1986). The study area consists of non-metamorphic rocks, carbonate rocks, ophiolitic rocks including peridotite, gabbro, serpentinite and metamorphic rocks. Large parts of NW Euboea are covered by Post Alpine formations, Quaternary and Neogene age sediments (Fig. 1A).

In the center of northern Euboea gulf the volcanogenic islands of Lichades are located (Georgalas, 1938). They are consisted mainly of trachyandesite lava flows, dated at 0.5 Ma (Pe-Piper and Piper, 2002). Karastathis *et al.* (2011) showed that there is a magma chamber, under N. Euboean Gulf, at 7-8 km depth, using low seismic P-wave velocity values and high Poisson ratios.

The study area is highly faulted due to extensional tectonics. A system of N.NE-S.SW and W.NW–E.SE to NW–SE normal fault zones prevails (Vavassis, 2001; Palyvos *et al.*, 2006). The fault zones are associated with the Northern Euboea graben, due to most recent (Quaternary) phase of the long-lasting extension established in the broader back-arc area of the Hellenic arc (Mercier *et al.*, 1989).

In Edipsos, thermogenic travertine deposits exist created by the local hot-springs (Kanellopoulos, 2006; 2011; 2013a; 2013b).

3. Materials and methods

3.1. Field work, groundwater sampling and analysis

A total of 12 hot groundwater samples were collected (Table 1) from springs and drills used mainly for spa therapy. Unstable parameters i.e. pH, Temperature, E.C. were measured in the field.

All the samples were vacuum filtered and stored in polyethylene bottles and preserved in a refrigerator. Part of each sample was acidified to a final concentration of 2% nitric acid.

All the 12 water samples were analyzed in the Laboratories of Institute of Geological and Mineralogical Exploration (I.G.M.E.). The major element and ion concentrations were measured using spectrophotometer, or/and titration or/and AAS or and ICP-OES (Table 2). The trace element concentrations were measured using ICP-MS (Table 3).

During the field work, all the major hot springs of the area were spotted and record with GPS and in several cases photos of them were taken with a thermal camera (FLIR T640, Fig. 3).

ArcGIS was used to create a new digital optimized geological map of the greater area of Edipsos (scale 1:10,000, Fig. 1). This map was based on new field observations and the published geological maps (Marinos *et al*., 1957; Katsikatsos *et al*.,1984) of scale 1:50 000 as well as, other detailed geological maps (Tzitziras, 1996; Vavassis, 2001). A spatial database was developed in ArcGIS; physicochemical parameters and elemental concentrations were linked to the sampling points and were used in order to create a temperature spatial distribution map.

4. Analytical results

4.1. Spatial distribution of temperature

In order to visualize the spatial distribution of the shallow hot groundwater temperature in Edipsos, an interpolated map was created, based on temperature measurements from all the major hot springs and shallow wells (depth <40m) of the area. ArcGIS software was used and kriging interpolation method was applied (Fig. 1B). Kriging is deterministic interpolation method that generates an estimated surface from a scattered set of points with z-values, in this case water temperature values.

Table 1 - Samples locality, physiochemical parameters, hydrochemical type and chemical geothermometers.

Code	Lon.[*1]	Lat.[*1]	Locality	T (ºC)	pH	TDS[*2] (mg/L)	EC (mS/cm)	Hydroc. type	Chemical geothermometers Qtz[*3]	Na-K-Ca[*4]	Na-K-Ca[*4] (Mg cort.)
STR-116G3	417122.1	4300593.0	Thermae Sylla	48.7	6.5	32330	46900	Na-Cl	57	158	76
STR-114P2	417610.0	4300710.0	Skourtanioti	64.3	6.2	30875	43900	Na-Cl	60	164	36
STR-114P4	417727.0	4300842.0	Skourtanioti-Ilios	58.1	6.8	27350	39900	Na-Cl	56	157	77
STR-115G7	417644.1	4300818.0	Kompogianni	71.8	6.2	33365	46000	Na-Cl	56	159	76
STR-114P8	417476.0	4301103.0	Pizou-Kapelari	60.2	6.0	32195	47100	Na-Cl	59	157	76
STR-114P1A	417376.0	4301182.0	Thermopotamos	69.0	6.2	27400	39100	Na-Cl	56	157	77
STR-113GA	417328.6	4300776.5	EOT-Artemis	79.6	6.2	33575	45900	Na-Cl	58	158	58
STR-113-01	417283.2	4300846.7	EOT-Ntamaria	70.1	6.0	32530	45900	Na-Cl	59	154	59
STR-114G20	417090.0	4301320.0	Koukoumos	82.2	6.5	33735	46200	Na-Cl	56	157	76
STR-114P5	417561.0	4300935.0	Ai pigai	54.5	6.6	30585	43900	Na-Cl	56	158	77
STR-114P9	417374.0	4301149.0	Papaioannou	43.9	6.4	18800	29600	Na-Cl	56	153	73
STR-BP1	417628.1	4300705.3	Vrysakia	54.0	6.6	20870	31200	Na-Cl	50	160	43

*[*1] = Geographical coordinates are in EGSA `87, [*2] = Measured at the laboratory, [*3] = Fournier 1977, [*4] = Fournier 1979*

Based on spatial distribution of the temperatures (Fig. 1B), the highest temperatures are detected along the major fault zones of the area and especially along the N.NE-S.SW to NE-SW and NW-SE directions. The temperature maxima were detected at fault intersections.

4.2. Chemical Analysis

The location of each sample is presented in Table 1 and in Tables 1, 2 and 3 are presented the physiochemical parameters analysed in situ and in the lab. In Figure 2A, the chemical analyses were plotted in Piper diagram (Piper, 1953), in order to evaluate them hydrochemically and identify their hydrochemical type. All the samples are plotted in the same areas in the Piper and Langelier-Ludwing diagrams (Langelier and Ludwing, 1942, Fig. 2A, C) and all of them have Na-Cl hydrochemical type (Table 1). In Giggenbach diagram (Giggenbach, 1980, Fig. 2B) all the samples are plotted in the same area and characterized as partially equilibrated waters.

Chloride and sodium are the dominant anion (up to 19570 mg/L) and cation (up to 10600 mg/L) and show high concentrations in all samples. The studied fluids showed high concentrations to a series of elements like B, Sr and Li, which could be associated with seawater. The concentrations of Na, Cl, K and TDS vary with the same way (Fig. 2D), suggesting common source (correlation coefficients >0.95). Similarly, Ni and Cu vary with the same way (correlation coefficient 0.82).

4.3. Geothermometry application

Chemical geothermometers are widely used tools in order to estimate the sub-surface reservoir temperatures in a geothermal system (Giggenbach, 1988). Geothermometers are based on the equilibrium of temperature dependent reactions between minerals and the circulating fluids (Fournier, 1973). Three geothermometers i.e. Quartz (Fournier, 1977); Na-K-Ca and Na-K-Ca with Mg correction (Fournier and Potter, 1979) were applied to the hot groundwaters of Edipsos (Table 1). The resulting temperatures are presenting large variations. The most probable reason for that could be the large percentage of sea water in the studied geothermal fluids, as the marine solutions to the geothermal fluids is one of the main causes for the disturbance for the chemical geothermometers (Dotsika, 2015).

Typically, the Quartz geothermometer is not affected by the seawater, but its results are too low (up to 60 ºC; hot spring in the area present temperatures up to 82 ºC). Possibly there is a mixing between the geothermal solution and superficial water affecting the Quartz geothermometer. The temperature which derives from the use of Na-K-Ca geothermometer is up to 164 °C.

5. Discussion - Conclusions

In Edipsos area many hot springs occur, as a result of both active tectonics of the area and recent volcanism (Lichades volcanic center). Their temperature is up to 82ºC. The hot groundwater in Edipsos is circulating using the major fault system related with the Northern Euboea graben. As it could be seen in Fig. 1B temperature shows its maxima in NE-SW direction related with a mapped fault, which intersect, with the covered by the travertines, NW-SE fault system.

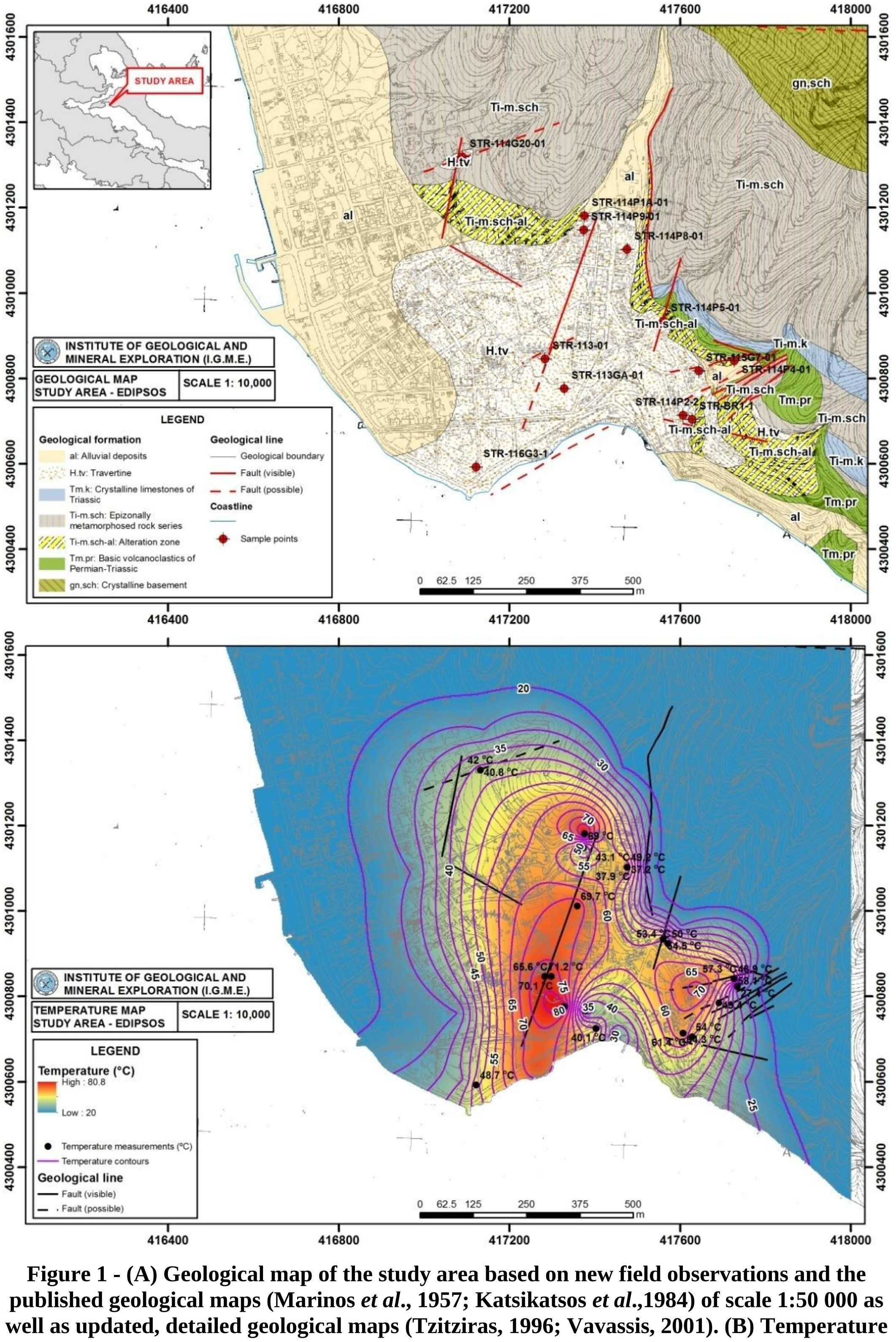

Figure 1 - (A) Geological map of the study area based on new field observations and the published geological maps (Marinos *et al*., 1957; Katsikatsos *et al*.,1984) of scale 1:50 000 as well as updated, detailed geological maps (Tzitziras, 1996; Vavassis, 2001). (B) Temperature distribution based on the hot springs and shallow wells of the area.

Table 2 - Concentrations of major ions (in mg/L).

Sample	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	NO_2^-	NH_4^+	F^-	SiO_2^-
STR-116G3	1357	484	10133	354	489	18298	1450	<5.0	<0.050	0.3	4.46	13.8
STR-114P2	1584	301	9668	330	678	17589	1050	<5.0	<0.050	0.4	4.58	16.5
STR-114P4	1346	264	8546	294	568	15601	1000	<5.0	0.40	0.5	4.42	17.6
STR-115G7	1675	313	10469	344	691	19006	1200	<5.0	<0.050	0.4	4.62	18.2
STR-114P8	1620	313	9679	335	626	18722	1200	<5.0	<0.050	0.4	4.52	17.1
STR-114P1A	1379	267	8551	293	593	15601	1000	<5.0	<0.050	0.6	4.12	16.4
STR-113GA	1650	322	10500	361	585	19290	1150	<5.0	<0.050	0.5	4.8	16.4
STR-113-01	1642	321	10219	351	620	18722	950	<5.0	<0.050	0.4	4.7	17.0
STR-114G20	1668	322	10592	363	610	19574	900	<5.0	<0.050	0.6	4.62	16.2
STR-114P5	1496	288	9459	321	657	17730	950	<5.0	<0.050	0.4	4.34	16.2
STR-114P9	864	174	5980	204	598	10567	700	<5.0	<0.050	0.4	3.66	17.7
STR-BP1	1079	220	6490	217	619	11843	700	<5.0	<0.050	0.3	3.42	16.3

Table 3 - Concentrations of trace elements (in µg/L).

Sample	Li	Fe	Cr	Mn	Ni	Zn	Rb	Ag	Be	Mo	Cd	Pb	Se	Co	V	Sb	B	I	Sr	Al	As	Cu	Ba	Hg	U
STR-116G3	1480	77	<50	270	70	<50	150	<5	<5	<10	<5	34	290	<10	100	<5	1030	580	11500	<10	72	190	130	<0,5	<5
STR-114P2	1900	2400	<50	200	90	<50	160	<5	<5	<10	5.6	29	290	<10	100	<5	5040	550	12750	<10	97	190	200	<0,5	<5
STR-114P4	1700	165	<50	180	80	<50	150	<5	<5	<10	<5	20	260	<10	100	<5	4670	410	11250	<10	100	180	200	<0,5	<5
STR-115G7	2100	3170	55	160	97	<50	170	<5	<5	<10	5	22	290	<10	110	<5	5000	415	13230	<10	97	200	220	<0,5	<5
STR-114P8	2100	1170	<50	<50	100	<50	170	<5	<5	<10	7	25	290	<10	120	<5	4900	420	13170	<10	100	205	210	<0,5	<5
STR-114P1A	1900	520	<50	<50	83	<50	150	<5	<5	<10	<5	25	290	<10	110	<5	4470	425	11220	100	78	170	270	<0,5	<5
STR-113GA	1360	540	<50	<50	74	<50	170	<5	<5	<10	<5	<10	340	<10	70	<5	5400	430	11300	<10	68	150	250	<0,5	<5
STR-113-01	1370	2500	70	53	66	<50	170	<5	<5	<10	<5	<10	320	<10	73	<5	5280	415	11300	<10	68	155	240	<0,5	<5
STR-114G20	1400	1020	<50	<50	70	<50	180	<5	<5	<10	<5	<10	310	<10	<50	<5	5160	445	620	<10	<50	85	130	<0,5	<5
STR-114P5	1320	2900	<50	140	69	<50	170	<5	<5	<10	<5	<10	300	<10	68	<5	4750	535	10700	<10	64	140	150	<0,5	<5
STR-114P9	860	880	<50	210	<50	<50	107	<5	<5	<10	<5	<10	200	<10	<50	<5	3700	300	640	<10	60	100	130	<0,5	<5
STR-BP1	940	870	<50	160	53	<50	130	<5	<5	<10	<5	<10	210	<10	<50	<5	3650	325	790	<10	<50	100	140	<0,5	<5

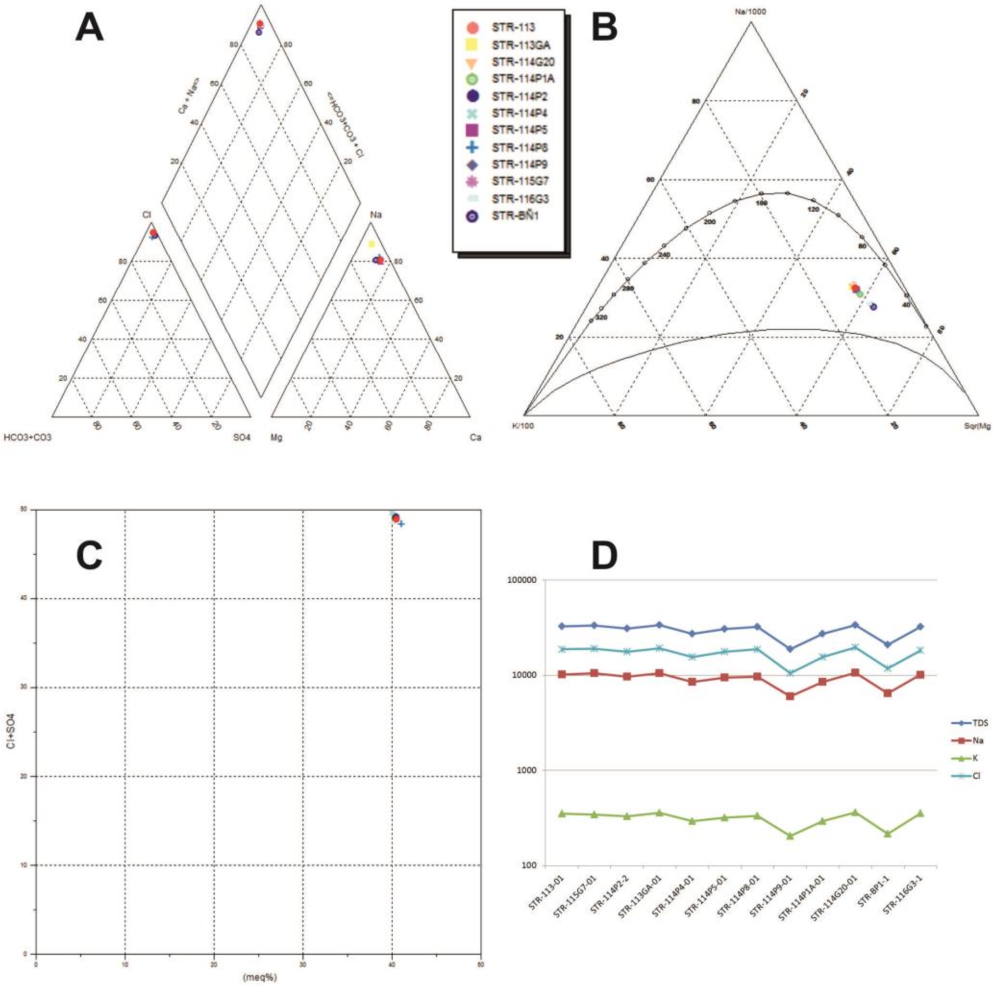

Figure 2 - Chemical composition of groundwater samples plotted in (A) Piper trilinear diagram. (B) Giggenbach trilinear diagram. (C) Ludwing-Langelier diagram. (D) Logarithmic diagram presenting the co-varying of TDS, Na, K and Cl.

The vast deposition of thermogenic travertines and the high Ca concentrations suggests that the hot groundwater at some point meet and dissolve carbonates rocks. So, the hot water enriches in Ca and deposits thermogenic travertine at the surface due to pressure and temperature change.

Similarly, the co-variation and the concentrations of Ni and Cu suggesting influence of the ultramafic rocks from the ophiolitic sequence. Kanellopoulos and Argyraki (2013) and Kanellopoulos and Mitropoulos (2013) have shown that element like Ni, Cr, Cu etc. are present in noticeable concentrations in the soil and the cold groundwater of the greater area of NW Euboea and are related with the ultramafic rocks from the ophiolitic sequence.

The high concentrations in Cl (up to 19570 mg/L), Na (up to 10600 mg/L) and in other elements that could be associated with seawater, combined with isotopic results (Mitropoulos and Kita, 1997; D`Alessandro *et al*., 2014; Dotsika, 2015) strongly suggests high seawater participation at the system.

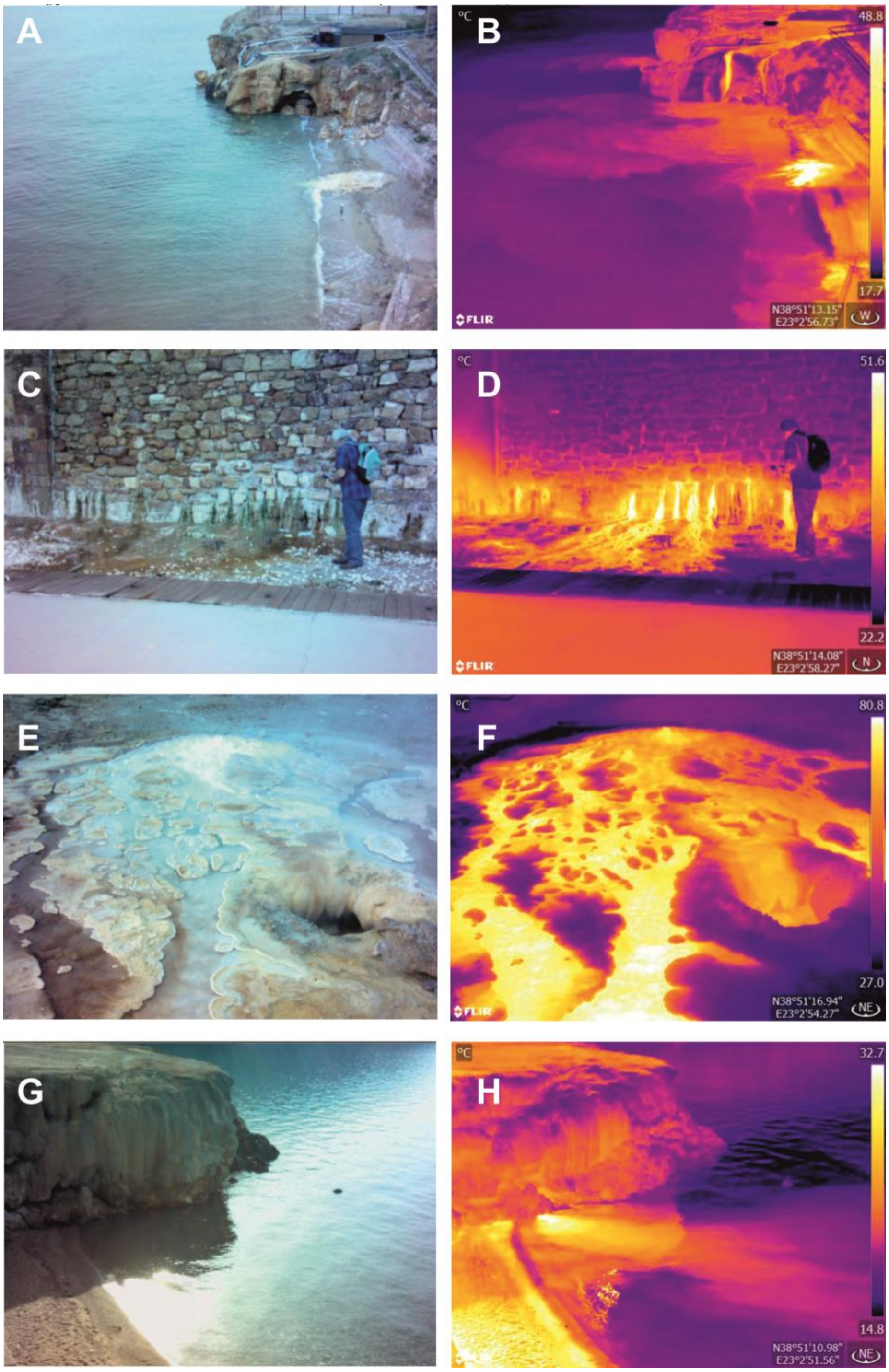

Figure 3 - Paired views of Edipsos hot springs pictures and corresponding thermal image of the same area. In the right side of each thermal picture, a colour column shows the temperature scale corresponding to the colors. (A and B) Near the sea hot spring discharge and the spring plume into the sea. (C and D) Wall with several small hot spring discharges. (E and F) Terrestrial hot spring discharge. (G and H) Submarine hot spring discharging in the base of a thermogenic travertine cape and the spring plume into the sea.

At the same time water and gas isotopic studies (Shimizu *et al*., 2005; D`Alessandro *et al.*, 2014; Dotsika, 2015) suggests that the hot springs of Edipsos are fed by deep parent geothermal fluid mixed with seawater. Possibly related with the volcanic center of Lichades and the magma chamber, which it has recently detected at 8 km depth (Karastathis *et al*., 2011).

Geochemical study in the cold groundwaters of the area, show that the main cold aquifers are not affected by the hot groundwaters (Kanellopoulos, 2006, 2011; Kanellopoulos and Mitropoulos, 2013). Suggesting that the hot reservoirs or/and the pathway of the hot groundwater, are not in hydraulic connection with the main shallower cold aquifers.

The application of chemical geothermometers in Edipsos hot groundwater is problematic. The samples are characterized as partially equilibrated waters (Fig. 2B) and the resulting temperatures are presenting large variations. The high percentage of seawater participation is most probably one of the main reasons (Dotsika, 2015). Taking under consideration that the hydrochemical type of the samples is Na-Cl and the fact that Na, K and Ca alongside with Cl are the main ions, support the idea that Na-K-Ca geothermometer could be considered the most representative geothermometer for the studied geothermal fluids. According to Na-K-Ca geothermometer estimations, the expected temperature of a potential geothermal reservoir is up to ~160 ^{o}C.

Therefore, the geochemical study of Edipsos hot groundwater shows that the water chemistry is controlled by the following three factors: i) a deeper magmatic source, ii) the chemical composition of the local rocks (ultramafic and carbonates) and iii) the high participation of the sea water.

Even though several studies have been conducted in the area, the detailed underground circulation of the hot groundwater still remains vague. Does the hot groundwater rise from greater depths using the dominant faults of the area, or is there a reservoir in the broader area, possibly in carbonate rocks? In that case which is the temperature of the geothermal fluid in the reservoir? A systematic geothermal deep drilling project could give the answers.

6. Acknowledgements

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