Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, τόμος L, σελ. 710-719
Πρακτικά 14ου Διεθνούς Συνεδρίου, Θεσσαλονίκη, Μάιος 2016

Bulletin of the Geological Society of Greece, vol. L, p. 710-719
Proceedings of the 14th International Congress, Thessaloniki, May 2016

HYDROCHEMICAL STUDY OF THE HOT GROUNDWATER OF AMPELIA AREA, EASTERN THESSALY, GREECE. A NEW AREA WITH GEOTHERMAL INTEREST

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Abstract

Ampelia area is a newly discovered area with geothermal interest and no surface manifestations (hidden resource). It is located in Farsala basin and belongs to the Enipeas graben. The geothermal anomaly is related with the E-W trending faults, which mainly control the basin development and the NNW-SSE trending faults of the area. The temperature values from the deep water boreholes (>200m depth) range from 20 to 41°C. The chemical composition of the studied groundwater samples varies in all chemical parameters. Most of the samples have affected by shallow cold aquifers (high E.C. and NO_3^- values). The most representative samples (T > 30°C) are from the deepest boreholes (hydrochemical type Na-HCO_3), which cut the fractured crystalline basement, i.e. limestones, flysch and ophiolitic rocks. They present the highest pH values (pH > 8) and the lowest E.C. compared with the rest of the samples. Their Ni and Cr concentrations are very low, indicating that the groundwater is not in contact with the ultramafic rocks from the ophiolite sequence. According to silica chemical geothermometers for the most representative samples, the expected temperature values of a potential geothermal reservoir range from ~ 60 to 100°C.

Keywords: *geothermal energy, hot groundwater geochemistry, trace element and ion concentration, Eastern Thessaly, Greece.*

Περίληψη

Η περιοχή της Αμπελίας είναι μια νέο-ανακαλυφθείσα περιοχή, η οποία παρουσιάζει γεωθερμικό ενδιαφέρον, χωρίς να παρουσιάσει επιφανειακές γεωθερμικές εκδηλώσεις. Εντοπίζεται στη λεκάνη των Φαρσάλων και ανήκει στο τεκτονικό βύθισμα του Ενιπέα. Η γεωθερμική ανωμαλία συνδέεται με τα ρήματα διεύθυνσης Α-Δ, που ελέγχουν την δημιουργία της κοιλάδας και τα διασταυρούμενα σε αυτά ρήγματα διεύθυνσης ΒΒΔ-ΝΝΑ. Οι θερμοκρασίες από τις βαθιές γεωτρήσεις (> 200 μ) κυμαίνονται από 20 έως 41°C. Η χημική σύσταση των δειγμάτων παρουσιάζει έντονες διαφοροποιήσεις. Τα περισσότερα δείγματα έχουν επηρεαστεί από κρύους επιφανειακούς υδροφόρους (υψηλές τιμές E.C. και NO_3^-). Τα πιο αντιπροσωπευτικά δείγματα με T > 30°C προέρχονται από βαθιές γεωτρήσεις που αναπτύσσονται και μέσα στο τεκτονισμένο κρυσταλλικό υπόβαθρο (ασβεστόλιθοι, φλύσχης, οφιολιθικά πετρώματα). Τα δείγματα αυτά παρουσιάζουν τις υψηλότερες τιμές pH (pH > 8) και τις χαμηλότερες τιμές E.C. Επίσης, παρουσιάζουν πολύ χαμηλές συγκεντρώσεις Ni και Cr, ενδεικτικό ότι δεν είναι σε επαφή με τα υπερβασικά πετρώματα των οφιολιθικών σχηματισμών. Βασιζόμενοι σε *πυριτικά χημικά γεωθερμόμετρα και εστιάζοντας κυρίως στις τιμές των πιο αντιπροσωπευτικών δειγμάτων εκτιμάται ότι η θερμοκρασία ενός πιθανού γεωθερμικού ταμιευτήρα στην περιοχή πρέπει να κυμαίνεται από ~ 60 έως 100°C.*

Λέξεις κλειδιά: *γεωθερμική ενέργεια, γεωχημεία θερμών υπόγειων νερών, συγκεντρώσεις ιχνοστοιχείων και ιόντων, Ανατολική Θεσσαλία, Ελλάδα.*

1. Introduction

In the next decades, the demand for energy could double or even triple as the global population rises and developing countries expand their economies. This increase coupled with continued demand for the same, limited natural resources will cause significant increase in consumption of energy. All life on Earth depends on energy and the cycling of carbon. Affordable renewable energy resources are essential for economic and social development as well as food production, water supply availability and sustainable healthy living (Glassley, 2015).

That huge demand for energy could be covered by the renewable energy resources, which at the same time have low CO_2 emissions. One of them, which Greece is blessed to have in several places due to its geological setting, is the geothermal energy. The high deformation rate of the Aegean area, the combination of magmatic and volcanic processes as well as intense tectonic activity which results in active fault systems, favour the rise of deep hot waters that in many times discharge at the surface as hot springs. In these cases, the areas with geothermal interest are easy to be discovered, by finding hot springs or/and boiling mud pot or/and fumaroles. However, there are many geothermally interesting areas that have little or no surface expression (hidden resources).

The Institute of the Geological and Mineralogical Exploration (IGME) since 1970`s, based on the first systematic study of all known Greek hot springs (Orfanos, 1975; Gioni, 1983; Sfetsos, 1988 etc.), has started to explore different areas of Greece in order to find potentially interesting areas for geothermal energy with no surface manifestations (Taktikos, 1985). One interesting province is Eastern Thessaly, in which there are several areas with hot and mineral springs e.g. Smokovo, Soulanta, Kaitsa and Ekkara. Recently, five new areas were identified to be potentially interesting for geothermal energy i.e. Paschalitsa, Nees Karies, Ampelia, Microthives and Paliouri (hidden resources; Fig.1). Paschalitsa and Nees Karies have explored from IGME with deep boreholes (Xatzis, 2001). The hydrogeology of Farsala basin was studied by Mariolakos *et al*. (2001a, 2001b). Stamatis *et al*. (2007) made the first attempt to evaluate the origin and quality of Ampelia thermal groundwaters.

The aim of this paper is to present the results of geothermal research of Ampelia area (Eastern Thessaly, Greece); which is a newly discovered area with geothermal interest and no surface expression and assess the hydrochemical characteristics and geothermometry applications of the hot groundwater of the area.

2. Geological and hydrological setting

Ampelia area is located in Eastern Thessaly, in the central part of Greece. The study area lies between the following coordinates X: 364000E, Y: 4356000N and X: 379000E, Y: 4344000N (EGSA `87). It is characterized by smooth topography and lowland areas.

Eastern Thessaly belongs geologically to the Sub-Pelagonian geotectonic zone (Aubouin, 1959; Mpornovas *et al*., 1969; Katsikatsos *et al*., 1983; Mountrakis, 1986). The study area is located in Farsala basin which is part of the Western Thessaly basin (Fig. 1) and consists of flysch (Upper Cretaceous age), karstified limestones (Upper Cretaceous), ophiolitic rocks including serpentinites, dunites, peridotites; in Farsala area occur pillow lavas and some ultrabassic intense serpentinised formations and schists (southern part of Farsala Basin, Mpornovas *et al*., 1969, 1964; Katsikatsos *et al*., 1983). Large parts of Eastern Thessaly are covered by Post Alpine formations i.e. Holocene deposits, Neogene formations and Plio-Pleistocene terrestrial deposits and layers of lignite

(Giakkoupis, 1995; Dimitriou and Arapogiannis, 2000, Fig. 1). The Post Alpine formations have been detail described by Giakkoupi, 1995. The tectonic structure of the study area is characterized by E-W trending faults, which mainly control the basin development and by NNW-SSE trending faults. Ampelia area belongs to the Enipeas graben. The sediments are mainly Holocene alluvial sands and Pleistocene terrestrial. The alpine basement is formed by flysch, Cretaceous limestone and ophiolitic rocks. The morphology of the top of the basement is controlled by the neotectonic activity, expressed by large folds with axis direction NE-SW as well as by E-W and NW-SE striking faults (Spyridonos *et al*., 2002).

Mariolakos *et al*. (2001a, 2001b) and Stamatis *et al*. (2007) describe the presence three different aquifers in the study area. One unconfined aquifer of important potentiality is developed in the unconsolidated deposits of the basin and suffers from overexploitation due to the supply of the irrigation needs of the area. The thickness of the unconsolidated deposits ranges from a few meters eastern of the basin to a few ten meters westwards, to more than 200 m in the central and northern parts of the basin, particularly within the tectonic graben (Mariolakos *et al*., 2001a, 2001b). Groundwater flows from the east to the west parts of the basin. Another karst aquifer of important potentiality is developed within the karstified carbonate formations. The major karst springs of the region, such as Vrisia and Chtouri springs, located west of the Farsala city, are fed from the carbonate formations of Narthakio and Filio Mountain in the west part of the basin (Mariolakos *et al*., 2001a, 2001b). The carbonate masses developed in the east part of the basin probably feed laterally the unconsolidated formations of the basin. Also, an aquifer of low potentiality is developed in the fractured crystalline formations. The discharge of the deep boreholes in the ophiolitic rocks does not exceed 30 m^3/h. Within the Neogene sandy and carbonate horizons an aquifer of low potentiality also occurs. The discharge of the boreholes, when the formation thickness and structure are favourable, reaches the 20-30 m^3/h.

3. Materials and methods

3.1. Groundwater sampling and analysis

After measuring the water temperature of several irrigation boreholes of the area, 12 groundwater samples were collected from irrigation wells with the highest temperature values (Table 1, Fig. 2). Unstable parameters such as, pH, Temperature, Electrical Conductivity (E.C.) were measured in the field. All the samples were vacuum filtered, acidified to a final concentration of 2% nitric acid, stored in polyethylene bottles and preserved in a refrigerator.

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 anion concentrations were measured using spectrophotometer, or/and titration or/and Atomic Absorption Spectroscopy (AAS) or and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Table 2). The trace element concentrations were measured using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Table 2).

ArcGIS software was used to create a digital geological map of the greater area of Eastern Thessaly (scale 1:70,000, Fig. 1). This map is based on the published geological map of scale 1:1,000,000 (Mataragkas *et al*., 2000). 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 the probability map of temperature using the Surfer software (Fig. 2).

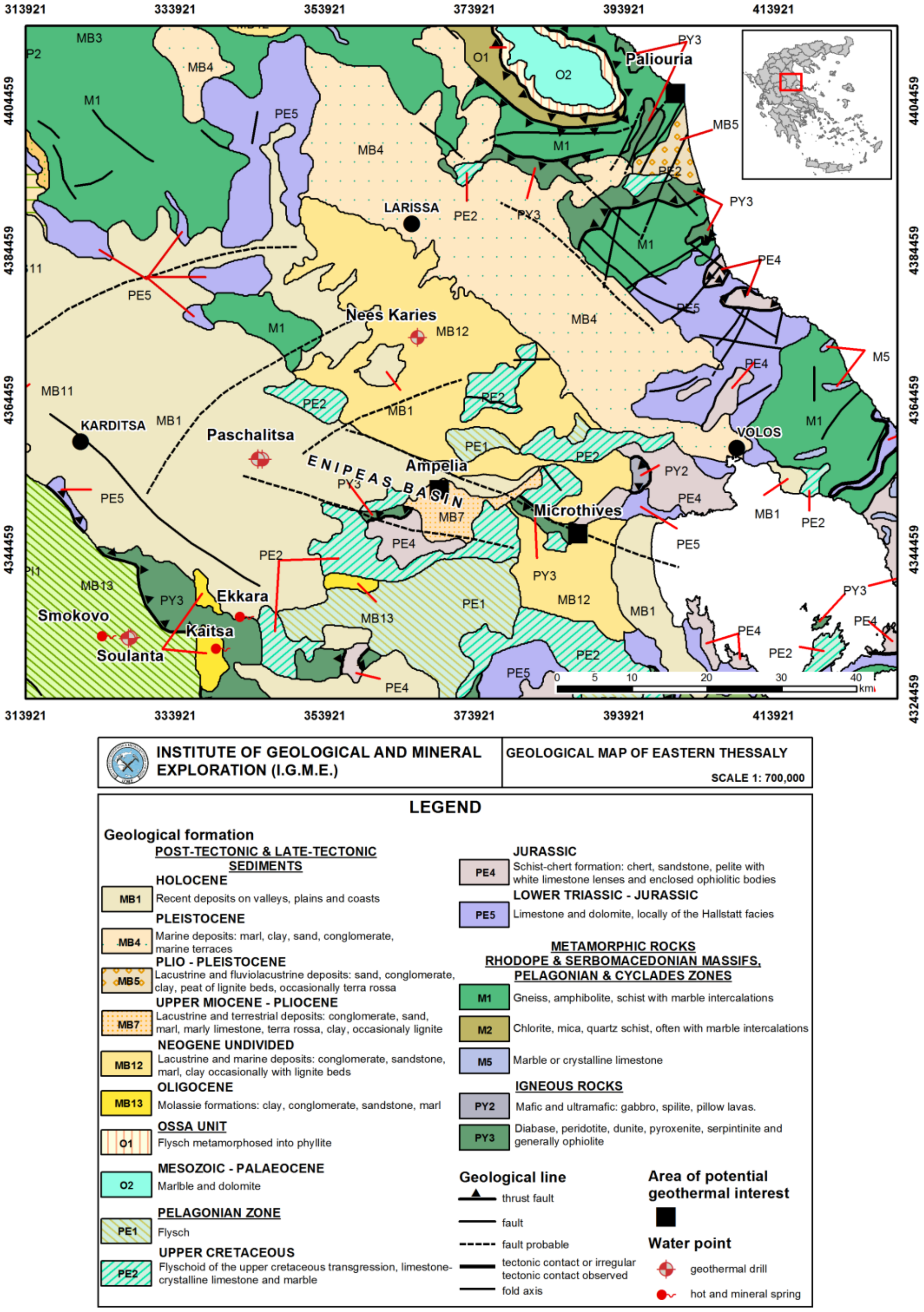

Figure 1 - Simplified geological map of eastern Thessaly (Mataragkas *et al*., 2000), presenting areas with hot and mineral springs and areas which are potentially interesting for geothermal energy data.

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

Code	Locality	Lon.^{*1}	Lat.^{*1}	Depth (m)	T (°C)	pH	TDS^{*2} (mg/lt)	EC (mS/cm)	Hydrochemical type	Chemical geothermometers		
										Qtz^{*3}	Chalcedony^{*3}	Na-K-Ca^{*4}
GTHES-001-D01	Ampelia	369248.59	4352419.58	410	41	8.1	310	458	Na-HCO$_3$	105	75	41
GTHES-006-D03	Ampelia	369552.34	4352218.85	235	35	8.6	305	393	Na-HCO$_3$	99	68	45
GTHES-036-D04	Ampelia	368347.00	4351854.00	-	22	7.1	770	1145	Ca-Mg-Na-HCO$_3$-NO$_3$	76	45	5
GTHES-037-D05	Stefania	369243.00	4353410.00	300	23	7.6	430	651	Ca-Na-HCO$_3$	63	31	107
GTHES-045-D08	Ampelia	368420.00	4352254.00	120	22	7.6	540	809	Ca-Mg-Na-HCO$_3$	71	39	14
GTHES-046-D11	Ampelia	369854.46	4351525.20	120	23	7.2	1100	1575	Ca-Mg-Na-HCO$_3$-Cl-SO$_4$	71	39	26
GTHES-058-D12	Mnimata	369100.73	4349245.65	300	26.3	7.6	570	857	Na-HCO$_3$-Cl	68	36	29
GTHES-060-D19	Mnimata	368415.29	4348989.36	-	29.5	7.6	417	700	Ca-Mg-Na-HCO$_3$-SO$_4$	55	23	29
GTHES-070-D16	Kastro	372664.00	4349467.00	300	25.1	7.4	389	620	Ca-Mg-HCO$_3$	88	58	103
GTHES-095-D17	Ampelia	366831.00	4351721.00	120	17.4	7.3	626	995	Ca-Mg-HCO$_3$	-	-	-
GTHES-098-D18	Ampelia	368828.00	4351353.00	150	23.5	7.0	718	1180	Ca-Mg-HCO$_3$-Cl	77	46	204
GTHES-093-D-14	Ampelia	368813.00	4350863.00	200	30.3	8.3	304	510	Na-HCO$_3$-Cl	57	25	35

** = Geographical coordinates are in EGSA `87, ** = Measured at the laboratory, *3 = Foumier 1977, *4 = Foumier 1979*

Table 2 - Concentrations of major anions and trace elements (in mg/L).

Sample	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+} mg/L	K^{+} mg/L	HCO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L	NH_4^+ mg/L	NO_2^- mg/L	SiO_2^- mg/L	Li μg/L	Cr μg/L	Ni μg/L	F μg/L	B μg/L	Fe μg/L	Sr μg/L	Ba μg/L	Al μg/L	Br μg/L	As μg/L	Cu μg/L	Hg μg/L	U μg/L
GTHES-001-D01	8.9	4.1	87.8	0.9	209	27.7	19.3	1.86	0.216	0.41	53.2	<5	<5	<5	320	1900	90	55	27	17	-	<5	<5	<0,5	<5
GTHES-006-D03	9.7	4	91	1.1	178	23.8	22.8	bld	0.537	0.175	46.7	7	10	<5	580	5400	88	50	29	34	-	<5	<5	<0,5	<5
GTHES-036-D04	89.2	64.3	63.1	0.96	420	70.9	66.7	161	<0.05	<0.05	27.7	23	<5	<5	668	23	21	790	7	11	890	<5	14	<0,5	<5
GTHES-037-D05	31.6	14.5	99	2.55	354	28.4	22.3	5.8	<0.05	<0.05	19.9	15	<5	<5	552	165	18	190	8	,5	470	<5	6	<0,5	<5
GTHES-045-D08	68.1	41.3	52.9	1.34	404	39	26.6	33.5	<0.05	<0.05	24.1	22	<5	<5	430	53	190	495	24	104	-	<5	8	<0,5	<5
GTHES-046-D11	100.6	99.71	104	2.34	566	145.4	191	18.8	<0.05	0.218	24.1	57	<5	18	724	114	2020	903	150	500	1550	<5	73	<0,5	<5
GTHES-058-D12	28.9	19	139.3	1.07	323	94	49.1	3.9	<0.05	<0.05	22.3	18	<5	<5	505	166	2950	167	138	36	1130	9	8	<0,5	<5
GTHES-060-D19	36.4	27.4	73.8	1.5	255	44.3	72.8	19.84	0.5	0.08	15.9	13	<5	<5	620	190	200	265	40	150	600	<5	<5	<0,5	<5
GTHES-070-D16	42.5	44.42	19	0.8	281	25.2	48.7	33.48	<0.05	<0.05	37.2	7	<5	<5	230	94	40	190	5	28	500	<5	<5	<0,5	<5
GTHES-095-D17	96.7	53	29	0.91	391	30	88.5	109.75	<0.05	<0.05	25.5	<5	<5	6	420	33	10	220	20	18	500	<5	<5	<0,5	<5
GTHES-098-D18	81.4	67.5	1.7	1.5	446	89	58	109.13	-	-	28.4	25	<5	<5	510	65	10	720	32	12	1100	<5	7	<0,5	<5
GTHES-093-D-14	9.39	2.2	103	0.71	195	43.6	30.9	0.62	<0.05	0.48	17	<5	<5	<5	100	650	75	34	21	31	500	<5	15	<0,5	<5

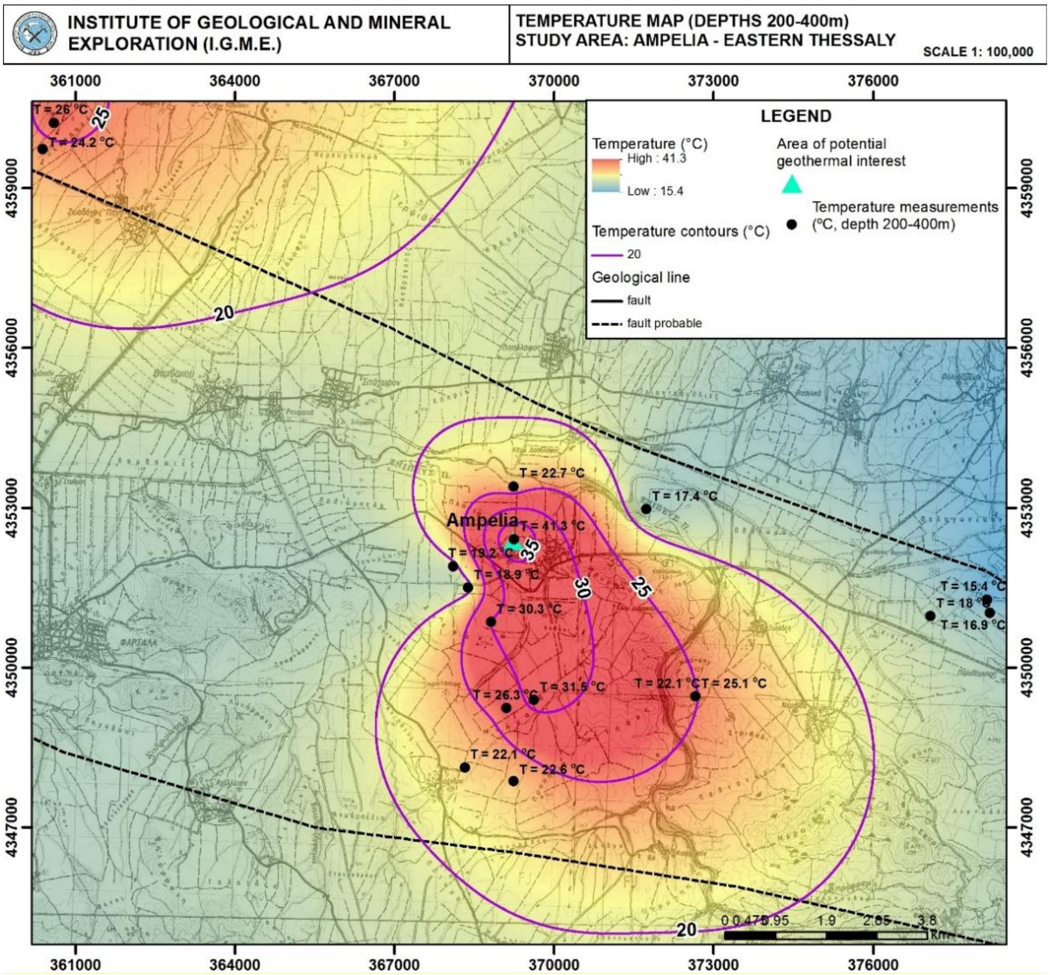

Figure 2 - Groundwater temperature distribution in Ampelia area, based on boreholes with depth >200 m.

4. Analytical results

4.1. Spatial distribution of temperature

In order to visualize the spatial distribution of the hot groundwater temperature an interpolated map was created based on boreholes with depth >200 m, using Kriging method (Fig. 2). Kriging is a deterministic interpolation method that generates an estimated surface from a scattered set of points with z-values, in this case water temperature values.

In Figure 2, the interpolated map reveals that the geothermal anomaly is constrained by the E-W trending faults, which mainly control the basin development and presents a direction N.NW-S.SE similar with N.NW-.SSE trending faults of the area. Also, reveals another geothermal anomaly in Zodochou Pigi area (NW edge of the map, Fig. 2).

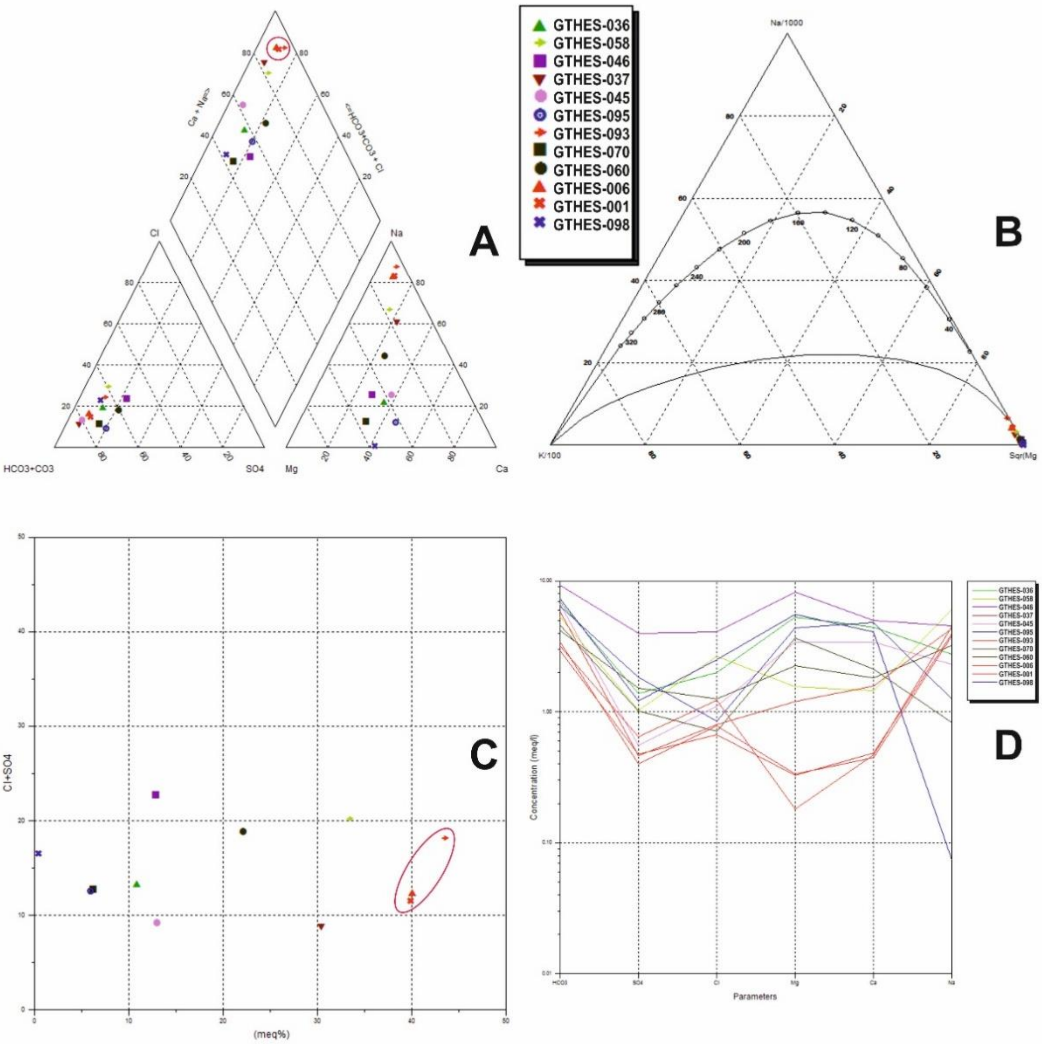

Figure 3 - Chemical composition of groundwater samples plotted in (A) Piper trilinear diagram. (B) Giggenbach trilineardiagram. (C) Ludwing-Langelier diagram. (D) Schoeller diagram. The three samples with temperature value over 30 °C are symbolized with red color.

4.2. Chemical Analysis

The locations of the samples are presented in Figure 2 and in Tables 1 and 2 are presented the chemical parameters analyzed in situ and in the lab.

All samples present temperature values over 20°C, except the sample GTHES-095-D17 which present temperature value 17.4°C. The GTHES-006-D03 and GTHES-093-D-14 samples present temperature value over 30°C and the GTHES-001-D01 over 40°C. These three samples show the lowest Electrical Conductivity (393-510 mS/cm) and the highest pH values (pH > 8) compared with the rest of the samples.

In Figure 3A, the results of the chemical analyses were plotted in Piper diagram (Piper, 1953), in order to evaluate them hydrochemically and identify their hydrochemical type. The three samples with T > 30°C are plotted, in the Piper and Ludwing-Langelier diagrams (Langelier and Ludwing, 1942, Fig. 3A, C) in the same area, while the rest of the samples are plotted scatter in the diagrams

(Fig. 3A, C). The three samples with T > 30°C have Na-HCO_3 as hydrochemical type supplemented by Cl for the GTHES-093-D-14 (Table 1). Also, they present the lowest concentrations of Ca^{2+}, Mg^{2+}, HCO_3^- and NO_3^-. Even though, the chemical composition of the samples varies in all the measured chemical parameters; these three samples show only small variation, characteristic is the diagram Schoeller (Fig. 3D, Table 2).

4.3. Geothermometry application

Chemical geothermometers are widely used tools in order to estimate the subsurface 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), Chalcedony (Fournier, 1977) and Na-K-Ca (Fournier, 1979), were applied to the hot groundwaters of Ampelia (Table 1).

According to Giggenbach's (Fig. 2B) triangle diagram all the samples are plotted between the fields of non-equilibrated and partially equilibrated waters, meaning that they can`t be considered equilibrated with minerals in the reservoir rock. For that reason, the chemical geothermometers give temperatures, which are diverse from one geothermometer to another and very variable between samples (Table 1). Another cause for that is the mixing of the hot groundwater with groundwater from swallower cold aquifers of the area. Therefore, the initial reservoir temperature could not be clearly estimated.

The estimated temperatures of the samples GTHES-001-D01, GTHES-006-D03 and GTHES-093-D-14 could be considered as indicative for the temperature estimation of a potential subsurface reservoir. Based on these three samples, the estimated temperatures by Na-K-Ca geothermometer, are from 35 to 45°C. That temperature range is very close to the maxima measured temperature. Silica geothermometers are typically inferred to reflect recent and/or shallower geothermal-reservoir temperatures (Fournier, 1981; Giggenbach, 1988; Ayling and Moore, 2013). For that reason, they are more suitable in the case of Ampelia. According to Quartz geothermometer, the calculated temperatures range from 57 to 105°C and based on the Chalcedony geothermometer the calculated temperatures range from 25 to 75°C.

5. Discussion – Conclusions

The study area is located in Farsala basin which is part of the Western Thessaly basin (Fig. 1). More specifically, Ampelia area belongs to the Enipeas graben. The sediments filling of the basin are mainly Holocene alluvial sands and Pleistocene terrestrial sediments. The alpine basement is formed by flysch, Cretaceous limestones and ophiolitic rocks (Fig. 1). The morphology of the top of the basement is controlled by the neotectonic activity, expressed by large folds with axis direction NE-SW as well as by E-W and NW-SE striking faults (Spyridonos *et al*., 2002).

Even though in Ampelia area, no surface expression of geothermal system exists, the temperature values from the deep water boreholes (> 200 m depth) range from 20 to 41°C. The Farsala Basin tectonic regime, combined with the existence of permeable and impermeable formations, create appropriate conditions for the development of an active geothermal system (Xatzis, 2001; Stamatis *et al*., 2007). The geothermal anomaly observed in the study area seems to be directly connected to the fractured zones by active fault system of the sub-basement formations. Based on the interpolated map (Fig. 2) the geothermal anomaly is constrained by the E-W trending faults, which mainly control the basin development and presents a direction NNW-SSE similar with NNW-SSE trending faults of the area.

The chemical composition of the studied groundwater samples varies in all chemical parameters. Characteristic are the several different hydrochemical types of the samples (Table 1) and the scattered projections of them in the discrimination diagrams i.e. Piper, Ludwing-Langelier and Schoeller (Fig. 2A, C, D). Most of the samples have high Electrical Conductivity values (up to 1575 mS/cm) and at the same time they present high concentrations in NO_3^- (up to 109 mg/L), revealing relation to the shallow cold aquifers which are affected from fertilizers. All these suggest that there is a mixing of the deep hot groundwater with shallower cold aquifers.

The most representative samples of the deep hot groundwater are the samples GTHES-001-D01, GTHES-006-D03 and GTHES-093-D-14. These samples have temperatures over 30°C and especially the GTHES-001-D01 which has the highest measured temperature (41°C). It is interesting that all these boreholes have depth over 200 m and the deepest borehole of all (GTHES-001, 410 m depth) presents the highest temperature. In that borehole the main water supply originates from its deepest part, which is cutting the fractured crystalline basement i.e. karstified limestones, flysch and ophiolitic rocks. The Ni and Cr concentrations of these samples are very low, in most cases below detection limit, indicative that the groundwater is not in contact with the ultramafic rock from the ophiolite sequence. These three samples show the highest pH values (pH > 8), the lowest Electrical Conductivity (393-510 mS/cm) and the lowest concentrations of Ca^{2+}, Mg^{2+}, HCO_3^- and NO_3^- compared with the rest of the samples; indicative of the low degree of influence by the shallower cold aquifers which are degraded by the use of fertilizers. Characteristic is that these three samples show only small variation in most of the measured chemical parameters.

According to Giggenbach's triangle diagram (Fig. 2B) all the samples are plotted between the fields of non-equilibrated and partially equilibrated waters. It is also apparent that mixing of the deep hot groundwater with swallower cold aquifers, which have different chemistry, takes place for the majority of the samples. For these reasons, the resulting temperatures are different for each geothermometer and with large variations between samples (Table 1). However, the estimated temperatures for the samples GTHES-001-D01, GTHES-006-D03 and GTHES-093-D-14 from the silica geothermometers could be used as indicative for the estimation of the temperature a potential subsurface geothermal reservoir. According to their geothermometric estimations, the expected temperature values of a potential geothermal reservoir range from ~ 60 to 100°C.

Many questions remain unanswered about the geothermal potential of Ampelia area e.g. about the underground circulation of the hot water; about the related reservoir etc. A systematic geothermal deep drilling project, will give valuable information concerning the geothermal potential of the region and it will help the economic development of the area.

6. Acknowledgements

This study was funded by the National Strategic Reference Framework (NSRF, 350913). The authors would like to thank the local population for their co-operation during the field work. The corresponding author would like to thank Dr. George Vougioukalakis who critically commented on an earlier version of this manuscript.

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